Applications of Molybdenum Metal and its Alloys

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Contents

Introduction

The first molybdenum metal application – lead wires in incandescent lamps – appeared in the early days of the 20th century. Molybdenum was chosen for this application because of its stability and strength at elevated temperatures. Since that first application, scientists and engineers have discovered that other properties of molybdenum make it the material of choice for many applications. Some of these take advantage of molybdenum's strength and stability at high temperatures, just as the first lamp wires did. However, molybdenum has many other properties that make it attractive for applications outside traditional high-temperature components, including:

- High thermal conductivity,
- High electrical conductivity,
- Low coefficient of thermal expansion

- Resistance to attack by molten metal,
- Compatibility with most glass compositions,
- Thermal shock resistance,
- High stiffness, and
- Strong bonding with glass used in lamps and electronic devices.

Because so many of its properties are attractive to engineers and designers, molybdenum metal and its alloys are used in:

- Lighting,
- Electrical and electronic devices,
- Medical equipment,
- Materials processing equipment,
- High temperature furnaces and associated equipment,
- Thermal spray coatings, and
- Aerospace & defense components.

Applications in all these areas require unique combinations of several properties. Molybdenum and its alloys, and composite materials that employ molybdenum metal, provide unique combinations of thermal and electrical conductivity, thermal expansion, high-temperature strength and creep resistance, vapor pressure, environmental stability, and resistance to abrasion and wear that make them ideal. This brochure intends to help the reader understand why this unique material finds use in so many varied applications. It also presents information on machining and fabrication techniques for molybdenum and its alloys.

Hot rolling molybdenum creates spectacular heat and smoke.
© Luoyang Hi-Tech Metals Co.

How molybdenum metal products are made

Because pure molybdenum melts at such a high temperature and because it oxidizes at relatively low temperatures, traditional smelting processes cannot extract the metal from its ore. Instead, ore is processed in a series of grinding and separation steps to isolate its MoS_2 (molybdenum disulfide) from other components. This isolated material, containing up to about 90% MoS_2 and the remaining unseparated mineral content called gangue, is roasted in air to produce MoO_3 (molybdic oxide) and SO_2 (sulfur dioxide). The sulfur dioxide is converted to sulfuric acid and sold

```
                    ┌──────────────────┐
                    │   Mo tech oxide  │
                    └──────────────────┘
                     Chemical treatment
                            ↓
    ┌─────────────────────────┐   Calcination    ┌──────────────┐
    │  Ammonium dimolybdate   │ ───────────────→ │  Pure MoO₃   │
    └─────────────────────────┘                  └──────────────┘
         First-stage hydrogen reduction  ←──────────────┘
                            ↓
                      ┌──────────┐
                      │  MoO₂    │
                      └──────────┘
              Second-stage hydrogen reduction
                            ↓
  ┌──────────────────┐               ┌──────────────────┐               ┌──────────────────────┐
  │ Pellets for      │  Press &      │                  │  Spray dry    │ High-speed pressing  │
  │ Ni-base &        │ ← sinter ──── │  Mo metal powder │ ───────────→  │ powder,              │
  │ stainless steel  │               │                  │               │ thermal spray powder │
  │ alloy additions  │               └──────────────────┘               └──────────────────────┘
  └──────────────────┘
         Add alloy ••••→  Blend
                            ↓
                  ┌────────────────────┐
                  │ Pure or alloy      │
                  │ powder             │
                  └────────────────────┘
```

Mo tech oxide → Chemical treatment → **Ammonium dimolybdate** — Calcination → **Pure MoO₃**

Ammonium dimolybdate → First-stage hydrogen reduction ← **Pure MoO₃**

First-stage hydrogen reduction → **MoO₂**

MoO₂ → Second-stage hydrogen reduction → **Mo metal powder**

Mo metal powder ← Press & sinter → **Pellets for Ni-base & stainless steel alloy additions**

Mo metal powder — Spray dry → **High-speed pressing powder, thermal spray powder**

Add alloy ••••→ Blend → **Pure or alloy powder**

Pure or alloy powder → Press-sinter-melt arc casting → **Cast ingot**

Pure or alloy powder → Press & sinter → **Pressed & sintered ingot**

Cast ingot → Extrude

Mill processing: Flat roll, swage, rotary forge, upset forge, etc.

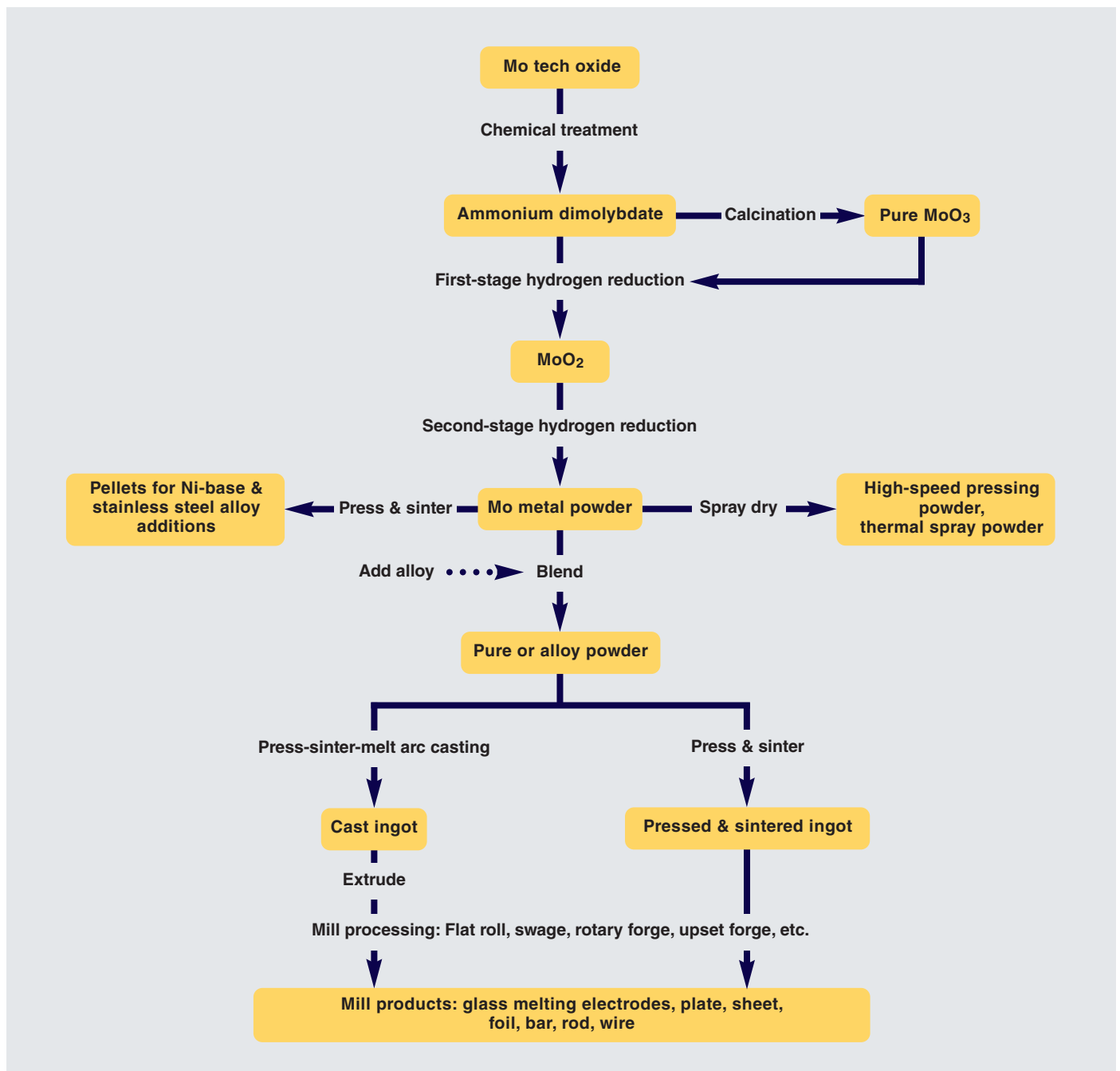**Mill products: glass melting electrodes, plate, sheet, foil, bar, rod, wire**

Figure 1. Flowsheet describing the production of molybdenum metal mill products.

for chemical applications. The roasted product, called technical oxide or tech oxide, contains about 57% Mo and less than 0.1% S. The roasting process does not remove gangue, but this is not a problem for the vast majority of tech oxide used to manufacture molybdenum-alloy steel. During melting, the gangue ends up in the slag. However, tech oxide must be purified chemically to use it in the manufacture of molybdenum metal.

Figure 1 is a flow chart of molybdenum metal manufacturing, starting with tech oxide. The oxide is first dissolved in ammonium or sodium hydroxide, and this solution is processed by precipitation and filtration, solvent extraction, or a combination of both to remove impurities. High-purity ammonium molybdate, or ADM, is extracted by crystallization or precipitation and filtration. This high-purity chemical is the starting material for molybdenum metal powder production. The molybdate can be calcined (heated to high temperature in air) to produce a high-purity molybdic oxide. Whether ADM or calcined oxide is used as the starting material for metal production, the subsequent process is the same. The ADM or calcined oxide undergoes a two-stage chemical reduction in hydrogen gas to create pure molybdenum metal powder. First-stage reduction occurs in the temperature range 450−650°C, and reduces the input material to MoO_2, often called brown oxide because of its color. Second-stage reduction is performed in the 1000−1100°C range, and this process results in molybdenum metal powder that is typically > 99.97% Mo.
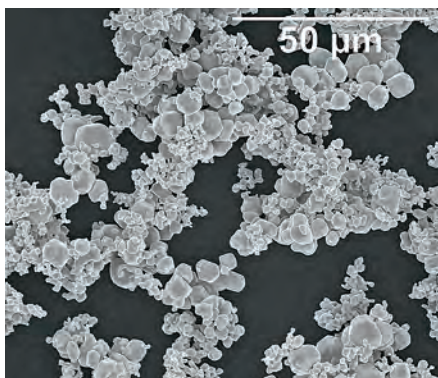

Figure 2. As-reduced molybdenum metal powder. © H. C. Starck

The two stages are necessary because attempting to reduce the input material directly to metal at high temperature can result in significant evaporation of molybdic oxide, which has a high vapor pressure at temperatures as low as 800°C. The as-reduced powder shown in Figure 2 is typical. Note the extremely fine and highly irregular particles, each larger particle made up of agglomerated finer particles. This morphology promotes high as-pressed strength in pressed shapes, but it produces very poor flowability that makes powder handling difficult. In striking contrast is Figure 3, an image of a spherical stainless steel powder like that used for thermal spray and powder-injection-molding (PIM) applications where flowability is paramount.

Powder is the starting point for all virgin molybdenum metal products. Substantial quantities of powder are pressed and sintered into pellets or other simple shapes

and sold as alloying additions for nickel-base superalloys and some stainless steels. Some powder is spray-dried (see sidebar) to manufacture spherical powders. The binders used in spray-dried powders can be either organic (in the case of powders used for high-speed pressing operations) or ammonium molybdate (in the case of thermal-spray powders).

The majority of powder is used to make mill products like sheet, plate, foil, rod, bar and forgings. Most mill products are made from pressed and sintered starting ingots. In this process, molybdenum powder or molybdenum powder blended with appropriate alloy components is placed in an elastomeric mold. After filling, the mold is evacuated, sealed, and
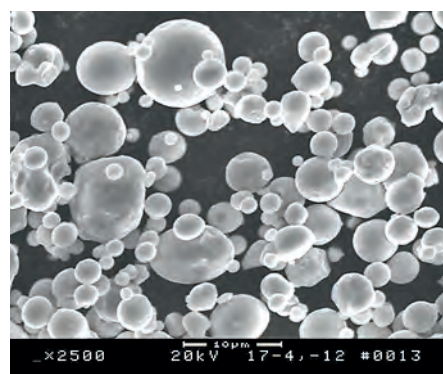

Figure 3. Standard gas-atomized 17-4 PH stainless steel powder. © Materials Processing, Inc.

placed with other filled molds in a cold isostatic press (CIP). After pressing at pressures of approximately 200 MPa, the ingots are removed from the molds and sintered in hydrogen at 1700−1800°C. Hydrogen is an ideal atmosphere in which to sinter molybdenum because it chemically reduces adsorbed oxygen and surface oxides on the powder particles, enhancing densification and maintaining low oxygen content in the metal. Pressed and sintered molybdenum typically contains about 5 wppm carbon, 20−30 wppm oxygen, less than 5 wppm nitrogen, and

Spray drying mixes powder with a liquid to form a slurry, atomizes the slurry into small droplets, and dries the droplets as they fall through a hot gas. The liquid contains binders to hold the powder particles together, so when the dried droplets are collected the result is a fine spherical powder made of individual powder particles held together by the binder. The choice of binder depends upon the properties desired in the spherical powder; the choice of gas atmosphere depends upon the properties of the binder and the pyrophoricity of the powder being spray dried.
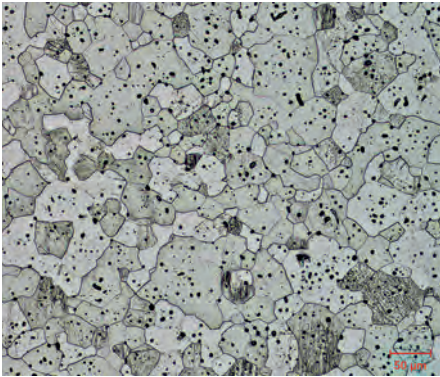
Figure 4. Microstructure of pressed and sintered molydenum. © H. C. Starck; sample prepared by NSL Analytical Services

1 wppm or less hydrogen. Figure 4 illustrates the microstructure of pressed and sintered molybdenum containing equiaxed grains and residual sintering porosity.

A small amount of molybdenum metal is produced by the press-sinter-melt (PSM) process developed by Climax Molybdenum in the 1950s. It is a semi-continuous process in which a vacuum-arc furnace electrode is built up from powder, fed into an arc-melting furnace, and melted in a water-cooled copper crucible. The process employs carbon as a deoxidizer, which results in very low oxygen contents (typically below 5 wppm) but significant quantities of carbon (50–100 wppm). Nitrogen and hydrogen are also quite low in these materials. The melting process creates very large as-cast grains that result in poor workability, so arc-cast ingots must be extruded at high temperatures to refine their grain size before further processing. This combination of factors mean the arc-cast process produces a narrower range of mill product sizes and geometries than the press-sinter process.

Not shown in Figure 1 is electron-beam (EB) melting, which is used primarily to reprocess scrap. Unlike the PSM process, EB melting does not require powder. Dual-gun units produce ingots with better as-cast grain size control than PSM furnaces because the heat input to the molten pool can be much lower. This restricts the formation of large, elongated as-cast grains that degrade workability.
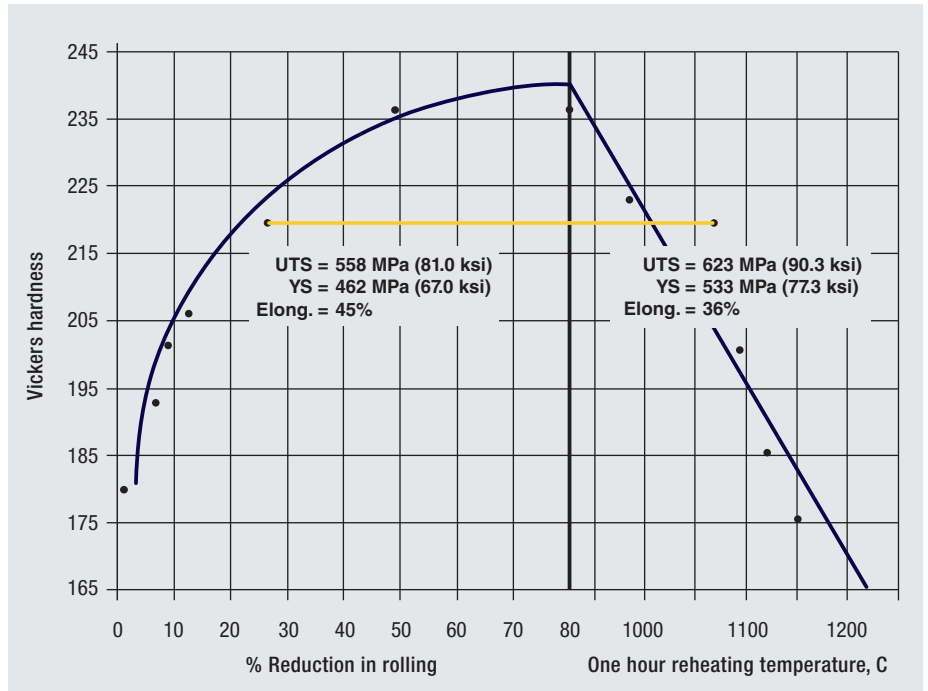

Figure 5. Effect of deformation and annealing hardness of molybdenum. Source: H. C. Starck

Mill processing of molybdenum metal can be performed on standard equipment as noted in the boxes in Figure 1. Because of its high melting point, molybdenum is processed at temperatures much higher than those used for other engineering materials. Process temperatures can be lowered as deformation accumulates. Most mill products are finished at ambient temperatures.

The deformation imparted by mill processing accomplishes more than one goal. First, it increases strength, raising the hardness and strength as shown on the left side of Figure 5[1]. As is normal for all metals, the hardening attained saturates at some point, but this effect can be reversed by annealing, which is illustrated in the right half of the figure. By appropriate choice of annealing temperature and time, the material can be "stress relieved," reducing its strength and hardness and recovering much of the ductility lost in the deformation process. The yellow reference line shows that as-rolled material does not have the same tensile properties as stress-relieved material of the same hardness. Tensile properties are path-dependent; they

result from the specific combination of deformation and thermal treatment steps used to create the final microstructure. Multiple deformation/annealing steps allow large deformations to be imparted to the workpiece without exhausting its ductility and making it brittle. A final stress-relief anneal is nearly always performed using a temperature-time combination that recovers some ductility with very little loss of strength. Figure 6 shows a microstructure typical of heavily deformed sheet after rolling and final stress-relief annealing.
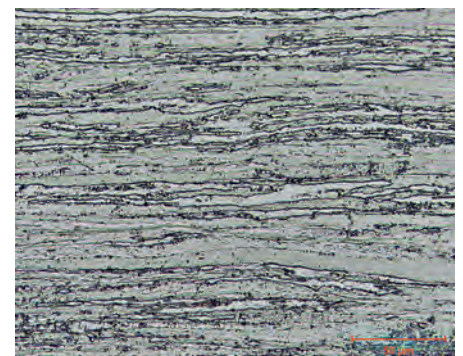

Figure 6. Typical microstructure of 0.77 mm (0.030 in) molybdenum sheet. © H. C. Starck; sample prepared by NSL Analytical Services

The second important effect of mechanical deformation is to decrease the material's ductile-brittle transition temperature (DBTT). Figure 7[2] illustrates the change in molybdenum's tensile ductility that occurs as the test temperature is lowered. Often the DBTT value is defined as the temperature at which the ductility drops to half its value on the "upper shelf." Using this measure, the DBTT for this particular material is about 0°C.

Many factors influence molybdenum's ductility, and thus its DBTT behavior. These include alloy composition and impurity content, test strain rate, the presence of intentional notches or surface defects in the sample, and thermomechanical processing. Figure 8[3] illustrates the effect of thermomechanical processing on DBTT, using a data set containing bend test results from several lots of material. In these tests, the bend angle at fracture is the measure of ductility.

The tests were performed on 1.59-mm sheet using a bend radius equal to the sheet thickness. Because the data set contains test results from multiple lots of material that contained variability in the other factors affecting DBTT, the plot shows scatter bands rather than individual points. The bands overlap because of this sample-to-sample variations. Therefore, it is unwise to interpret the overlap region to mean that there are cases where specific deformed and recrystallized material has a lower transition temperature than the same material in the deformed and stress-relieved condition. Bearing this in mind, the advantage of stress-relief over recrystallization for improving DBTT is clear.
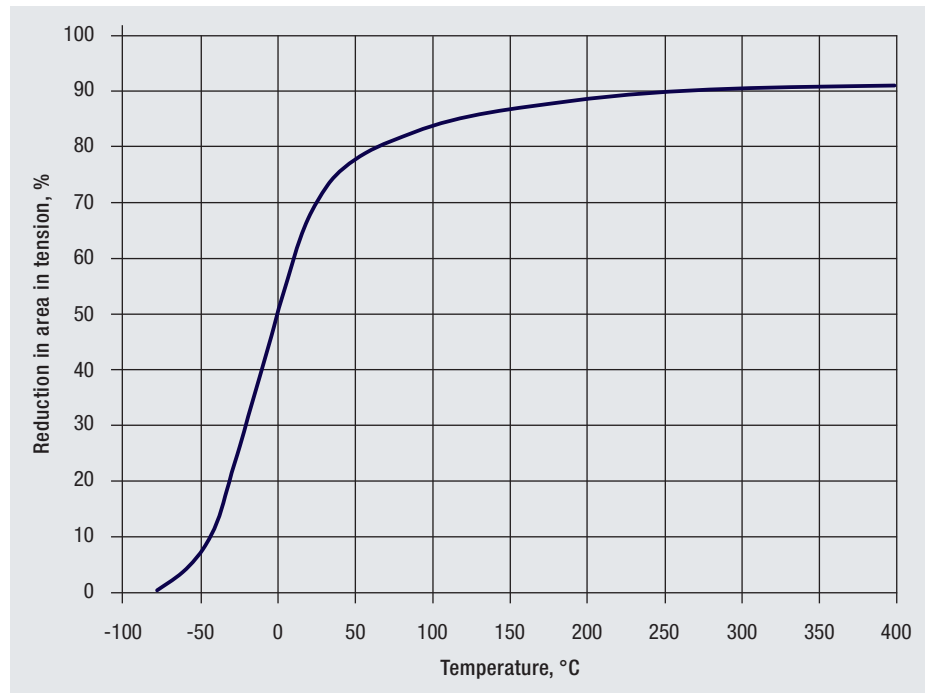
Figure 7. Ductile-brittle transition behavior in molybdenum, as measured by reduction in area in a tensile test. Source: H. C. Starck

Figure 8. Ductile-brittle transition behavior of sheet in the deformed and stress-relieved condition compared to the deformed and recrystallized condition, as measured by the angle at which cracking occurs during a three-point bend test. t = 1.59 mm (1/16"); bend radius = 1t; deflection rate = 483 mm/min (19 in/min). Source: H. C. Starck

Properties and applications of molybdenum

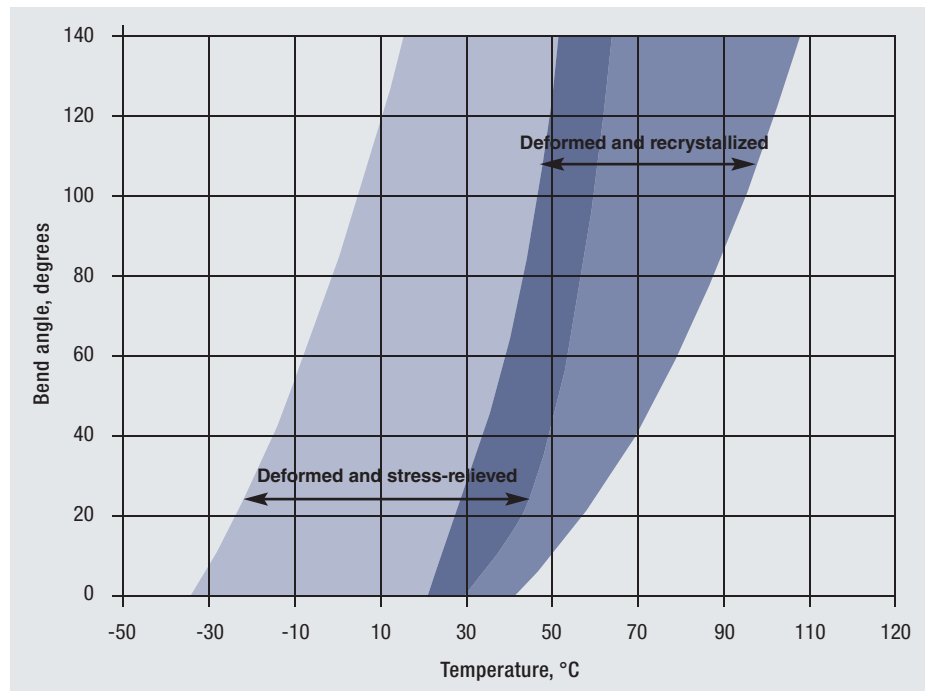An unbreakable link exists between a material's properties and its applications. In some applications, a particular property (e.g. electrical conductivity) is paramount. In others, a combination of properties taken together makes a material the optimum choice. Optimum is an important word in this context. It means that while other materials may have an advantage in one property or another, the material of choice provides the best combination of solutions to the various engineering design problems confronting the material in a given component. Sometimes the optimum solution is not a single material, but a combination of materials, or composite, that allows a designer to tailor the properties of interest to meet a challenge presented by a particular application. In all cases, cost-effective solutions are the ones that ultimately win the competition. This means that materials like molybdenum metal, which by common engineering material standards are quite expensive, must demonstrate a significant advantage over competitors.

Table I summarizes the nominal chemical composition ranges of commercially available molybdenum-based materials circa 2012. The table includes both molybdenum-based alloys and composites of molybdenum with other materials. Alloys provide higher strength than pure molybdenum, and retain that strength at temperatures higher than pure molybdenum can tolerate. The alloy section of the table is subdivided into "Substitutional," "Carbide-stabilized," and "Dispersion-strengthened" subsets.

A substitutional alloy is the simplest kind of alloy. In it, alloy atoms substitute for molybdenum atoms on the alloy's body-centered cubic (BCC) crystal structure (Figure 9). When an alloy atom substitutes for a molybdenum atom, it strains the crystal lattice, thereby increasing the material's strength.

Even though alloying increases strength, the main way molybdenum is strengthened in all cases is by mechanical deformation. This is normally done by standard rolling, swaging, and forging processes. Deformation can increase molybdenum's strength by a factor of as much as four, depending on the amount of deformation applied. For heavily worked material like wire, this factor can be even higher. Annealing removes the effects of working, causing recovery of unworked properties. Substitutional alloys may have slightly higher maximum use temperatures than pure molybdenum. However, to provide significant improvement in high-temperature strength metallurgists have resorted to other alloying approaches.

Carbide-stabilized alloys contain fine particles of reactive metal carbides in the molybdenum matrix. They also benefit from a small amount of substitutional alloying conferred by the reactive metals not present as carbides and additional interstitial hardening from carbon and oxygen atoms not contained in the carbide particles. This combination maintains molybdenum's strength to temperatures higher than possible with either pure molybdenum or simple substitutional alloys because the fine particles force recovery processes to take place at higher temperatures. Processing is a key element in the success of these alloys. The process must ensure that the reactive metals and carbon first dissolve in the molybdenum matrix, then precipitate in the required fine dispersion during the balance of the process.

Dispersion-strengthened alloys use oxide second phases, or in the case of Al/K/Si-doped materials dispersed elemental phases, that do not dissolve in the molybdenum matrix. In this case, the extremely small and stable second-phase particles must be present in the material at the very start of deformation processing. Processing is designed to create a special array of these particles that produces extraordinary high-temperature strength and stability.
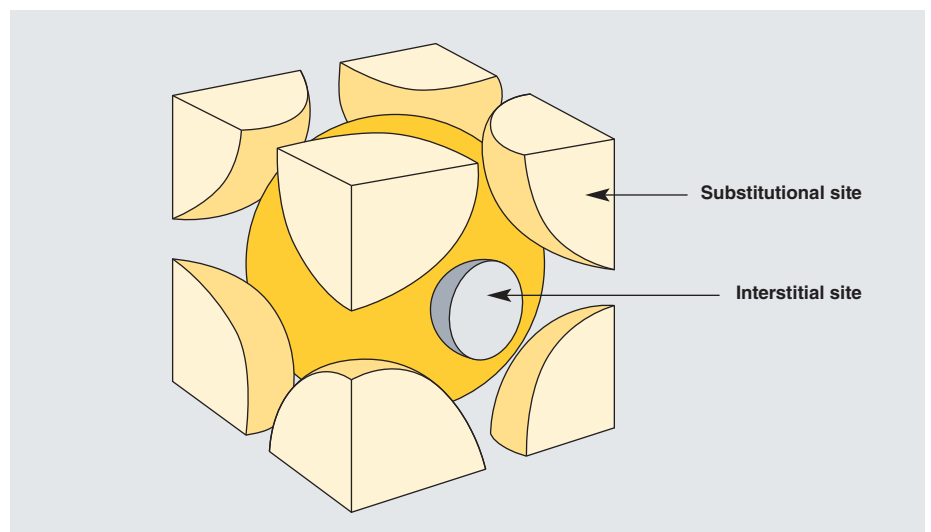

Figure 9. Molybdenum atoms are arranged on a lattice represented by a "body-centered" unit cell with atoms at the corners and center. Replicating this cell face-to-face in three dimensions will construct a complete crystal.

Table I. Nominal chemical composition ranges of commercial molybdenum-based materials

Material	Nominal composition (wt. % unless noted) or structure	Application examples
Pure molybdenum		
Mo	Min. 99.95–99.97 Mo (depending on the producer)	Constitutes the majority of Mo metal products: furnace and glass melting components, power semiconductor heat sinks, sputtering targets used to manufacture thin films in flat-panel displays and thin-film solar cells, powders spray-dried with either organic binders for high-speed pressing, or ADM for thermal spray applications
Alloys		
Substitutional alloys		
Mo-W	10–50 W	Equipment for handling molten Zn, glass stirrers
Mo-Re	3 Re, 5 Re, 41–47.5 Re	Thermocouples (low Re) and applications requiring low-temperature ductility (high Re)
Mo-Ta	10.7 Ta	Thin films in touch-screen displays
Mo-Nb	3.0–9.7 Nb	Thin films in touch-screen displays
Carbide-stabilized alloys		
TZM	0.5 Ti-0.08 Zr-0.03 C	Isothermal forging dies, injection molding tooling, metalworking tools, X-ray targets
MHC	1.2 Hf-0.08 C	Extrusion dies, metalworking tools
Dispersion-strengthened alloys		
$Mo\text{-}La_2O_3$	0.43–1.20 La, 0.075–0.21 O	Furnace heating elements, sintering boats, lamp components
$Mo\text{-}ZrO_2$	1.24 Zr, 0.43 O	Glass-melting furnace components
$Mo\text{-}Y_2O_3\text{-}Ce_2O_3$	0.37–0.43 Y, 0–0.06 Ce, 0.11–0.12 O	Halogen lamp components, evaporation boats
K/Si doped	0.01–0.07 Si, 0.005–0.03 K, 0.01–0.07 O	Lamp components, heating elements
Composite materials		
Laminates		
Cu-Mo-Cu	Various Cu/Mo ratios possible; typically between 13% and 25% Cu thickness per side	Heat sinks for semiconductors and integrated circuits
Mo-Ni	Typically 5% Ni thickness bonded to one side	Power semiconductor heat sinks
Powder composites		
MoCu	15 Cu, 30 Cu	Heat sinks for power integrated circuits: hybrid vehicles, mobile telephone cell transmitters
Mo-Ti	50 atomic % Ti	Sputtering targets to manufacture thin films in flat-panel displays and thin-film photovoltaic devices
Mo-Na	1–3 Na	Sputtering targets to manufacture electrodes in thin-film photovoltaic devices
Thermal spray powders		
Pure Mo	99.0 Mo	Piston rings, synchro rings, continuous casting & ingot molds
Mo-C	Up to 6 C	Piston rings, synchro rings, pump impeller shafts
17.8Ni-4.3Cr-1.0Si-1.0Fe-0.8B	17.8 Ni-4.3 Cr-1.0 Si-1.0 Fe-0.8 B	Piston rings, synchro rings

Composite materials fall in two classes: laminates and powder composites. Laminates are produced by roll-bonding Cu or Ni to a molybdenum core. Powder composites are produced by either blend/press/sinter (sometimes augmented by hot isostatic pressing, or HIPing) or liquid-phase infiltration techniques.

Table II cross-references a selection of properties and applications, noting the properties important for each application. Neither the property nor the application list is exhaustive. Manufacturing properties like machinability and formability come into play in the economic decision to manufacture a specific component, but the basic material options are defined by the application's requirements. It is apparent from the table that no application is built around only a single property. For example, heat sinks for power semi-conductors must have thermal expansion coefficients that minimize thermal stresses during operation, but they must also conduct heat and electricity efficiently, since their job also requires them to both pass current and remove the heat from the semiconductor. If the power devices are in aircraft or spacecraft, density becomes a much more important factor than if they are part of equipment like power controls for large stationary motors.

Thus, one must think in terms of a "suite" of properties when matching a material to an application. Once the required suite for a given application is understood, the appropriate alloy or composite may be selected for the application. When no existing material system is available, consideration can be given to developing a new material with a set of tailored properties. This decision must be made with an understanding of the landscape of competitive materials systems and their cost, availability, and reliability compared to the molybdenum-based option.

Molybdenum-based materials systems are used in all the applications in Table II and many more because as noted earlier, they have unique property suites that make them ideal for those applications. The remaining sections of this brochure present short descriptions a few of of molybdenum's many applications, and discuss the properties that enable molybdenum to succeed.

Table II. Selected applications and properties required of molybdenum

Property	Application								
	Halogen lamps	Heat sinks	LCD & photovoltaic	Semiconductor manufacturing	X-ray tubes	Hot-work tooling	Liquid-metal and glass processing	Furnace components	Surface coating
Physical properties									
Density		X							
Electrical conductivity	X	X	X		X		X	X	
Thermal conductivity		X			X	X	X		
Thermal expansion	X	X	X		X	X	X	X	
Mechanical properties									
Elastic modulus	X	X		X	X	X	X	X	
Hot strength	X			X	X	X	X	X	
Creep resistance				X	X	X	X	X	
Other properties									
Wear/Erosion resistance						X	X		X
Corrosion resistance	X		X	X			X		X
Bond strength with substrates	X	X	X		X				X

Lighting

Incandescent lighting was the first molybdenum metal application. Its use, dating back to about 1910 [4], was in the form of wire filament supports in incandescent lamps (Figure 10). Lighting applications continue to account for large quantities of molybdenum metal [5] production today as both lamp components and wire used as mandrels to coil tungsten filaments. At the time of writing, this is changing dramatically as the incandescent lamp is being replaced by compact fluorescent lamps (CFL) and light-emitting diode (LED) lamps. Lighting technology is far more advanced today than it was a century ago, but molybdenum is still used for support wire and glass feed-throughs in halogen lamps and as mandrel wire around which tungsten filaments are coiled during manufacturing. Halogen and high-intensity discharge (HID) lamps operate at much higher temperatures than standard incandescent lamps, so require more sophisticated materials solutions. Lower power (<100 W) halogen and HID lamps employ vitreous silica glass envelopes to withstand the higher temperatures generated by their sources. The coefficient of thermal expansion (CTE) of vitreous silica varies between

Figure 11. Halogen lamp showing molybdenum feedthroughs (left) and reflector (arrow right). © Plansee SE

3.0×10^{-7} K^{-1} and 8.0×10^{-7} K^{-1}, between room temperature and 1500°C. Molybdenum's CTE averages 5.8×10^{-6} K^{-1} between 0°C and 1000°C. Thus, even though molybdenum is required as a feed-through material because of the lamp's temperature, significant thermal stresses develop as the lamp heats. To accommodate them, a carefully profiled thin molybdenum sheet is used for the feedthrough, allowing plastic deformation in the molybdenum sheet to relieve the stresses. For lower-power lamps, or those having larger dimensions, the glass envelope can be made from alkali-free borosilicate glass (average CTE approximately 5×10^{-6} K^{-1} between room temperature and 500°C) or aluminosilicate glass (average CTE approximately 4.6×10^{-6} K^{-1} between room temperature and 300°C). Figure 11 shows two views of an automotive halogen lamp. The lamp envelope on the left shows the molybdenum foil feed-throughs, while the assembly on the right shows a molybdenum reflector (arrow) designed to minimize "blinding" of approaching drivers. The feed-through employs molybdenum foil because of its low CTE, good electrical conductivity, and strong bonding with silica glass. Molybdenum's excellent high-temperature strength and mechanical stability, and resistance to corrosion by the halogen gases inside the lamp envelope (a critical feature for the application), make it ideal for the reflector. These properties also make it a material of choice for similar components of high-intensity lamps.
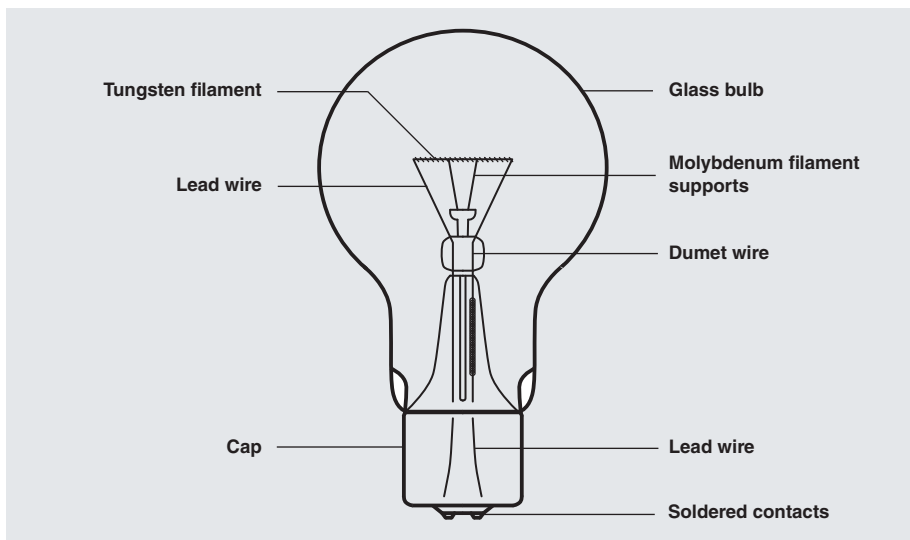

Figure 10. Schematic of incandescent lamp. Drawing courtesy GE Lighting, simplified for clarity

Tungsten filament

Lead wire

Glass bulb

Molybdenum filament supports

Dumet wire

Cap

Lead wire

Soldered contacts

Electrical and electronic devices and manufacturing

Electrical power devices

Electron vacuum tube manufacturers capitalized on molybdenum's lighting experience, using it for filament supports and grids because of its high-temperature strength and mechanical stability. Solid-state electronics long ago eliminated vacuum tubes from common use. As molybdenum's use in vacuum tubes declined, solid-state device designers discovered that properties other than high-temperature strength continued to make molybdenum indispensible. Molybdenum's CTE is close to that of silicon, and molybdenum has excellent thermal and electrical conductivity. These properties make it ideal as a substrate for fragile silicon devices. Molybdenum provides a strong, rigid base that conducts electricity to and from the device and removes heat efficiently. Its low CTE minimizes differential expansion stresses. Thus, the driving force for molybdenum's use in electronic devices shifted from mechanical properties (high-temperature strength and stiffness) to physical properties (thermal expansion, electrical conductivity, and thermal conductivity). In fact, by 2009 the use of molybdenum by electronic devices equaled that for lighting products[6].

Table III lists selected physical properties of several materials used in electronic devices, including molybdenum. The

Table III. Physical properties of electronic packaging materials at room temperature[7]

Material	Coefficient of thermal expansion (CTE) α, 10^{-6}/K	Thermal conductivity k, W/(mK)	Young's modulus E, GPa	Density ρ, g/cm^3	k specific, W/(mK)*	E specific, GPa*
Si	2.6[8]	150	130−169[9]	2.3	65.2	56.5−73.5
GaAs[10]	5.7	55	83.9	5.3	10.4	15.8
Al_2O_3	6.7	21	380	3.9	5.4	95.0
BeO	8.0	275	345	2.9	94.8	119.0
AlN	4.5	250	327	3.2	78.1	102.2
Si_3N_4	3.3	–	304	3.2	–	95.0
Diamond	1.7	2300	785	3.5	657	224
Epoxy/Glass FR4 12/70	15.8**; 80−90***	1.7	17.2	1.9	0.9	9.1
Al (1100)	23.0	240	69	2.7	88.9	25.6
Cu	16.9	398	125	8.9	44.7	14.0
Mo	5.0****	140	324	10.2	13.7	31.8
Kovar®	5.3	17	138	8.3	2.0	16.6
Mo30Cu[11] (Infiltrated powder composite)[11]	7.1	205	–	9.7	21.1	–
W20Cu[11] (Infiltrated powder composite)[11]	8.7	235	–	15.5	15.2	–

* Specific properties are ratioed to specific gravity   ** In-plane   *** Through-thickness   ****This value is somewhat lower than the more commonly used value of 5.2
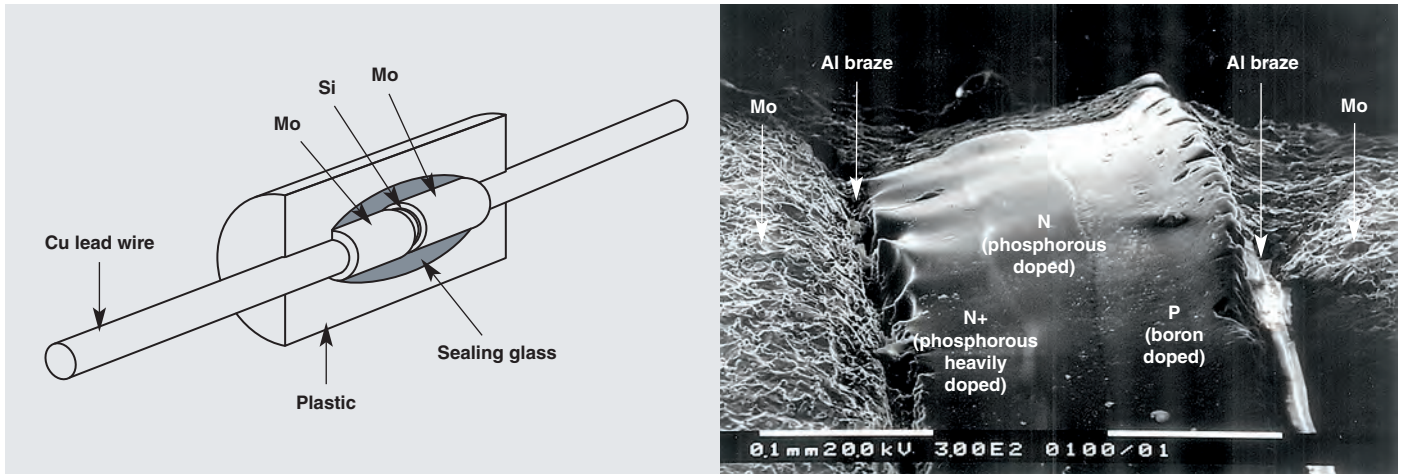
Figure 12. Left-hand image shows a schematic of a small power semiconductor diode using pressed and sintered molybednum heat sinks. Right-hand image shows the semiconductor junction and brazed assembly details, showing the size of a typical device.
© Prof. K. S. Hwang

table summarizes coefficient of thermal expansion (α), thermal conductivity (k), elastic modulus (E), and density (ρ). The table also includes specific thermal conductivity and elastic modulus, obtained by dividing the individual properties by specific gravity. These "specific properties" are important in weight-sensitive applications like aerospace components. Table II includes device materials, substrate materials used in integrated circuits, packaging and interconnect materials, and thermal management materials. Demands for ever increasing device performance have pushed operating temperatures higher. In response, thermal management materials have evolved toward highly engineered composite systems designed to optimize the combination of matched thermal expansion and high thermal conductivity.

The left side of Figure 12 [12] illustrates a thermal management application that has used pure molybdenum for many years, a diode heat sink found in the rectifier circuits of countless consumer products. The right side of Figure 12 is a high-magnification SEM image of a brazed diode assembly. The Si chip is doped on the left hand side with phosphorous to make it an N type semiconductor, then additional P is doped near the surface making this region an N+ semiconductor. The additional doping is needed to

counteract the effect of the aluminum brazing material, which tends to make the silicon a P-type semiconductor. The right hand side is doped with boron to make it P type. The heat sinks are pressed and sintered from molybdenum powder. They conduct power through the diode and remove heat from it. Millions of these tiny cylinders are made each day using automated high-speed presses. Standard molybdenum powder, shown in Figure 2, is incompatible with this equipment because it does not flow readily. It does not have a good morphology for powder used with automatic feeders. To solve this problem, the powder is spray dried with a water-based organic binder solution. The spherical aggregates thus produced are shown in Figure 13. The spherical agglomerates have high flowability, while the binder enhances the green strength of the as-pressed parts and lubricates the particles and die walls, reducing pressing loads, extending tool life, and minimizing tool failure.

Pressed and sintered heat sinks work very well for low-power rectifiers, but the parts are not fully dense. Residual porosity is always present in pressed and sintered parts, and the pores reduce the heat sink's thermal conductivity. Sintered molybdenum also has lower toughness than wrought (deformed) material. High-power semiconductor applications

demand maximum performance, so heat sinks for these devices are manufactured from fully dense molybdenum sheet. Molybdenum heat sinks for high-power devices have been an important part of solid-state electronics technology for many years. Power semiconductors handle large electric currents; they are used in applications like motor controls for transit vehicles and industrial equipment, and electrical power generation.
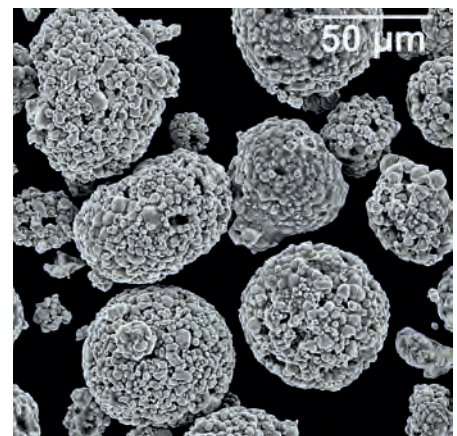

Figure 13. Spray-dried molybdenum powder, showing the highly flowable spherical particles.
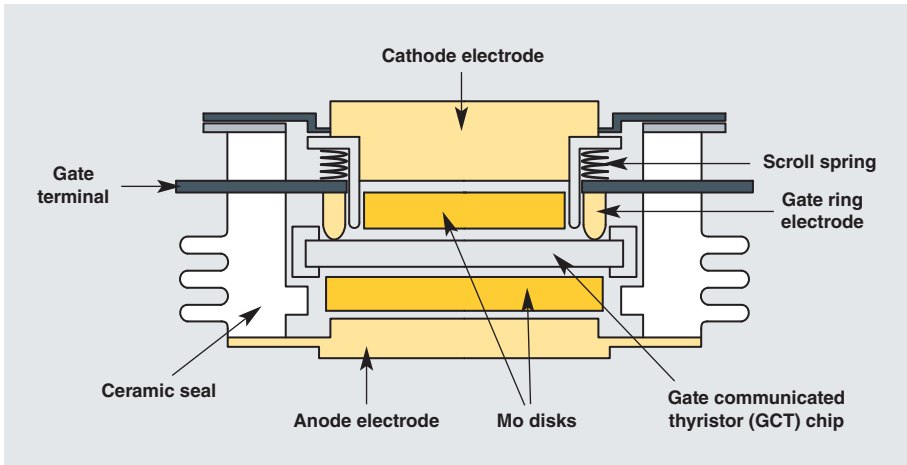© H. C. Starck

13

Figure 14. Schematic of power semiconductor device. Source: Powerex
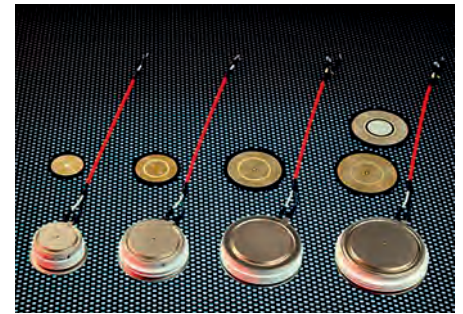

Figure 15. Power semiconductor devices. © Powerex, Inc.

Figure 14 is a schematic of a semiconductor thyristor showing the stack of molybdenum plates and the power semiconductor inside the device. Figure 15 shows examples of several power semiconductor packages that employ molybdenum heat sinks.

Some applications require a CTE higher than that of pure molybdenum. One example would be the case of epoxy-glass circuit boards containing surface-mount ceramic integrated circuit packages, the application that led to the development of copper-clad molybdenum. Another is the need for thermal management of ceramic packages directly mounted on the heat sink, which led to the development of Mo-Cu powder composites. Combining molybdenum and copper can increase the CTE and at the same time increase thermal conductivity. Two approaches are possible: manufacturing laminated copper/molybdenum/copper (CMC) sheet and producing molybdenum/copper (MoCu) powder composites by either solid-state sintering or liquid infiltration.

Figures 16 and 17 show the effect of copper/molybdenum cladding ratio on thermal conductivity and thermal expansion of CMC sheet, respectively. Copper increases the thermal expansion coefficient, allowing designers to tailor a match with ceramic substrate materials like alumina (Al_2O_3) and beryllia (BeO).
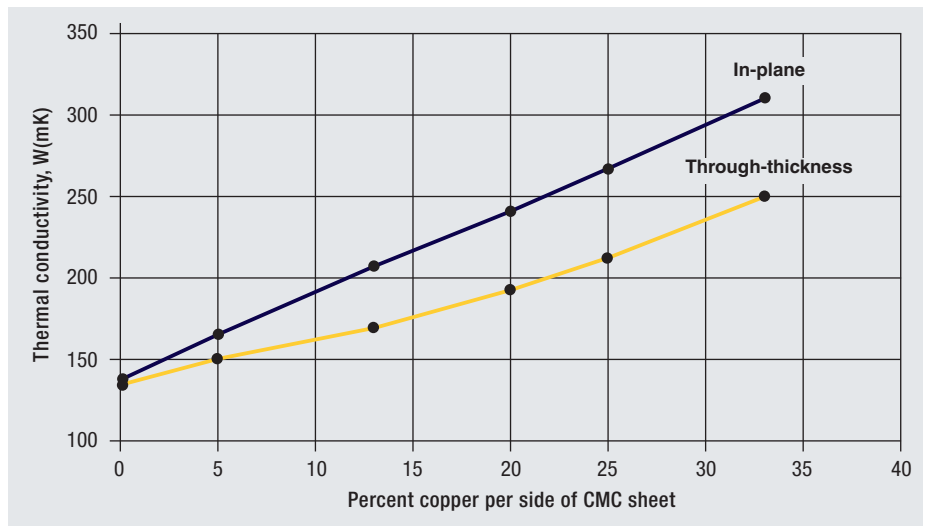

Figure 16. Effect of copper on thermal conductivity of CMC sheet. Source: H. C. Starck
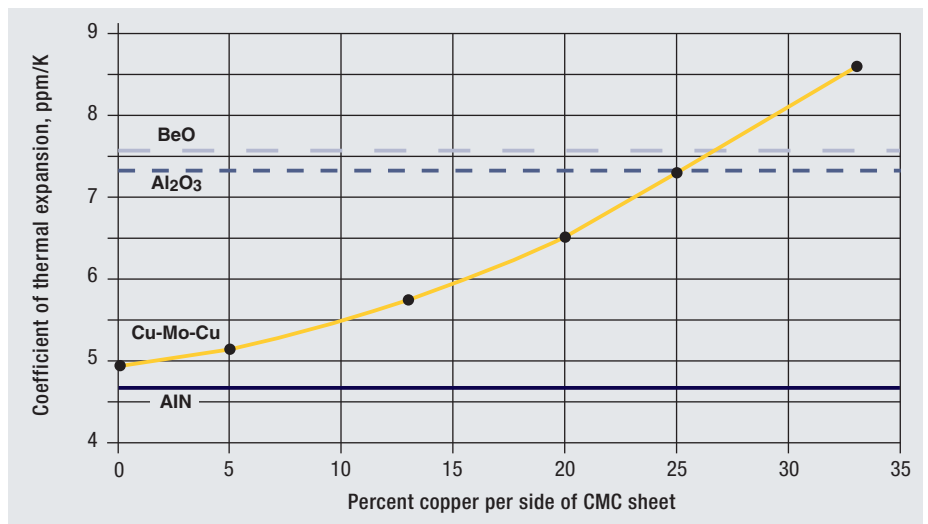

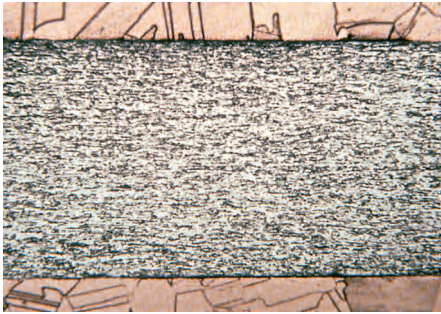Figure 17. Effect of copper on CTE of CMC sheet. Source: H. C. Starck

14

Figure 18. Microstructure of CMC sheet.
© H. C. Starck; sample prepared by NSL Analytical Services

Figure 19. Microstructure of an infiltrated MoCu heat sink material containing 30 wt.% copper.
© Plansee SE

Figure 18 illustrates the microstructure of this unique material. The anisotropic properties shown in Figure 16 can be an advantage when lateral heat spreading is more important than through-thickness conduction, because devices attach to the high-conductivity copper surface.

If isotropy of thermal properties is paramount, MoCu composites having several copper/molybdenum ratios are available. MoCu is typically made by presintering a molybdenum skeleton to attain a controlled volume fraction of interconnected porosity, then filling the pores with liquid copper by infiltration. This process is possible for only a limited range of compositions because it requires a presintered molybdenum skeleton having open porosity to accommodate the copper. However, it produces a superior combination of properties in the finished component, because of the mechanical restraint imposed by the sintered molybdenum lattice. Figure 19 illustrates the micro-structure of such a MoCu heat sink.
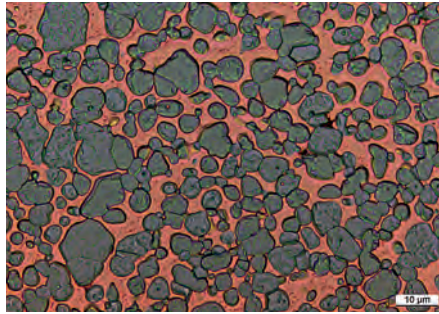
It is possible to produce MoCu using traditional blend/press/solid-state sinter processes. However, this approach produces inferior properties because residual porosity is always present in these materials after sintering. The pores cannot conduct heat, so degrade the composite's thermal conductivity. These composites also do not have the beneficial constraining effect of the molybdenum

skeleton, so they have higher TCE values for any given composition, an undesirable effect. Figure 20 illustrates this point for tungsten with data presented in the original patents for this class of materials.[13, 14, 15, 16] Tungsten-copper (WCu) and MoCu are analogues because the chemical and physical properties of molybdenum and tungsten are very similar to one another, and because WCu composites use the same manufacturing processes as MoCu composites. For a given thermal expansion coefficient, the infiltrated composite always has a higher thermal conductivity than the blended and sintered material. The advantage is about 10%, a significant increment in these applications.

Infiltrated MoCu is found in heat sinks for integrated gate bipolar transistor (IGBT) power devices used in hybrid vehicles. While tungsten-copper has a better combination of TCE and thermal conductivity than molybdenum-copper, the need to save weight and minimize costs in automotive applications makes MoCu the preferred choice.
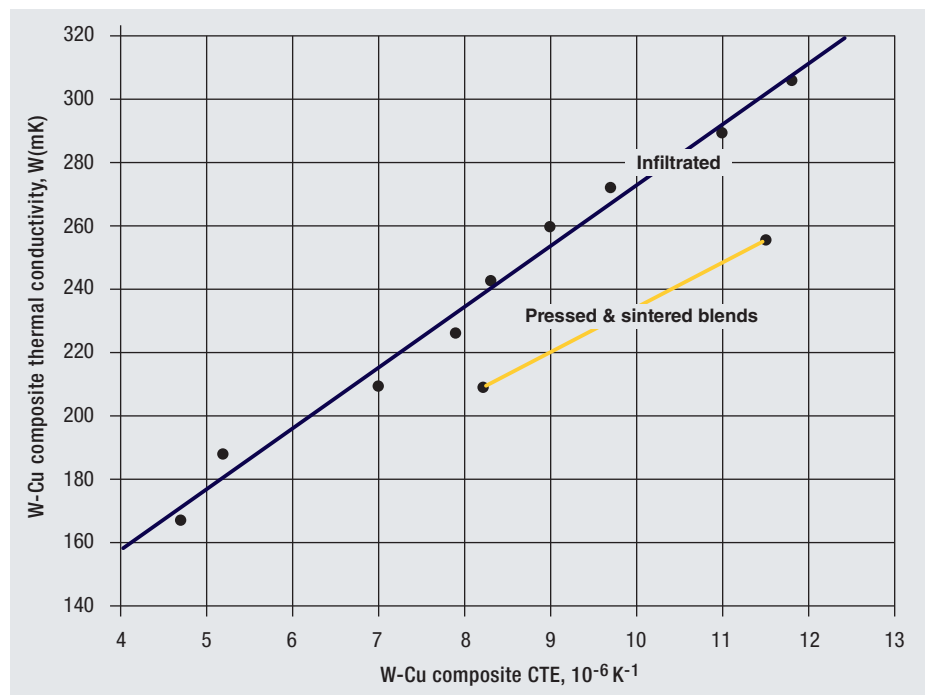

Figure 20. Thermal conductivity vs. thermal expansion for WCu composites made by solid-state sintering and liquid infiltration. MoCu composites behave in a similar fashion.
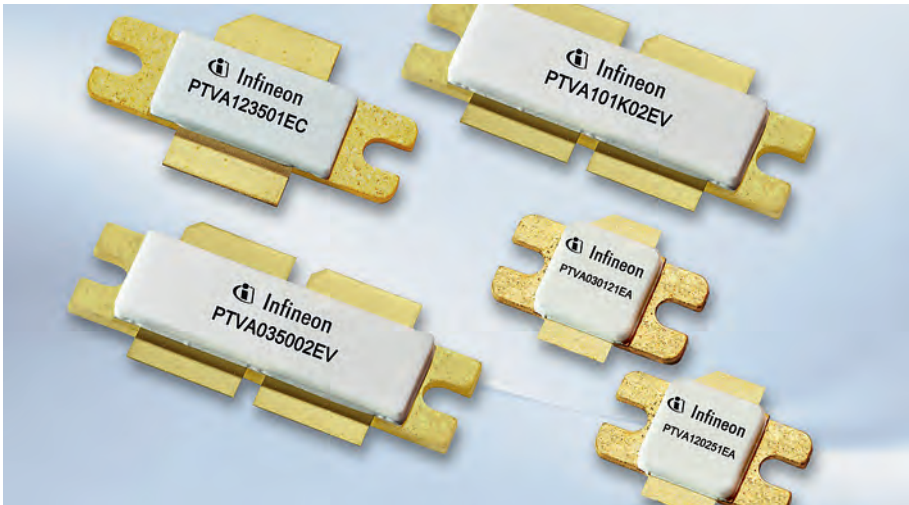
Figure 21. Power transistors of a design that employs Cu-MoCu-Cu composite heat sinks. © Infineon

The two approaches (sintering and cladding) to creating composites are not mutually exclusive. Manufacturers have clad a MoCu infiltrated core materials with copper to further increase the performance of the system[17], improving the thermal properties compared to those of either composite alone. Figure 21 shows an example of power semiconductor devices that employ this "composite-composite" material. Figure 22 shows the cross-section of the doubly composite material. Cu-MoCu-Cu composites can also be rolled to produce thin foils that are used in sapphire-based LED chips. Cu-MoCu-Cu wafer substrates with a CTE of 6.1 to 6.7 10^{-6} K^{-1} provide a thermal expansion buffer

between the sapphire base and the LED semiconductor during soldering, and also provide long-term heat dissipation during lamp operation.

Thin films and sputtering targets

Molybdenum has played an important part in eliminating long-standing technologies like cathode-ray tubes. The thin film transistor liquid crystal display (TFT-LCD) technology that revolutionized instrument, computer, telecommunications, and television displays relies on yet another set of molybdenum properties. LCD displays have a light source (either LEDs or cold-cathode fluorescent lamps) behind the screen that illuminates the

various picture elements (pixels). For each pixel, individual TFTs control the electric field surrounding each liquid crystal, allowing the liquid crystal to admit the appropriate amount of light to illuminate the pixel. Molybdenum thin films are used in the gate metallization and source/drain electrodes of the TFT, while the main electrically conductive layer is usually aluminum or copper, which both have higher electrical conductivity than molybdenum. Molybdenum serves several purposes:

- It bonds strongly to the glass substrate, promoting adhesion of aluminum and copper conductors.
- In contrast to Al, it forms a low resistivity contact to the indium tin oxide (ITO) pixel electrode.
- Its high melting point, combined with the low diffusivity of aluminum and copper in molybdenum, makes it an excellent diffusion barrier to prevent current-driven diffusion, or electromigration, that can cause device failure.
- It is compatible with the chemical processes used to produce displays, and can be patterned by wet etching along with aluminum and copper.

Flat panel displays use the same manufacturing technology as traditional silicon solid-state devices, with multiple steps of applying a thin film, etching unneeded material away, and applying and etching many subsequent layers to build the device up from the glass substrate. One type of physical vapor deposition (PVD), known as sputtering, is commonly used to deposit these thin films. Sputtering has been described as a game of "atomic billiards," because it uses collisions between ions and atoms to liberate the thin film atoms from a reservoir called a sputtering target.

Figure 22. A "composite-composite" structure showing a MoCu core and a copper surface layer. © Plansee SE
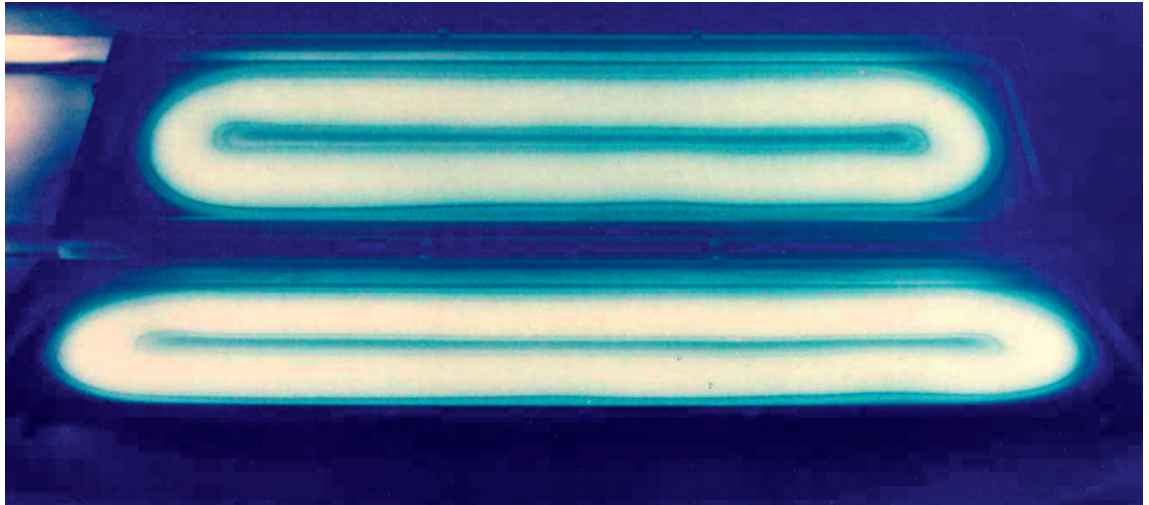
Figure 23. A sputtering target during operation, showing the blue glow associated with its Ar plasma. © Materials Science, Inc.

Figure 23 shows a sputtering target during operation. Low-pressure argon gas is ionized by applying a voltage to the target, creating a plasma consisting of positively charged argon ions (Ar+), free electrons, and neutral argon atoms. The plasma produces the striking glow seen in Figure 23. The Ar+ ions are accelerated towards the negatively charged target (acting as a cathode) by the electric field. They hit the target surface with high kinetic energy, knocking out some target atoms. The typically neutral target atoms fly away from the target in straight lines and deposit on the substrate surface. Because of this line-of-flight deposition, the target and substrate must be closely matched in size and close to one another to maximize yield. To maximize productivity, multiple screens are produced on a single sheet of glass, so as display size increases the target area must keep pace. In a short time from inception of the technology, target sizes increased to the point where they began to exceed molybdenum plate manufacturing capability, multiple-target arrays were developed as alternatives to large monolithic targets. Figure 24 shows a flat target and tubular targets.
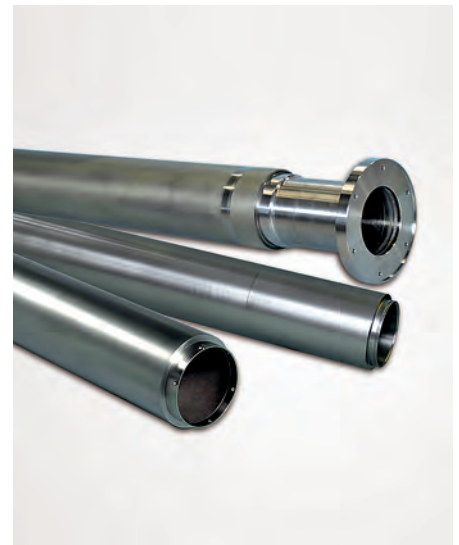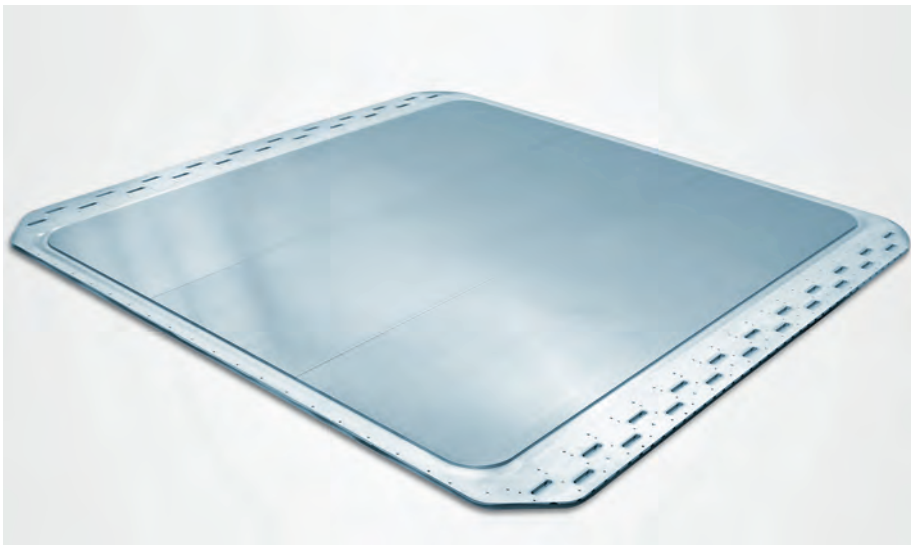

Figure 24. Sputtering targets are now produced in an array of sizes and forms. © Plansee SE

Material development continues to evolve as new higher-performance designs evolve to meet increased display performance requirements. Composite Mo-Ti targets manufactured using a powder metallurgy (PM) approach that employs combinations of blending, pressing, sintering, and hot isostatic pressing (HIP)[18]. Figure 25 shows the microstructure of a typical Mo-Ti target.

TFT-LCD and touch-screen panel applications employ Mo-Nb and Mo-Ta alloys that exhibit greater corrosion resistance in humid ambient atmospheres, but retain low electrical resistivity and excellent wet etching characteristics.

All these materials must fulfill several requirements. The molybdenum layer must bond strongly with substrate and semiconductor materials, forming low-resistivity contacts to allow efficient electrical conduction. It must have a good thermal expansion match and good thermal conductivity to dissipate heat. It must also be compatible with the chemistry used in panel manufacturing processes, capable of being etched precisely while protecting underlying layers from potentially damaging environments.

An emerging market that requires molybdenum thin films is solar power[19]. Early solar panels employed single crystal silicon as the power conversion element in their design. However, compared to emerging thin-film cell technologies these devices are quite expensive. Thin-film technologies offer high conversion efficiencies[20] at attractive costs compared to traditional single-crystal solar cells. One of the two main thin-film photovoltaic materials is copper-indium-(gallium)-selenide (CIGS). In these cells, the photoelectrically active absorber layer is a compound semiconductor layer having a crystalline or amorphous structure is based on chalcopyrite in the form of $Cu(In_x, Ga_{(1-x)})(Se_y, S_{(1-y)})_2$. Molybdenum is an important part of the CIGS solar cell structure, forming the back contact that lies beneath the entire panel. Figure 26 is a color-enhanced scanning-electron-microscope (SEM) image of a
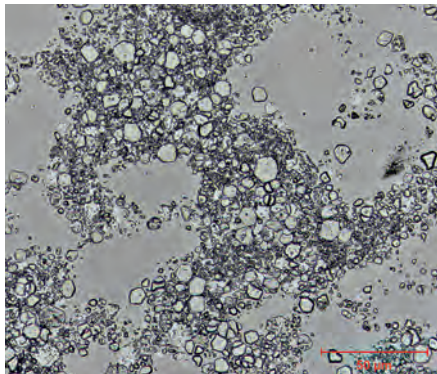

Figure 25. Microstructure of a Mo-Ti target.
© H. C. Starck; sample prepared by NSL Analytical Services

CIGS solar cell cross-section. Because CIGS cells can use polymer or metal substrates as well as the glass substrate shown in the image, they allow for low-weight flexible (i.e. bendable) designs. Solar cells and flat panel displays use molybdenum for the same reasons: reliable adhesion to both the substrates and to the display components or active solar cell material, good CTE matching to minimize thermal stress and related cracking, good electrical conductivity, and compatibility with processing environments.

High-efficiency CIGS cells incorporate alkali metals into the absorber layer. Studies have shown that sodium produces the greatest increase in efficiency, followed by potassium and lithium, while cesium has virtually no influence[21]. Typical sodium concentrations are in the order of 0.1 atomic %, with sodium, being distributed preferentially at grain boundaries in the CIGS layer. This improvement in efficiency is attributed to both electronic and structural effects. The structural effects include the favorable influence of alkali metals on the growth and the morphology of the CIGS layer. One electronic effect is an increase in effective charge carrier density and therefore conductivity, which increases in the open-circuit voltage of the cell.

Doping of the absorber layer with the alkali metal can be accomplished by diffusion of sodium from the soda-lime glass substrate through the molybdenum back electrode layer. However, the use of this method is restricted to rigid glass substrates. To enable manufacture of high-efficiency cells on substrates other than glass and to better control the doping process, molybdenum-sodium sputtering targets that incorporate sodium directly in the back contact layer are now available.
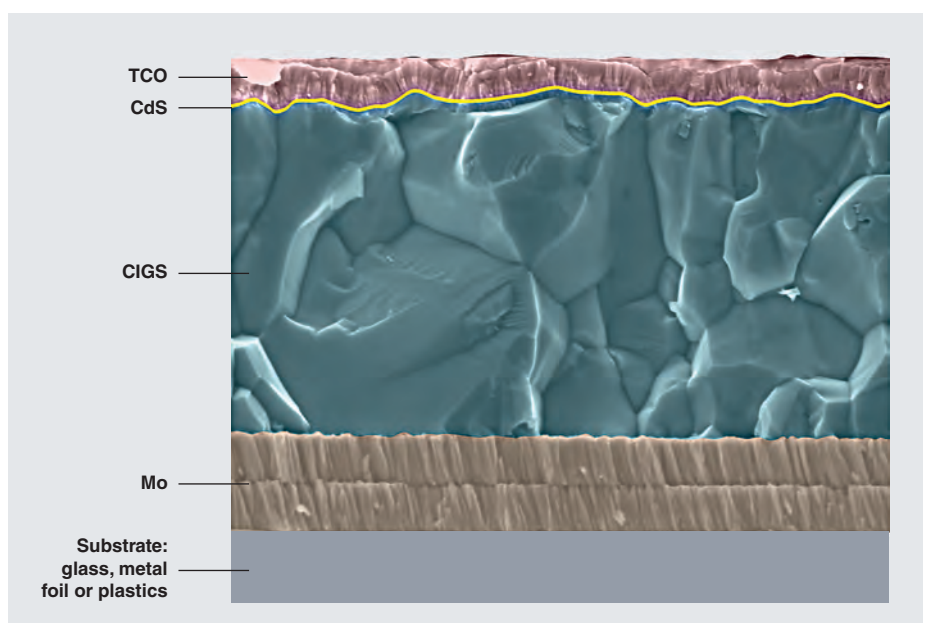

Figure 26. A highly magnified SEM image of the structure of a CIGS solar cell. This figure was prepared by the National Renewable Energy Laboratory for the U.S. Department of Energy.

The molybdenum layer can also be made up of two coating layers, one coating doped with sodium and the second layer consisting of pure molybdenum. Both coating layers can be produced by means of DC sputtering[22].

Solar cells rely on molybdenum for the same reasons that TFT-LCD panels do. Molybdenum's ability to establish strong ohmic contact with the thin-film cell structure is especially important because molybdenum's purpose is to harvest electrons generated in the cell and conduct them out to be used for electrical power.

Semiconductor manufacturing

Semiconductor manufacturing equipment has long used molybdenum for components requiring strength at temperature and compatibility with aggressive process environments. Figure 27 is a schematic diagram of the ion implantation process used to dope silicon wafers with atoms to create semiconductor devices. Highly reactive gases containing the dopant are ionized in the ion source, and accelerated by high voltage toward a magnet that "bends" the ion beams of different elements in arcs with diameters that depend on their mass/charge ratio. That way, impurities entrained in the ion beam by reaction and erosion of the ion source wall, are separated from the dopant beam directed toward the silicon substrate. Ion sources employ molybdenum because it resists reaction with dopant gases and erosion by the plasma inside the chamber. Figure 28 shows a typical molybdenum ion-source component.
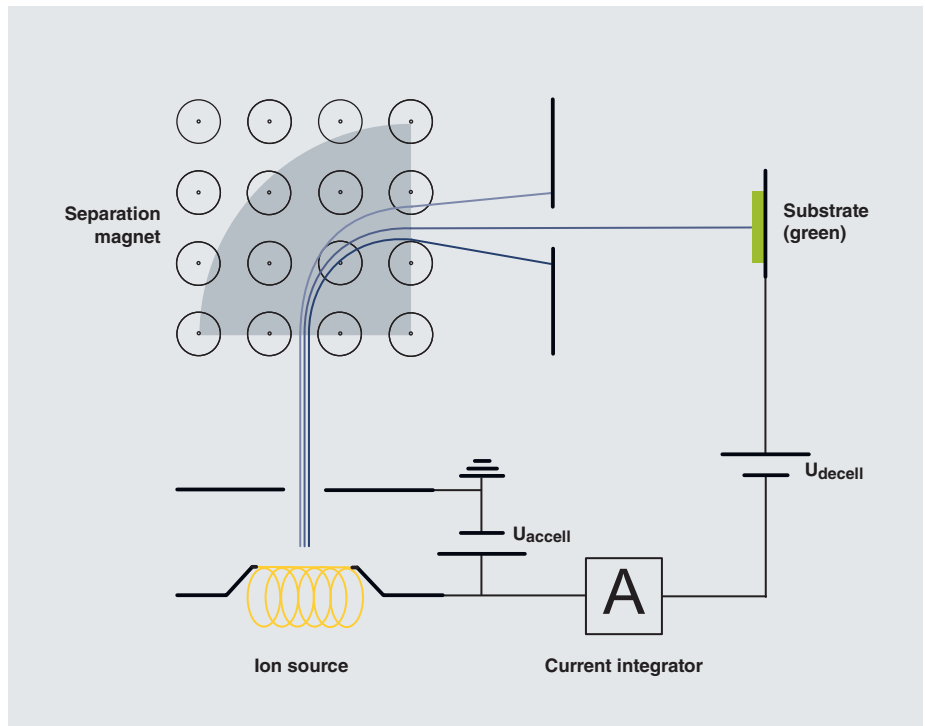

Figure 27. Schematic drawing of the ion implantation process.
Source: D. Schwen / CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/)
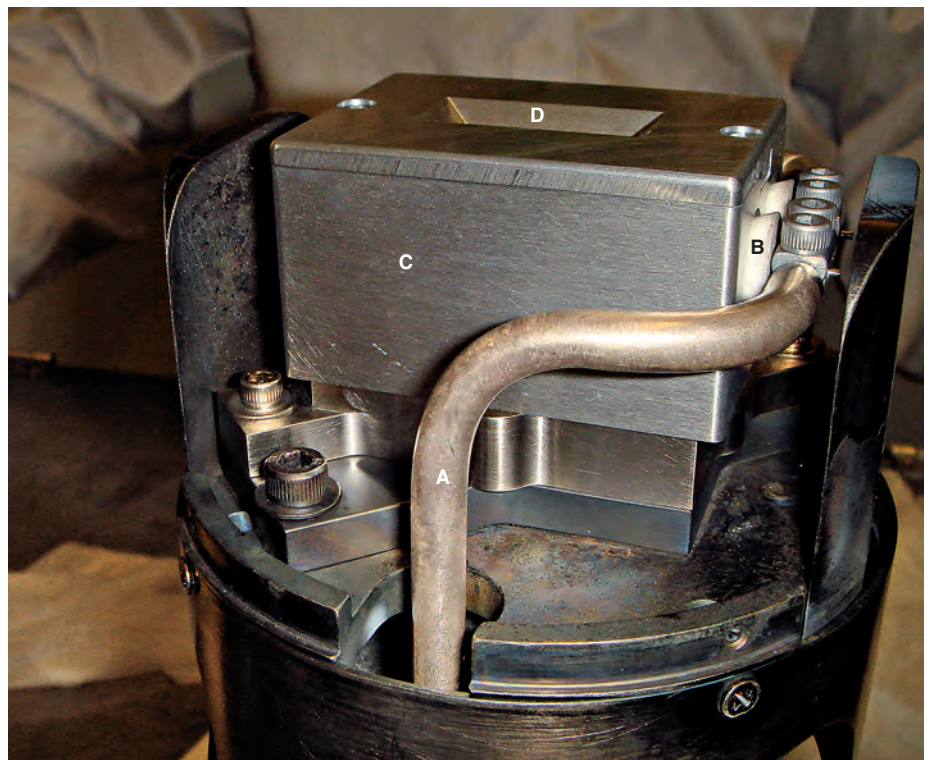

Figure 28. Assembled ion source. The power leads (A) supply power through Al_2O_3 insulating feedthroughs (B) to a tungsten filament inside the molybdenum ion chamber (C). The appropriate doping gas is ionized inside the chamber and ions are accelerated through the beam slit (D) in order to implant dopant into the silicon wafer. © Signet Products, Inc.

19

Molecular beam epitaxy (MBE) machines are used to "grow" semiconductor materials in place, atom by atom. Figure 29 is a schematic of this process. "Effusion cells" containing the elements used to make the semiconductor, e.g. gallium and arsenic, are heated to evaporate the elements. The evaporated atoms travel across the high-vacuum chamber, depositing on the substrate material where they create a semiconductor crystal aligned with the substrate's crystal structure. Molybdenum is used in this process as shutters, substrate carriers, and other internal components of the vacuum chamber. Molybdenum's chemical stability, stiffness and strength at elevated temperatures all are factors in its choice.

Photo-etched molybdenum foils serve as masks in the physical vapor deposition of circuits on semiconductors. The application requires a material that can be etched precisely and reproducibly, and that has high stiffness and flatness to ensure accurate reproduction of the etched design. Molybdenum meets these requirements.
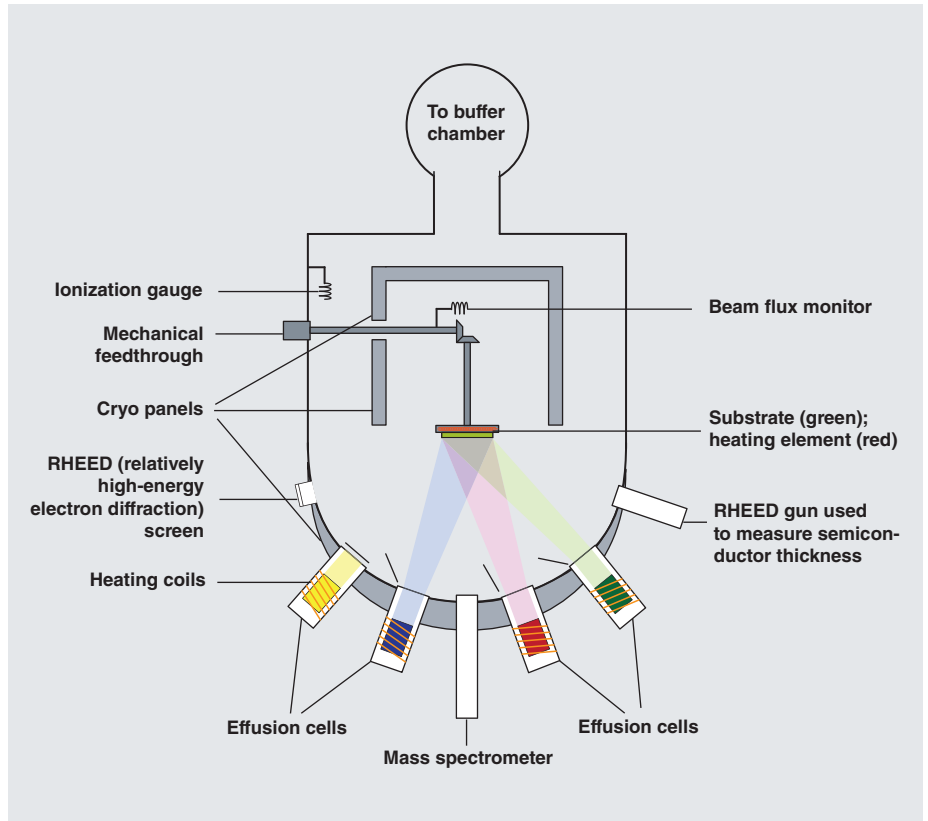

Figure 29. Schematic of molecular beam epitaxy machine.
Source: Vegar Ottesen / CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/)

Medical equipment

Molybdenum components are essential to the operation of high-power X-ray tubes used in computerized axial tomography (CAT, or CT) scanning equipment. The vacuum tube that generates X-rays is analogous in many ways to the vacuum tubes used in early electronic equipment, but it must withstand much more severe thermal and stress environments. Figure 30 is a photograph of a contemporary X-ray tube. The tube has elements similar to those in electronic tubes: a cathode (electron source), and an anode, or target (electron receptor). Electrons in an X-ray tube do not carry a signal as in electronic tubes, but instead deposit their energy into the target, thereby generating X-rays. Large electron currents and high accelerating voltages increase the X-ray

Figure 30. X-ray target showing rotor (A), stem (B), and molybdenum-alloy target (C) with tungsten-rhenium alloy track (D) for X-ray generation. Also shown are the graphite heat sink (E) and cathode cup (F) that contains the tungsten filament. © Plansee SE (X-ray tube produced by Dunlee)
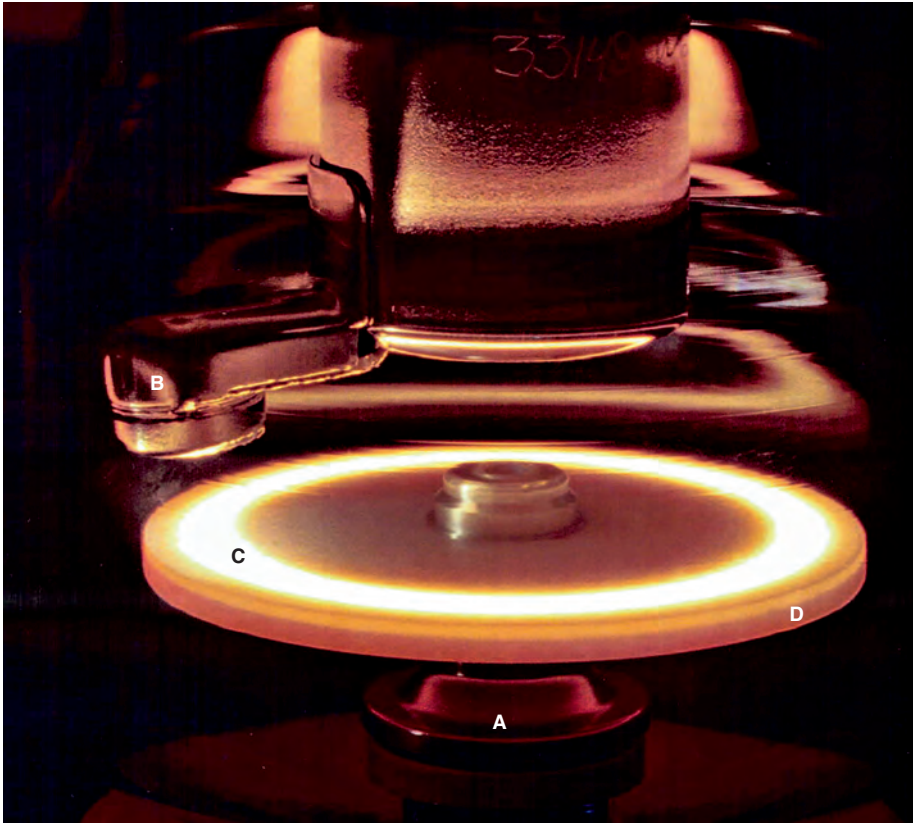
Figure 31. The target rotates at high speed, driven by the Mo-TZM rotor (A). The tungsten filament, heated to high temperatures within the cathode cup (B), emits electrons that are focused onto the W-Re focal track (C) that is integral with the Mo-TZM target (D). © Varian Medical

signals for analysis, but for different reasons. Figure 32 shows how the X-ray tube and detector array rotate around the patient during a scan. The two components are coupled with one another on a large gantry assembly designed to hold constant their geometric relationship with one another. This is necessary because of the precision required by the mathematics used to analyze the signals.

The detectors are individual cells that use molybdenum foil as collimators (walls that separate the detectors from one another). Molybdenum is used because it has a high elastic modulus that resists bending under centrifugal loading during operation, and because it effectively shields neighboring detectors from errant radiation. Extremely tight tolerances on sheet thickness are maintained so the entire detector array remains within overall dimensional tolerances, and does not suffer from tolerance "stack up" that would degrade image quality. Very thin molybdenum foils are also used as filters in mammography imaging systems.

yield from the process, which is inherently inefficient. Most of the beam energy creates heat, not X-rays, so the target must survive very high temperatures. The cathode assembly employs molybdenum parts machined from mill products. These parts must withstand the thermal loads imposed by the filament inside. The rotor also uses machined molybdenum or Mo-TZM alloy round bar because it supports the spinning load of the large target, and conducts heat down and away from the target. High-temperature strength is paramount in this component as well. The target is probably the most important part of the tube, as it must endure extremely high temperatures, associated high thermal stresses, and mechanical stresses from the centrifugal forces present in the spinning target, which may operate at speeds up to 10,000 RPM. The target is typically made from Mo-TZM, or proprietary carbide-strengthened alloys similar to TZM

in order to withstand these stresses. It contains an integral track made from tungsten-rhenium alloy on the outer surface, which can exceed 70% of its melting temperature during operation. The target and track are made together as a single unit, pressed from powders in a steel mold and sintered to densify the target and bond the tungsten-rhenium alloy track to the Mo-TZM substrate. The sintered target is then hot forged to slightly densify it and improve its strength, machined to finish dimensions, and brazed to a carbon heat sink whose purpose is to store the heat created while the tube is operating and release it in a controlled fashion. Some target designs call for coating the graphite heat sink to increase its thermal emissivity. Figure 31 shows a finished tube during a post-manufacturing test.

Molybdenum sheet is also important in the detector array that captures the X-ray
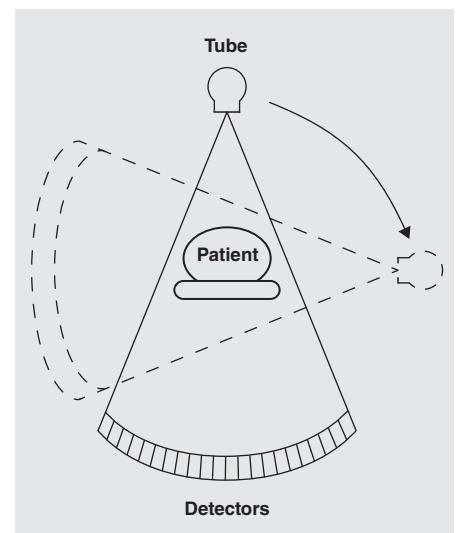

Figure 32. Sketch of CAT scanner X-ray tube and detector array.

21

High-temperature processing

Hot working

High-temperature strength and deformation resistance are important properties for hot-work tooling. Molybdenum alloy tools forge superalloys in the superplastic forming temperature regime above 1100°C. Molybdenum alloys are ideal for brass extrusion, molten metal casting, liquid metal handling, and even plastic injection molding.

Table IV[23] shows the temperature where full recrystallization occurs in one hour for commercially available molybdenum alloys used in high-temperature applications. Recrystallization temperature depends on manufacturing history. For example, a large forging having 50–60% hot reduction in height during forging recrystallizes at a higher temperature than heavily cold-worked sheet or bar that has received more than 70–80% reduction in cross-section. Therefore, the values in Table IV refer to materials with the specified reductions. The strength of dispersion-strengthened alloys is especially sensitive to reduction. Each application and product

must be evaluated to determine the appropriate material, product form, and manufacturing process.

Carbide-strengthened alloys can be used where high strength is required at

temperatures up to about 1500°C. Figures 33 and 34 show the "nominal" yield and ultimate tensile strength of stress-relieved pure molybdenum, TZM and MHC alloys as a function of temperature[24].

Table IV. Commercially available molybdenum alloys and their 1-hour recrystallization times

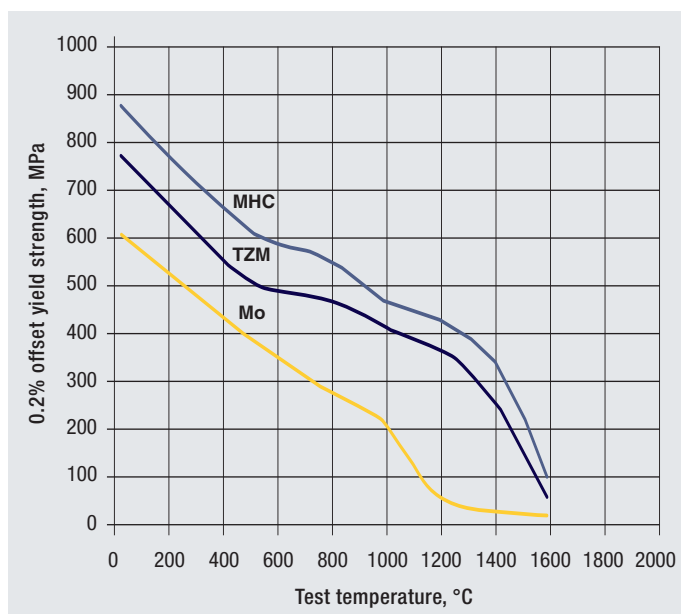| Alloy		Deformation, %	$T_{Recryst}$, °C
Mo		90	1100
TZM		90	1400
MHC		90	1550
30 W		90	1200
50 Re		90	1300
Lanthanum-doped	low reductions	90	1300
	high reductions	99.9	2000
Yttrium/cerium-doped	low reductions	90	1100
	high reductions	99.9	1350
K/Si-doped	low reductions	90	1200
	high reductions	99.9	1800

Figure 33. 0.2% offset yield strength of stress-relieved molybdenum, TZM, and MHC 25-mm bar as a function of temperature. Source: Plansee SE
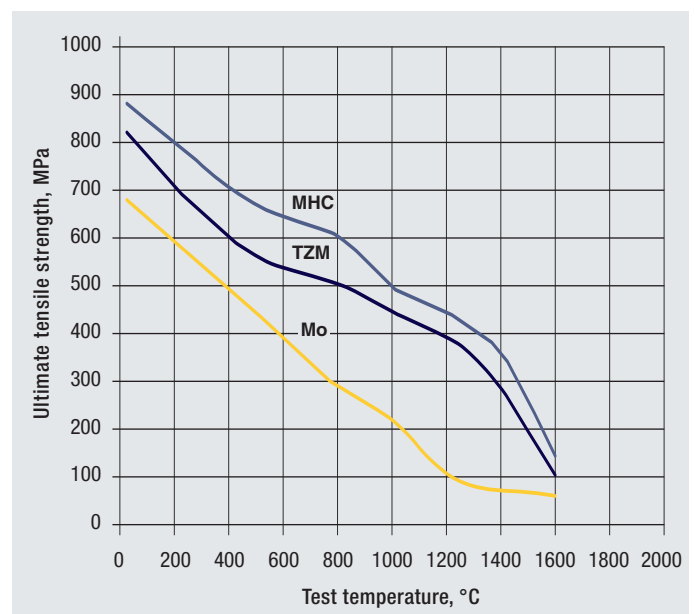

Figure 34. Ultimate tensile strength of stress-relieved molybdenum, TZM, and MHC 25-mm bar as a function of temperature. Source: Plansee SE
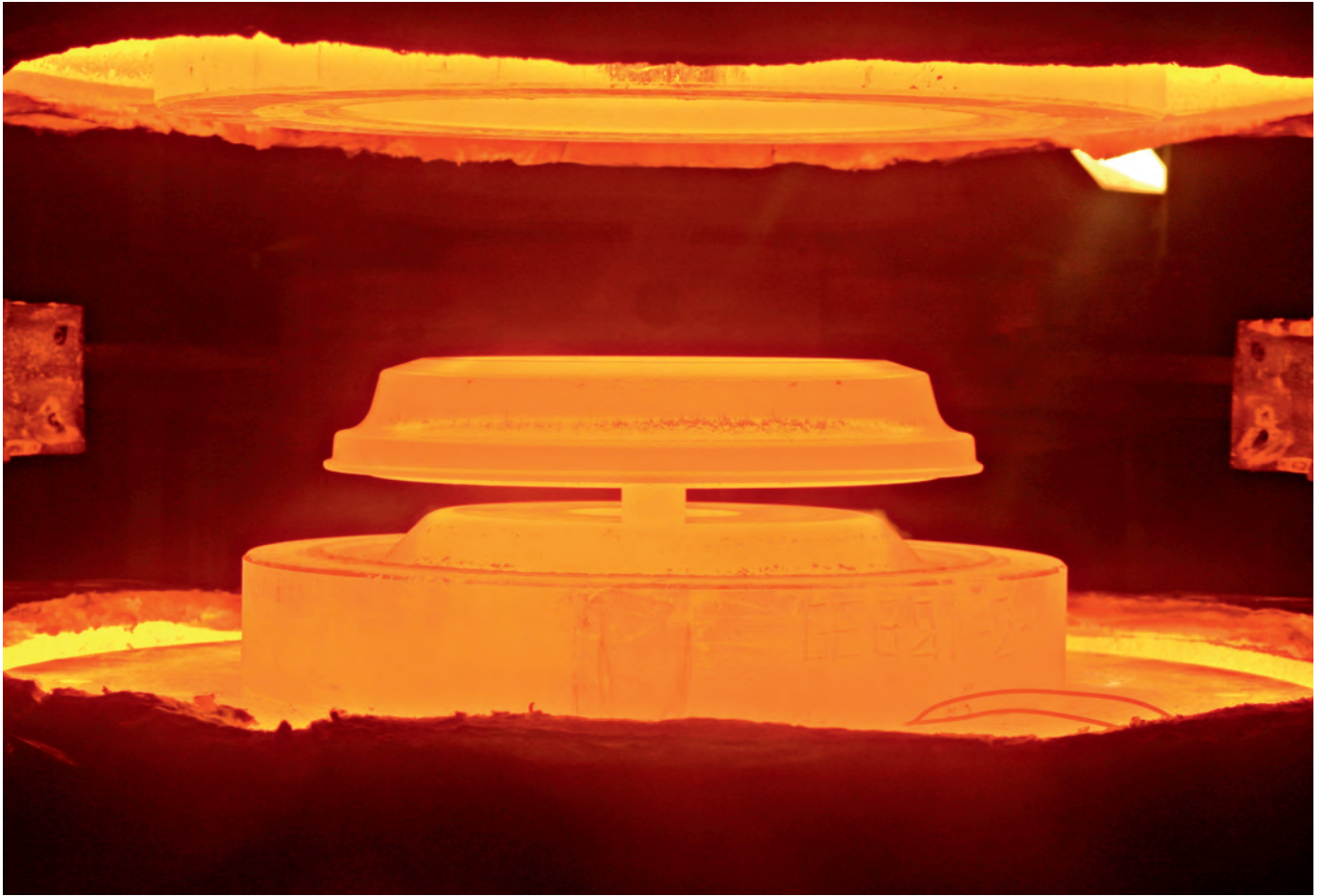
Figure 35. Isothermal forging of superalloy turbine discs using TZM alloy tooling. © ATI Ladish

Figure 35 shows the isothermal forging process used to produce superalloy gas turbine engine discs. This process uses TZM tooling to forge nickel-base superalloy billets in the 1100–1200°C temperature range. To prevent oxidation of the molybdenum tooling, the forging billet and tooling stack are contained in a protective chamber integrated with the forging press. The superplastic forming process enables large deformations and produces highly defined forgings. Forgings produced this way have much finer grain size and higher strength than those produced by conventional forging processes. They also require less machining than conventional closed-die forgings. The cost saved in machining more than compensates for the higher cost of forging.

High strength at elevated temperatures and high thermal diffusivity make the carbide-strengthened alloys ideal for hot-work tooling because this combination of properties makes them resistant to thermal shock and cracking that arise when the tool surface is heated rapidly to high temperatures. The thermal expansion of the surface is constrained by the colder metal inside the tool, which places the surface in compression and the interior in tension. If these thermal stresses are high enough, they can initiate cracks in the tool that propagate and cause tool failure. If the surface is not strong enough, it will deform when hot to alleviate the stress. The stress pattern is then reversed on cooling. Multiple heating/cooling cycles can lead to thermal fatigue failure. Several parameters can be used to describe thermal shock resistance, depending on the imposed thermal conditions. One is the robustness parameter, R′, for the case of heat flow through a material[25].

$R′$ = $(1-v)k\sigma_U/\alpha E$, where
v = Poisson's ratio,
k = Thermal conductivity, W/mK
σ_U = Ultimate tensile strength, MPa
α = Coefficient of thermal expansion, 10^{-6} K^{-1}, and
E = Young's modulus, GPa

The expression shows that high strength and thermal conductivity, and low elastic modulus and thermal expansion coefficient, increase R′.

Table V. Values of the room-temperature robustness parameter R´ for three tooling materials

Material	ν	k, W(mK)	σ_U, MPa	α, K^{-1} x 10^6	E, GPa	R´
H-13[26, 27]	0.27	17.6	1455	10.7	209	8.36
IN 718[28]	0.3	11.1	1240	7	200	6.9
Mo[29, 30]	0.32	140	815	5.2	324	46.1

Table V shows room-temperature values of R´ and its component parts for pure molybdenum, H13 hot work tool steel, and the nickel-base alloy IN 718. H13 is much stronger than molybdenum, but because of its low thermal conductivity and high CTE, its resistance to thermal shock is only a fraction of molybdenum's. Figure 36 illustrates how the parameters change with temperature. Molybdenum's resistance declines slightly with increasing temperature due to strength loss and decrease in conductivity, while the resistance of H13 remains approximately constant. Even so, molybdenum retains a 3:1 advantage at elevated temperature. This advantage would be even greater for TZM or MHC alloy, both of which retain their strength at elevated temperatures.

Both MHC and TZM alloys are widely used for copper extrusion dies, though MHC is the preferred material in this
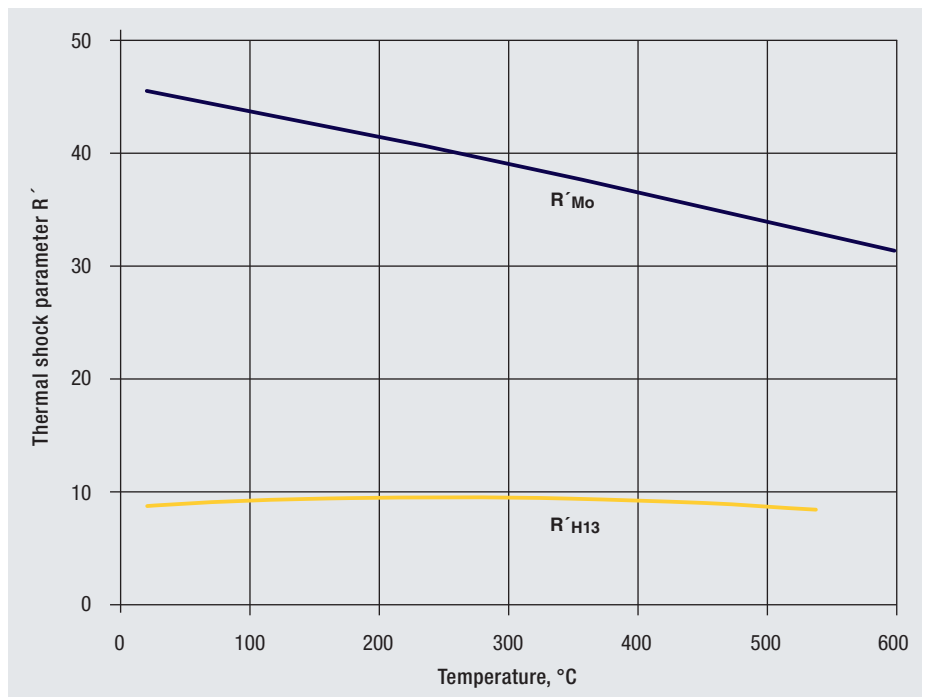
Figure 36. Estimated robustness parameters for molybdenum and H13 as a function of temperature.
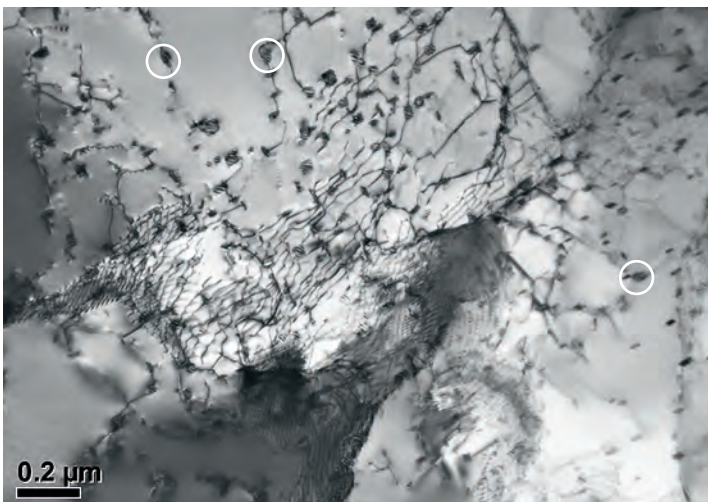
Figure 37. Microstructure of carbide-strengthened alloy. The hafnium carbide precipitates (circled) decorate the dislocations, producing high strength.
© Plansee SE

application. The carbides in these alloys (Figure 37) boost strength and improve the dies' resistance to mechanical erosion. Die design requirements for molybdenum and its alloys are different from those for other die materials because of molybdenum's low coefficient of thermal expansion. Molybdenum inserts require more shrink fit than steel or nickel alloy dies in nickel alloy cases, because the insert expands less than the case as the assembly heats up to its normal operating temperature.

Tubing manufacturers rely on TZM alloy piercing plugs to make seamless tubing with excellent dimensional control and tooling life. Figure 38 shows a machined TZM piercing tool. During use the tool

loses some material due to evaporation of MoO_3. However, the oxidation provides additional lubrication between the plug and workpiece, enhancing tube surface quality and tooling life.

The plastic injection molding industry has found molybdenum TZM to be an important material for the hot runner die inserts that control the flow of liquid plastic into the die cavities that form the parts. While process temperatures are not nearly so high as in metalworking or metal casting, TZM provides the thermal shock and abrasion resistance required in the application.

Figure 38. A molybdenum tube-piercing plug. © Plansee SE

Processing liquid metals

Aluminum die casters use molybdenum TZM die inserts (such as cores and pins) to solve thermal checking and cracking problems in areas of high heat flux and large temperature gradients. Resistance to thermal shock and fatigue are paramount in this application also. Molybdenum's resistance to molten metal corrosion by aluminum is an additional factor in its favor. Molybdenum tooling is more costly than steel, so inserts are used in critical areas of the die to provide thermal cracking resistance and improve casting microstructures. Molybdenum's high thermal conductivity allows it to extract heat rapidly from the casting. This reduces aluminum dendrite arm spacing and improves the casting's properties in these areas. Molybdenum-tungsten alloys are another example of molybdenum's ability to provide cost-effective solutions to liquid-metal processing. Tungsten was once the only metal known to resist molten zinc corrosion, but its cost was prohibitive and it was fragile. Alloying molybdenum with tungsten resulted in an equally resistant material at a greatly reduced cost. The Mo-25% and Mo-30% tungsten alloys that evolved from this work are found in impellers, pump components, and piping used to handle molten zinc.

Melting glass

Pure molybdenum is compatible with many molten glass compositions, so it is used in glass handling equipment, tooling, and furnace components. Glass melting electrodes (GMEs) are the most common application. Glass is electrically conductive when molten, so molybdenum electrodes that pass current through the melt can increase the energy input in conventionally fired furnaces, increasing throughput and productivity. Many electrode designs exist, but all immerse the molybdenum electrode in the glass melt, which protects the electrodes from oxidation. Figure 39 illustrates a design where the electrodes penetrate the side of the furnace[31]. The electrode is held by a sheath, and molten glass is allowed to infiltrate the region between the electrode, sheath, and refractory brick. The infiltrating glass cools and forms a seal, preventing bath leakage and product loss. The portion of the electrode exposed to the atmosphere must be protected from oxidation. A number of approaches have been taken over the years to provide oxidation protection, including internal or external cooling, protective atmospheres, or protective coatings based on a variety of coating materials[32]. As the erosion consumes the electrode during furnace operation, new electrode segments are threaded into the exposed external end, the glass
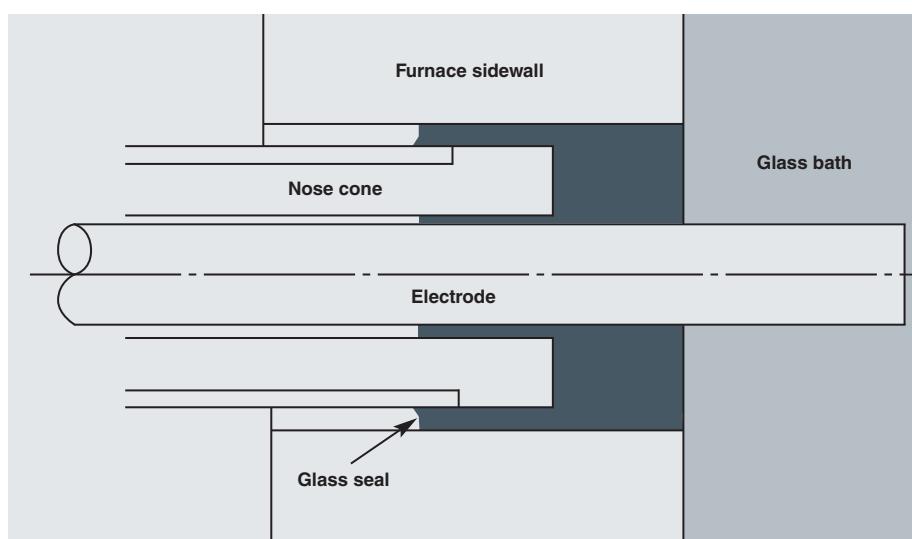

Figure 39. Schematic of a sidewall glass-melting electrode. Source: H. C. Starck

seal is melted, and the newly extended electrode is pushed into the bath. In addition to the side-entry electrode shown, both top- and bottom-entry designs are used. Figure 40 shows an example of a furnace using bottom-fed electrodes.

Molybdenum-zirconium oxide dispersion-strengthened alloys are used in some glass melting applications because they offer improved corrosion resistance in certain glass compositions that use aggressive refining agents such as antimony oxide, which cause strong grain boundary corrosion in pure molybdenum. Glass for solar cell substrates is an example of this kind of application. The zirconia-dispersed materials also provide better creep resistance than pure molybdenum.
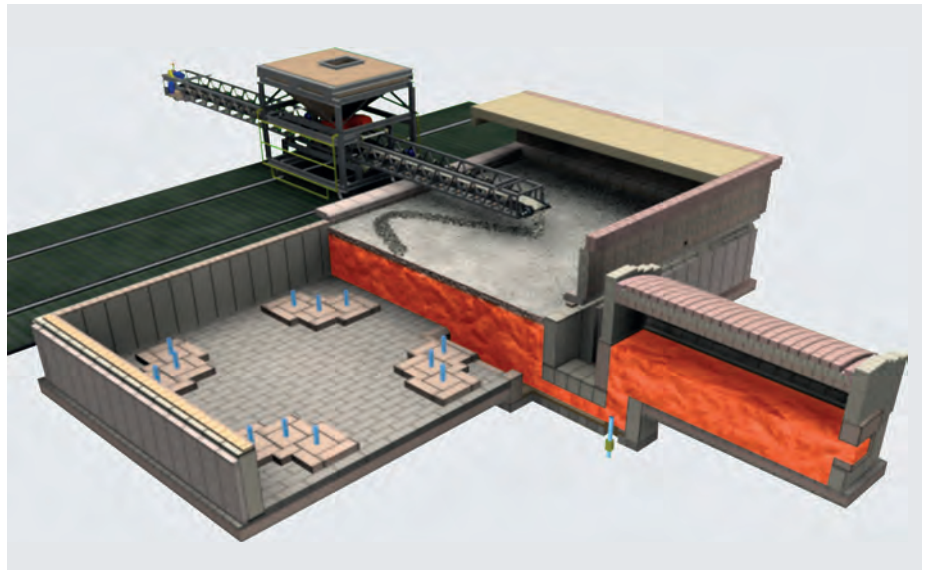

Figure 40. A cutaway of an electric furnace design using bottom-fed vertical electrodes (blue pillars). © Toledo Engineering Co.

Table VI. Glass-melting materials

Advantages	Disadvantages
Molybdenum	
High current density Excellent strength and sag resistance Thermal shock resistance 1700°C capability Excellent total-life cost	Oxidation Incompatible with lead glass Moderately high material cost
Carbon	
Very low material cost 2000°C capability	Requires chemically reducing conditions Low current densities require large electrodes Bubble formation
Iron	
Low material cost	Discolors glass Oxidation
Inconel® 600	
Corrosion resistant Moderate material cost Moderate strength	Low strength above 1200°C Poor sag resistance
Platinum	
Extraordinarily stable 1400°C capability	Extremely expensive Poor in chemically reducing conditions High frequencies (10 kHz)
Tin oxide	
No coloration of glass bath 1350°C capability	Poor oxidation resistance Low thermal shock resistance

Molybdenum is not the only candidate material for glass applications. Table VI summarizes the advantages and disadvantages of several candidate materials. Molybdenum's superior creep resistance, compatibility with a variety of glass chemistries, high electrical conductivity, slow erosion rate, and resistance to thermal shock all outweigh its higher initial cost with respect to most of the other materials, which are relegated to niche applications.

Other important glass furnace components beside GMEs use molybdenum for the same reasons. Furnace shields formed from molybdenum sheet and plate protect refractory brick in regions of high flow and erosion, extending furnace life and minimizing the need for expensive rebuilds. Stirrers made from platinum-clad molybdenum homogenize melts chemically and thermally, and provide the flow required to feed glass through the process.

Coating technology to increase molybdenum's oxidation resistance is important for glass melting. When a furnace is running at steady state there is little problem, because the molten glass protects immersed molybdenum components from oxidation. The main concern during operation is in the regions of transition from glass to air, as in the GME applications mentioned above. Actively cooling the electrode, or coating with traditional $MoSi_2$ compounds can cope with these conditions. However, when starting a new or rebuilt furnace, the glass must be transformed from a pile of solid nonconductive cullet to a molten, electrically conductive bath using external heating. If the GMEs and other molybdenum components are pre-positioned in the furnace, they must not oxidize while exposed to the atmosphere during this transition. In recent years, coatings with superior performance have emerged[33]. This is one reason for the increased use of molybdenum in applications like furnace shields, which must be in place before the glass is molten. Figure 41 shows the effect of coating molybdenum using advanced Mo-Si-B coatings. Uncoated
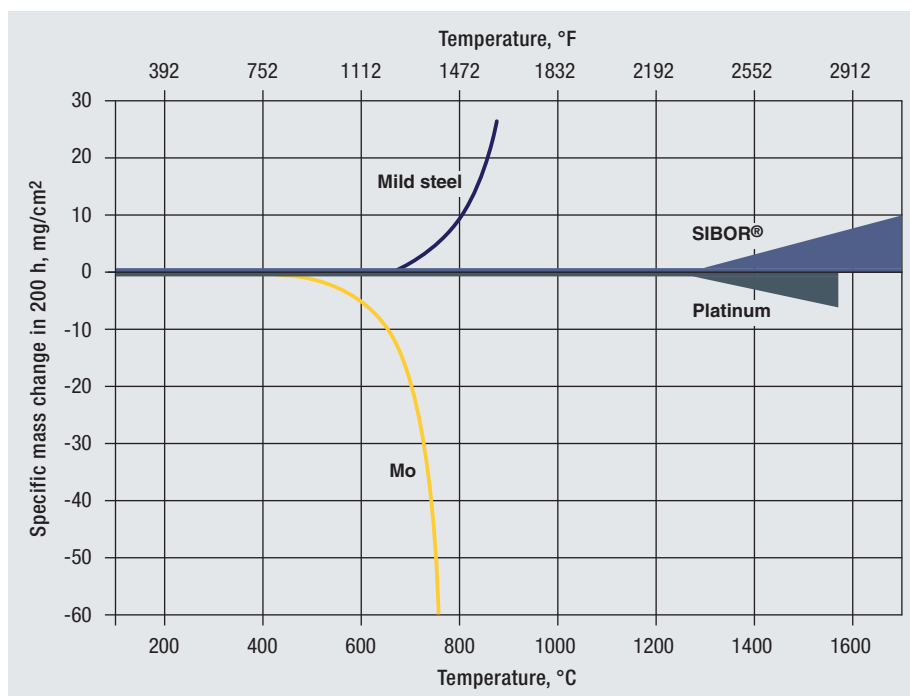

Figure 41. Oxidation resistance gained by the use of advanced oxidation-resistant coatings.
Source: Plansee SE

molybdenum loses weight catastrophically at low temperatures due to evaporation of MoO_3. Coated molybdenum shows no change in weight until above 1200°C, where a protective SiO_2 coating forms.

Furnaces

Molybdenum's strength and stability at elevated temperature make it an attractive material for high-temperature furnaces and their fixtures and tooling. Figure 42 shows the vapor pressure of molybdenum as a function of temperature[34]. For the range of temperatures and pressures encountered in typical vacuum furnaces noted by the figure's yellow region, molybdenum's vapor pressure is several orders of magnitude below the furnace pressure. Therefore evaporation of molybdenum internal components is negligible at typical vacuum-furnace operating temperatures. Tantalum and tungsten, both of which have lower vapor pressures than molybdenum, are much more expensive, and tungsten is much more difficult to fabricate than molybdenum, so they find use only in furnaces operating above 1500°C.
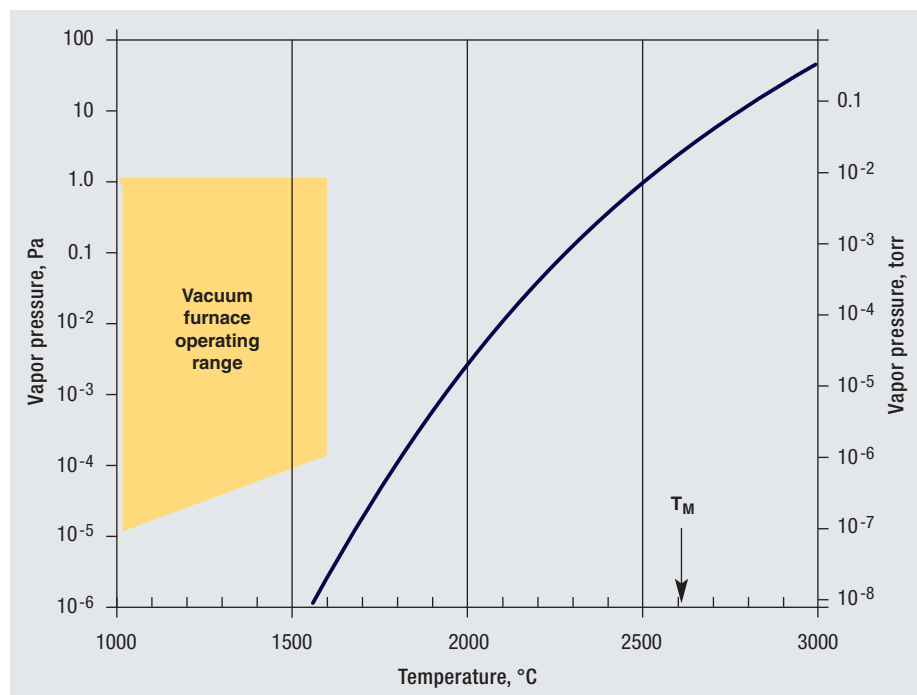

Figure 42. Vapor pressure of molybdenum as a function of temperature.

Figure 43. Vacuum furnace employing an all-metal hot zone. © Thermal Technology LLC
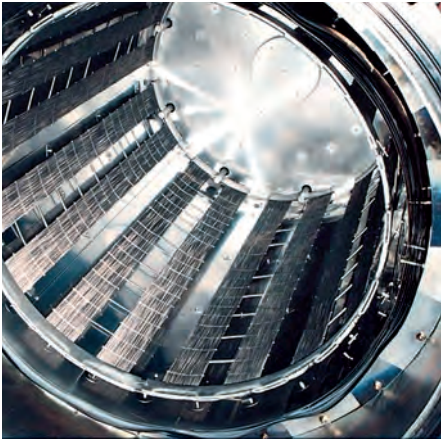
Figure 43 shows an all-metal hot zone employed in a modern vacuum furnace. Metal hot zones offer the utmost in vacuum cleanliness for materials like titanium, niobium, and tantalum that cannot tolerate carbon or oxygen contamination. Therefore, metal hot zones are often found in furnaces serving in the aerospace, lighting, medical, electronics and powder injection molding (PIM) industries. Hot isostatic pressing (HIP), used to consolidate powder materials and improve the integrity of cast metals, relies heavily on molybdenum internal components for their strength at temperature and dimensional stability. Molybdenum and its alloys are widely used as materials of construction for HIP vessels, and are found in heating elements, mantles, and support structures. Figure 44 shows a molybdenum mantle fabrication for a large HIP unit, being hoisted for positioning in the hot zone. The molybdenum internals are illuminated by evocative lighting.

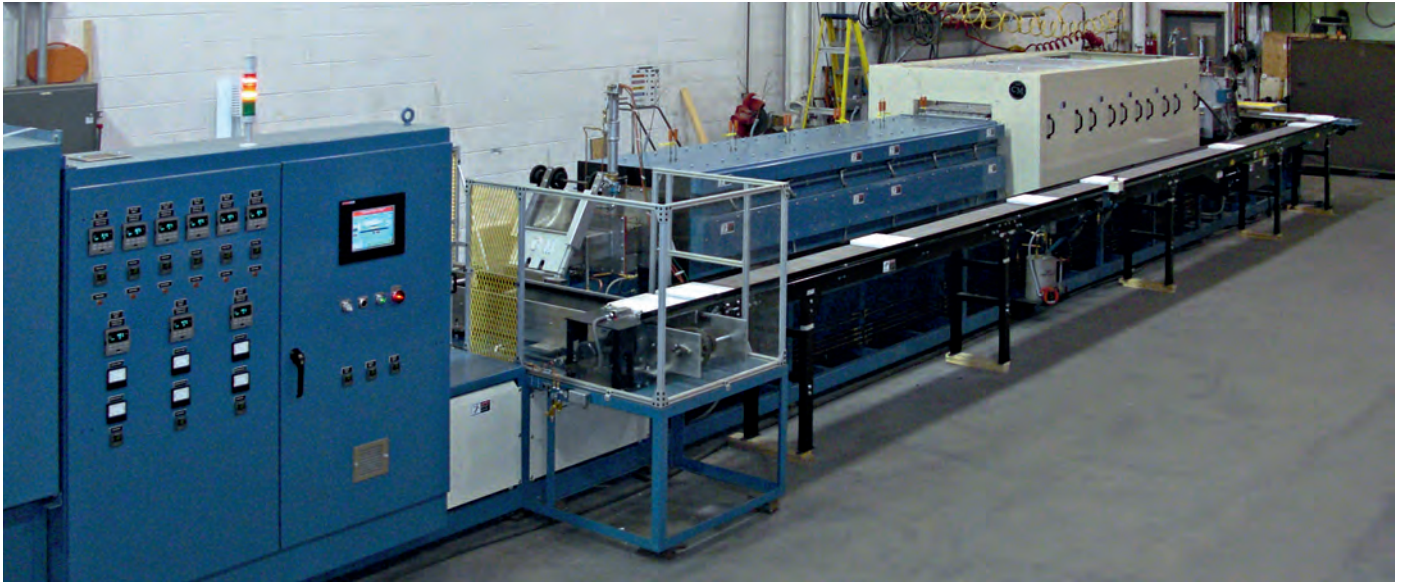Figure 44. HIP mantle being lowered into place. © Bodycote

Figure 45. High-temperature hydrogen-atmosphere furnace employing molybdenum heating elments. © CM Furnaces

Ceramic processing technology uses molybdenum components extensively for furnace fixtures and sintering boats. Molybdenum and its alloys are the materials of choice for sintering ceramic nuclear fuels, while oxide ceramics processed by the electronics industry are sintered in hydrogen on molybdenum carriers. Molybdenum heating elements in high-temperature hydrogen atmosphere furnaces (Figure 45), which are used to sinter ceramics, refractory metals, and tungsten heavy alloys, provide long life and operational reliability.

Long-term mechanical stability of components is critical in furnace applications. Figure 46 compares the stress-rupture life of molybdenum with TZM and MHC[35]. The strength advantage and recrystallization resistance that alloying confers is reflected in the increased creep resistance of TZM and MHC at moderate temperatures (<1500°C). Above these temperatures, carbides begin to redissolve, the microstructure recrystallizes, and the alloys lose their creep resistance.
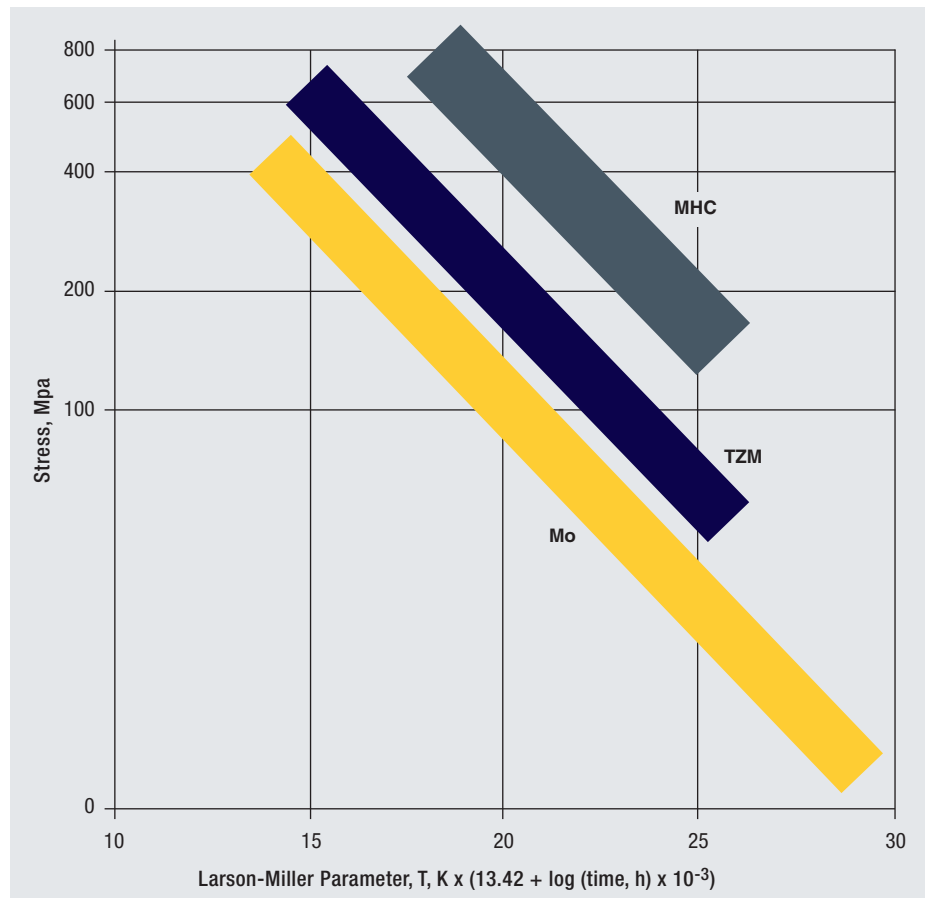

Figure 46. Stress-rupture plots for Mo, TZM, and MHC alloys. (Based on data from Ref. 36)

It is important to remember that rupture life is not the only determinant of creep performance. A component that lasts a long time before failure, but deforms significantly during use, may "fail" because it simply cannot keep its shape. A second measure of creep resistance is the steady-state creep rate observed during creep and stress-rupture tests. Dispersion-strengthened alloys have far superior creep rates at temperatures above 1500°C, as shown in Figure 47[37]. At the lower temperatures typical of standard vacuum furnaces, TZM is far more resistant to deformation than dispersion-strengthened alloys, as shown in Figure 48[38]. The difference arises because of the different deformation mechanisms that occur at high and low temperatures, and dissolution of carbides that provide creep resistance in TZM. The high-temperature superiority of dispersion-strengthened alloys is remarkable. These alloys are used in the most demanding furnace applications, such as heating elements (strip, wire, and cable), and sintering boats used for uranium oxide nuclear fuel production. The relative creep resistance changes among the alloys as temperature is lowered, so that users need to work closely with manufacturers to specify the appropriate material and thermomechanical processing.
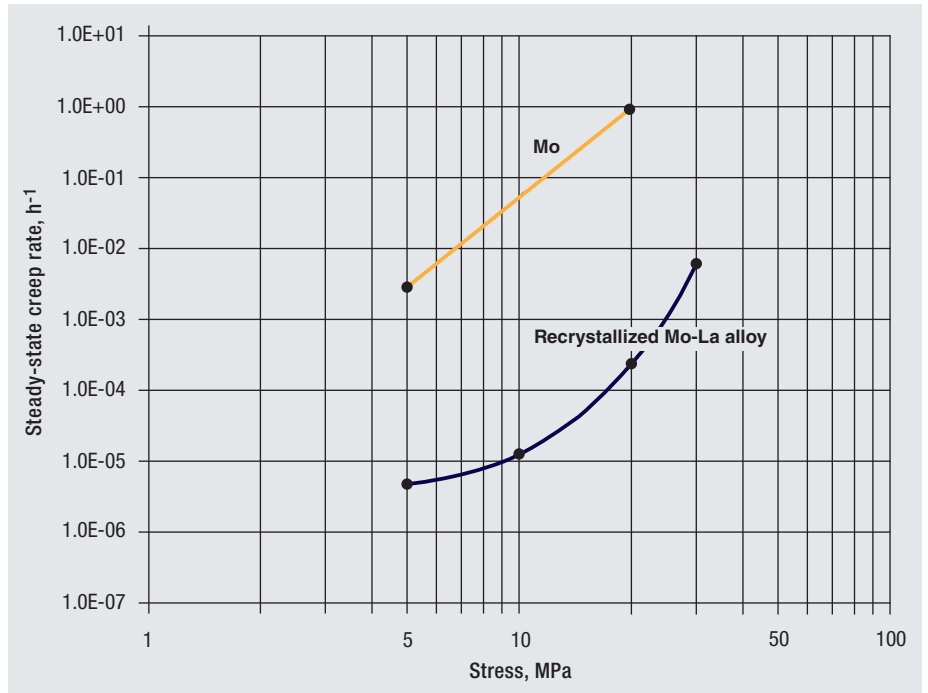

Figure 47. Steady-state creep rate of pure Mo and Mo-La at 1800°C. The creep rate of TZM at this temperature is similar to that of pure Mo. Source: Plansee SE
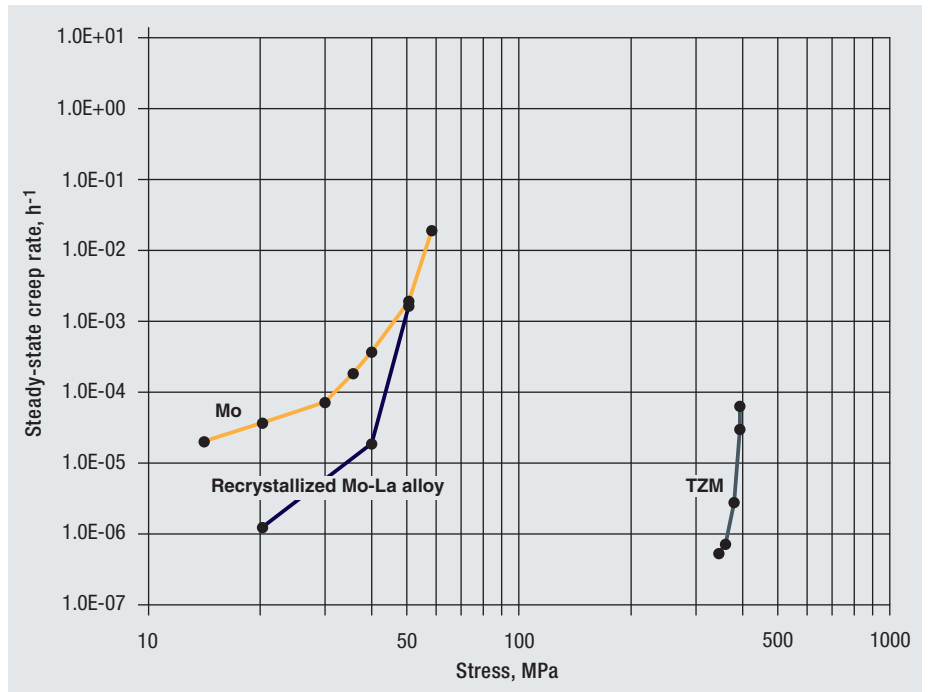

Figure 48. Steady-state creep rate of pure Mo, TZM, and Mo-La at 1100°C. Source: Plansee SE

Thermal spray coating

Thermal spray is a technology that creates a new, engineered surface on a substrate by spraying droplets onto it[39]. Thermal spray equipment feeds the coating material into a high-temperature jet of inert or reducing gas, which melts and atomizes the coating material and impels it onto the surface. There the droplets solidify in "splats," building up the surface coating. The coating material source can be wire, rod, or powder. Metals, ceramics, and cermets are all processed using thermal spray technology. The heat source for spraying may be a flame, an electric arc, or even a controlled explosion. This variety of heat sources, carrier gases, materials, and material forms has led to the development of many different processes, including flame spray, wire spray, detonation gun deposition, high-velocity oxyfuel (HVOF), and plasma spray. The coatings themselves can be designed to impart corrosion resistance, wear resistance, friction control, and thermal insulation to the substrate. Thermal spray is also used in some cases to rebuild regions of a component that have been worn or eroded away in service. Figure 49 illustrates a modern thermal spray setup, with multiple spray guns operated using sophisitcated digital controls.

Molybdenum thermal spray coatings were originally developed using wire spray technology, and this technology still uses substantial amounts of molybdenum wire. In recent years, wire spray has been increasingly supplanted by powder spray technologies. Pure molybdenum finds application as a spray coating for friction control on components in both automotive and aerospace industries. It is in this area that wire spraying is strongest, due to historical precedents and the fact that spray wire is available only as the pure metal. Journal and bearing shafts and piston rings are two major users of molybdenum coatings, applied using both wire and powder deposition processes.

Pure molybdenum is limited to temperatures of about 300°C due to oxidation concerns, so it is often blended with other elements in order to produce molybdenum-alloy coatings or with another base material such as nickel to enhance the coating.
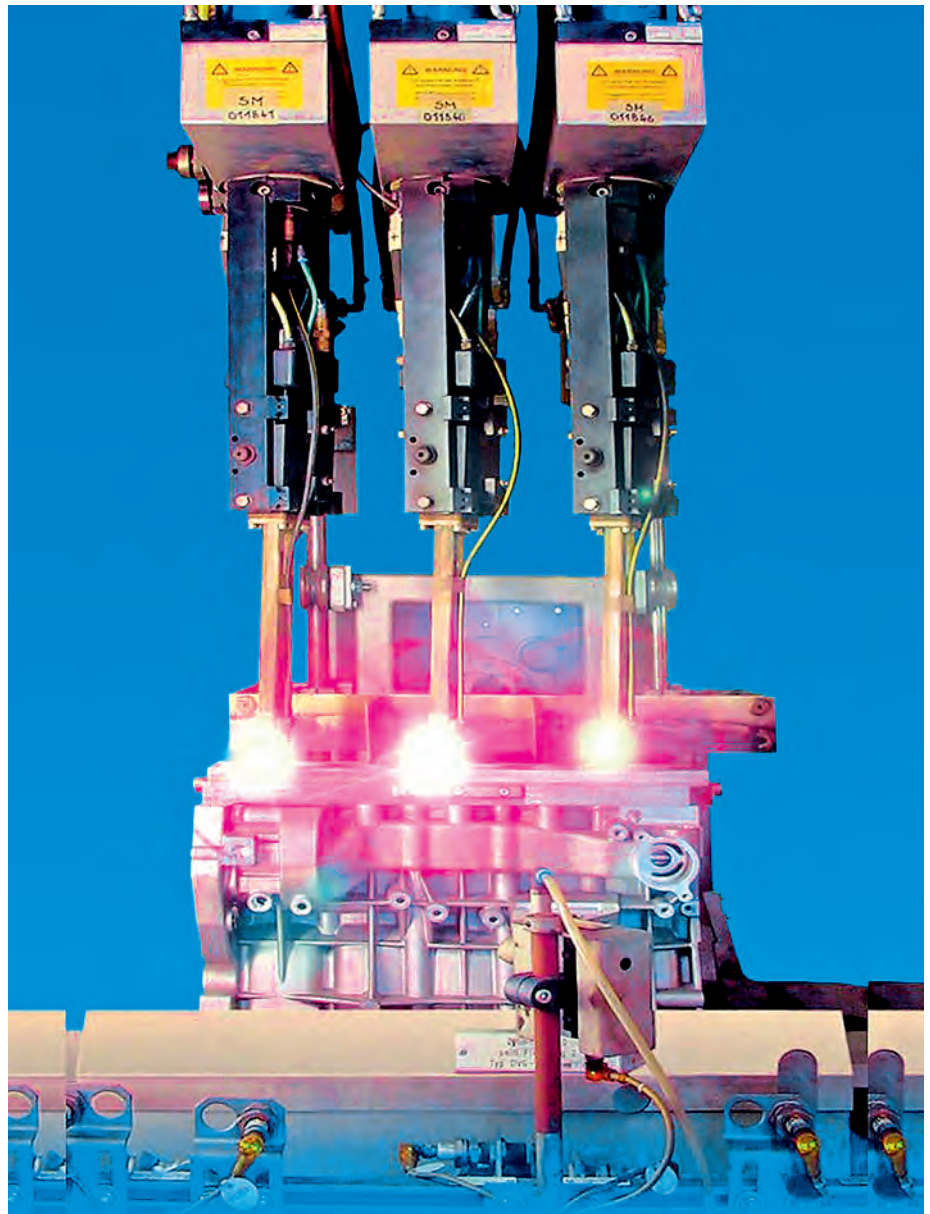

Figure 49. Automated ganged rotating-gun technology used to coat automotive cylinders. While this is not a molybdenum spray application, it illustrates the level of sophistication possible with current technology. © Sulzer Metco
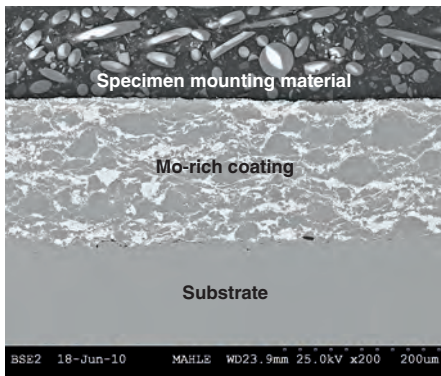
Figure 50. Molybdenum-containing thermal spray coating on substrate. © Mahle Group

Figure 50 illustrates the microstructure obtained when thermal spraying a molybdenum-based alloy powder[40]. When using powder spray equipment, varying the composition of the feed material to the jet in a controlled fashion can produce composite or graded coatings.

Powders used in spray applications are markedly different from those used to produce mill products. Mill products start as pressed and sintered billets, so require powder that will press to high density and produce large green billets with the strength to survive industrial handling. Flowability is not as high a priority as green strength for mill products because mold filling is frequently performed manually, not with mechanized equipment. Thus, powders that are best for mill products tend to be agglomerates of fine particles that mechanically interlock when pressed. Spray applications, like the powders used for automated pressing applications, place a premium on flowability. The solution to this problem is similar, but not identical, to that used to produce powders for high-speed pressing operations. The powder is spray dried, but instead of using a water-based organic binder, an aqueous solution of ammonium dimolybdate is used.

Table VII. Molybdenum-based spray powder compositions and typical applications

Powder composition	Morphology/ manufacturing process	Bulk density, g/cm^3	Coating method (powder particle size range)	
Mo-base alloys				
99.0% Mo	Spheroidal/ agglomerated & sintered	2.5	Air plasma spray (45–75 μm)	
	Irregular/ sintered & crushed	5.9	HVOF (15–45 μm)	
Mo-3Mo$_2$C	Spheroidal/ agglomerated & sintered	2–3	Air plasma spray	
Mo-17.8Ni-4.3Cr-1.0Si-1.0Fe-0.8B	Blend – Mo spheroidal/ agglomerated & sintered + NiCrSiFeB – gas atomized		HVOF (16–45 μm)	
Alloys containing Mo additions				
Ni-5.5Al-5Mo	Spheroidal/ clad or gas atomized	3.5	Air plasma spray or combustion	
Ni-9Cr-6Al-5Mo-2Fe-2B-2Si	Spheroidal and irregular/clad		Air plasma spray (45–125 μm)	
Ni-20Cr-10W-9Mo-4Cu (Superalloy)				
Co-28.5Mo-8.5Cr-2.6Si (T-400 type)	Water atomized	3.3	HVOF	
Co-28.5Mo-17.5Cr-3.4Si (T-800 type)	Spheroidal/gas atomized	5.1	Air plasma spray	
Ni-14Cr-9.5Co-5Ti-4Mo-4W-3Al (René 80 type)	Spheroidal/gas atomized	3.9–4.4	HVOF	

When spray dried, the powder/molybdate solution forms spherical droplets and the water evaporates as the drops fall to the bottom of the spray dryer chamber. Unlike the spherical pressing powder that uses organic binders, these powders are held together with the solid ammonium molybdate that remains after the water is removed. Heating the molybdenum/ammonium molybdate composite spheres in hydrogen chemically reduces the molybdate to molybdenum metal and partially sinters the sphere, providing the strength necessary to withstand shipping, handling, and processing in thermal spray equipment. Figure 51 shows a thermal spray powder that contains both spherical molybdenum powders ("lacy" surfaces) and alloying element powders produced by atomization from the melt (smooth surfaces).

Thermal spray powders are available in many compositions for a variety of applications. Table VII summarizes information about molybdenum-containing thermal-spray alloys, including composition, powder and coating physical properties, applications, and user specifications.
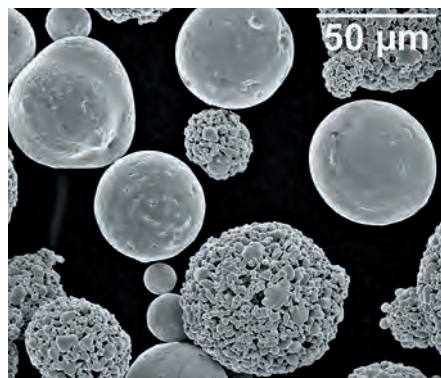

Figure 51. Spray-dried molybdenum powder alloy blend, showing highly flowable spherical particles. © H. C. Starck

Hardness HV0.3	Typical applications	Desired properties	Industry specifications
420–455	Piston rings, synchronizing rings, diesel engine fuel injectors, continuous casting & ingot molds	Lubricity	Pratt & Whitney PWA1313 Canadian Pratt & Whitney CPW213 Rolls Royce EMS 56705, Volvo PM 819-13 Honeywell EMS 57738
425–520	Piston rings, synchronizing rings, pump impeller shafts	Lubricity, wear resistance, resistance to molten metals in a non-oxidizing environment	
	Piston rings, synchronizing rings	Lubricity, wear resistance	
	Service T < 650°C Wear rings, exhaust fans, valve and pump seats	Wear resistance	GE B50TF166 CIA Honeywell EMS57749, Volvo PM819-29 Rolls Royce MSRR 9507/5
450	Service T < 750°C Bond coat, salvage and restoration	Wear resistance, corrosion resistance	
575 650			
			GE B50TF155 CIA Honeywell EMS52432, CI XVI Rolls Royce EMS56712, Volvo PM819-62
			GE B50TF190 CIA Honeywell EMS 52432, CI XV Rolls Royce EMS56713, Volvo PM819-15
	Service T < 1000°C Restoration and repair of superalloy & gas turbine components		

Machining and fabricating molybdenum

Machining

Molybdenum metal and its alloys are machinable by all common machining processes. Shops around the world manufacture a wide variety of parts in a range of sizes from molybdenum and its alloys every day. Excellent surface finishes and exacting tolerances can be attained with appropriate attention to detail.

Several points must be considered when machining molybdenum or any of its alloys. Although molybdenum retains its strength to high temperatures, it is not particularly strong at ambient temperatures. Neither is its ductility as high as carbon steel or brass. Furthermore, its (relatively speaking) high DBTT means that it is susceptible to stress risers and other geometric features that might initiate cracks.

Machines should be rigid and free from backlash, and work should be securely clamped. Tool sharpness is very important because dull tools can tear the material instead of cutting it cleanly, creating microcracks that can limit the life of the finished component. Carbide tools are preferred for most applications because of their hardness and wear resistance, but high-speed tools can be employed if close attention is paid to tool sharpness. Feeds and speeds for high-speed tools are reduced from those employed for carbide tools. Carbide grades perform particularly well where problems arise due to abrasion by chips and dust. They also demonstrate their economic value in jobs where long uninterrupted cuts are required, due to their substantially better life compared to steel tools. Tooling material suppliers are an excellent source of knowledge about the relative performance of different tool material grades.

Some heavy machining (e.g. ingot scalping and rough turning) can be done without lubrication, but for most tasks, especially finishing work, emulsion lubricants are needed to flush dust away from the tool/workpiece interface and cool the workpiece and tool. Consult with lubricant manufacturers to determine the best lubricant system for a particular job.

Table VIII[41] summarizes some suggested basic machining parameters for molybdenum promulgated by one major manufacturer. Table IX[42] presents the

Table VIII. Basic machining recommendations for molybdenum [41]

| Turning	
Tool material (ISO grade designation)	HW-K10 - HW-K25 (uncoated WC/6-9% Co) HW-K25 (uncoated WC/6-9% Co) HW-M10 (uncoated WC/(Ti, Ta, Nb)C/6% Co)
Cutting speed (m/min)	100 – 140
Feed, m/min	0.05 – 0.35
Depth of cut (mm)	0.3 – 6
Coolant	Emulsion
Milling	
Carbide tools Use milling cutters with hardmetal indexable inserts	
Tool material (ISO designation)	HW-K10 - HW-K25 (uncoated WC/6-9% Co) HW-K25 (uncoated WC/6-9% Co) HW-M10 (uncoated WC/(Ti, Ta, Nb)C/6% Co)
Rake angle	≥ +10°
Inclination angle	0 – 10°
Cutting speed (m/min)	100 – 150
Feed (mm/tooth)	0.03 – 0.10
Coolant	Emulsion
High-speed steel tools	
Rake angle	≥ +10°
Cutting speed (m/min)	20 – 25
Coolant	Emulsion
Drill diameter up to 18 mm	
Drill	HSS (preferably with internal cooling channel)
Cutting speed (m/min)	10 – 15
Feed (mm/rev)	0.05 – 0.1

Table IX. Basic machining recommendations for molybdenum TZM alloy [42]

Operation	Tool material	Tool geometry	Tool	Depth of cut in.	Width of cut in.	Feed	Speed ft/min.
Turning	C-2 carbide	BR: 0°, SCEA: 15°, SR: 20°, ECEA: 15°, relief: 5° NR 1/32"	5/8 in. square brazed tool	0.030	–	0.009 in./rev	450
Turning				0.060	–		350
Face milling	T-15 HSS	AR: 0°, ECEA: 10°, RR: 20°, CA: 45°, clearance: 10°	4 in. dia single tooth	0.060	2	0.010 in./tooth	100
Face milling	C-2 carbide					0.005 in./tooth	350
End mill slotting	T-15 HSS	Helix: 30°, RR: 10°, CA: 45°, clearance: 10°	0.750" dia drill, HSS end mill	0.125	0.750	0.004 in./tooth	190
End mill peripheral cut	M-3 HSS						
Drilling	M-33 HSS	118° plain point clearance: 7°	0.250" dia drill, 2.5 in. long	½ through hole	–	0.005 in./rev	150
Reaming	M-2 HSS	0° helix angle CA: 45° clearance: 10°	0.272" dia six-flute chucking reamer		0.010 depth on hole radius	0.015 in./rev	700
Tapping	M-10 HSS	Four-flute plug 75% thread	5/16-24 NF tap				

results of an extensive research program funded by the U.S. Air Force into the appropriate techniques for machining molybdenum and its alloys in the early 1960s. The parameters in these tables are a good starting point for machining these materials. Experimentation on any specific job will allow a shop to optimize their procedures and minimize their manufacturing cost.

Electrical discharge machining (EDM) techniques can also be used to machine molybdenum and its alloys. Both wire EDM and plunge EDM are used widely. It is important to minimize the formation of a recast layer on the workpiece surface when machining molybdenum with EDM equipment. This layer often contains microcracks, so it must be removed by mechanical or chemical polishing prior to placing the part in service.

Both silicon carbide and aluminum oxide wheels are used to grind molybdenum. Manufacturers of grinding wheels and abrasives offer a variety of compositions designed for a range of applications. They should be consulted for specific recommendations choosing wheel compositions and grinding practices. Cooling is important in grinding operations to prevent overheating. Grinding coolants similar to those used for machining give good results.
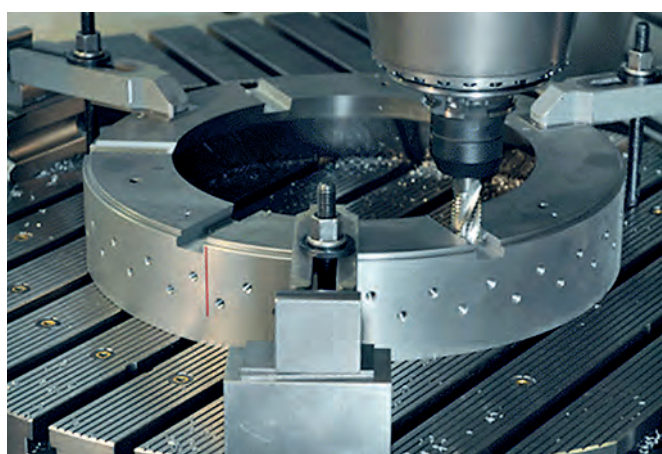
Machining a part that has already received different machining processes.
© Plansee SE

Forming and metalworking

Molybdenum and its alloys are formed by all common metalworking processes (e.g. bending, punching, stamping, drawing, and spinning). The ductile-brittle transition temperature of molybdenum and its alloys increases with increasing strain rate and triaxiality of applied stress, so successful forming depends upon the surface condition of the material, the size of the section being formed, the severity of the forming, and the deformation rate. Figure 52 shows a hot roll-forming operation commonly used to create cylindrical shapes from sheet. Note the use of hand-held burners to heat the workpiece above its ductile-brittle transition temperature and ensure good formability.

Figure 53[3] shows the effect of strain rate in a tension test on the measured reduction in area at fracture. The tests were performed on recrystallized molybdenum bar having an ASTM 6–7 grain size, and the results illustrate the strong effect of strain rate on ductile-brittle transition. The DBTT of wrought and stress-relieved molybdenum is lower than that of recrystallized material, but it is sensitive to strain rate in the same way as shown in Figure 53.

Figure 54[43] illustrates the importance of surface condition on DBTT. In these tests, 1.59-mm arc-cast molybdenum sheet
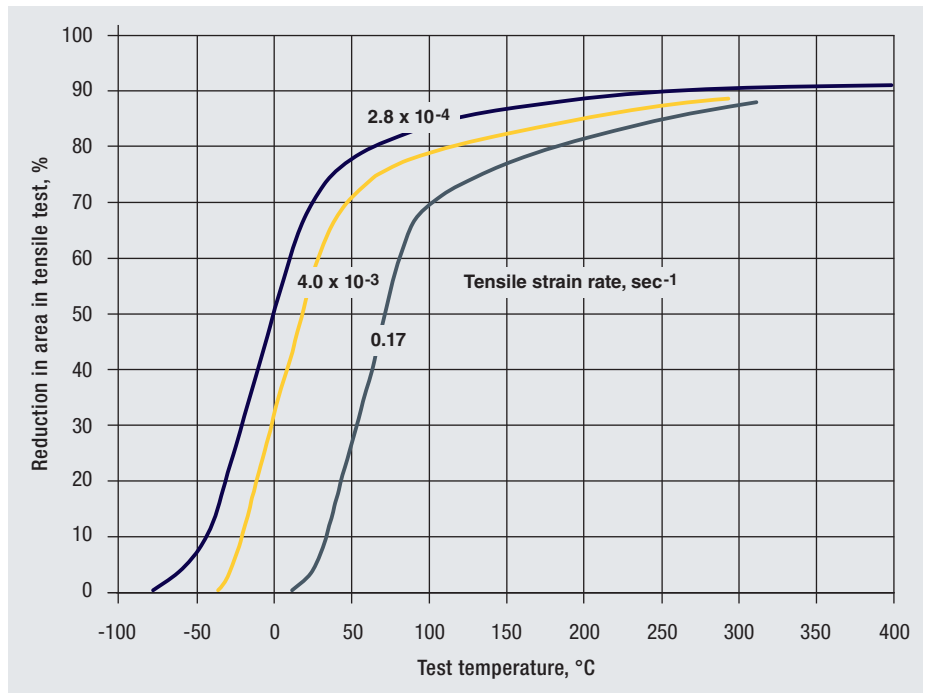

Figure 53. The effect of strain rate in tension on the ductility of molybdenum as measured by reduction in area. Source: H. C. Starck

stress relieved in hydrogen after surface treatment was bent over a mandrel having a diameter two times the sheet thickness. The bend angle is the angle at which cracking was observed on the tension side of the bend. High bend angles are desired for forming operations of all kinds. The tests were performed in the "easy bend" orientation, with the primary sheet rolling direction perpendicular to the bend axis. Tests done in the "hard bend" direction 90° to the "easy bend" direction would display much smaller bend angles. This directionality of test result has important implications for formability, and manufacturers often cross roll their sheet products in order to improve sheet ductility transverse to the rolling direction. As sheet thickness is reduced, it becomes more and more expensive to maintain significant amounts of cross rolling in the material because each time the sheet is turned, only a length of material as wide as the rolling mill can be cross-rolled. For demanding applications where formability is critical and users can afford to pay the necessary premium, this approach may be warranted. For most material though, manufacturers usually establish a point relatively early in the process and usually after hot rolling, where the product is turned for cross rolling and rolled in this new direction to final thickness. This processing usually establishes sufficient transverse ductility for most applications that require forming.

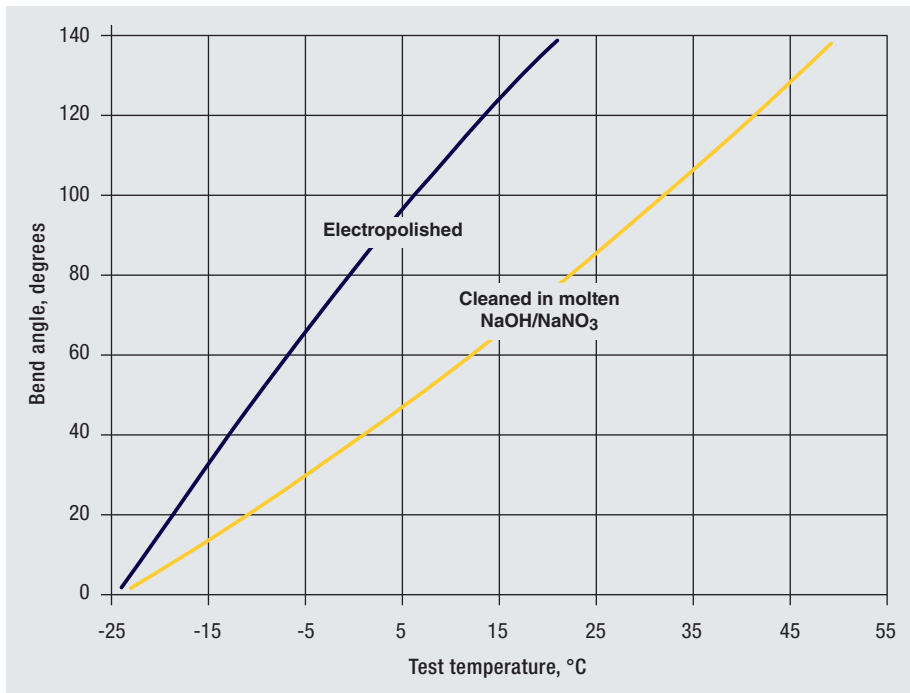Figure 52. Roll forming molybdenum sheet. © Plansee SE

Figure 54. The effect of surface treatment on the DBTT of molybdenum sheet, as measured in a bend test. Source: H. C. Starck
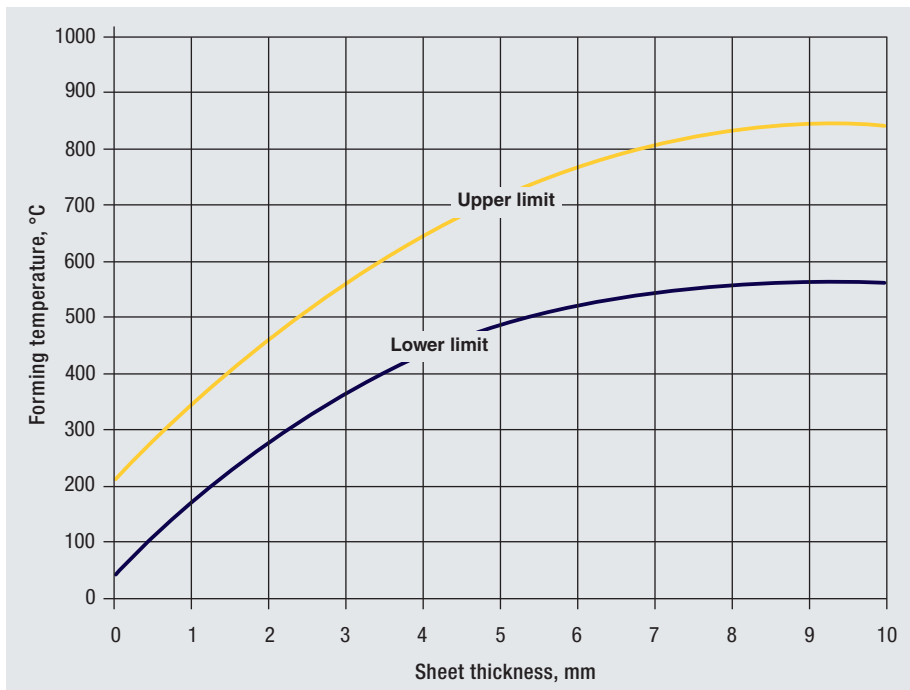

Figure 55. Forming temperature range for molybdenum sheet. Source: Plansee SE

Note that Figure 54 only presents two different finishing processes as ways to evaluate the effect of surface condition on bendability, both chemical cleaning and surface removal techniques. While electropolishing is clearly superior, molten caustic cleaning is far more economical and is the typical way material is cleaned after hot rolling. Cold rolling establishes a surface that is created by the finish on the rolling mill rolls, so this is a way to produce a variety of surface finishes. Most molybdenum sheet is made with a "bright" finish that has fine marks imparted by the grinding marks on the mill rolls. Because the roll grind marks are circumferential on the rolls themselves, they are oriented along the rolling direction of the sheet. This minimizes their impact on bendability in the easy-bend direction, but has negative effects on bendability in the hard-bend direction. A mirror finish can produced on the sheet by using highly polished rolls, but this is a specialty finish used for only a small number of applications.

The bend radius that can be achieved successfully without cracking at any given temperature is a function of the sheet thickness. Increasing section thickness demands a higher forming temperature. Figure 55[44] shows recommended forming temperatures for molybdenum sheet as a function of thicknesses. TZM forming temperatures are 50–100°C higher than those for pure molybdenum for a given section thickness, because of the alloy's higher strength and greater sensitivity to embrittling factors. Preheating methods are limited only by the creativity of the operator. Linear gas burners, infrared lights, air furnaces, hand-held torches, and hot plates have all been successfully employed as heat sources for forming operations.

Sheet shearing operations (e.g. slitting, stamping, punching, and blank shearing) can produce cracks, commonly called delaminations, in the plane of the sheet. Delaminations are intergranular cracks along grain boundaries parallel to the sheet surfaces. Incorrect tool clearances and sharpness are major contributors to this phenomenon[45]. Dull and damaged tool blades also invite delamination.
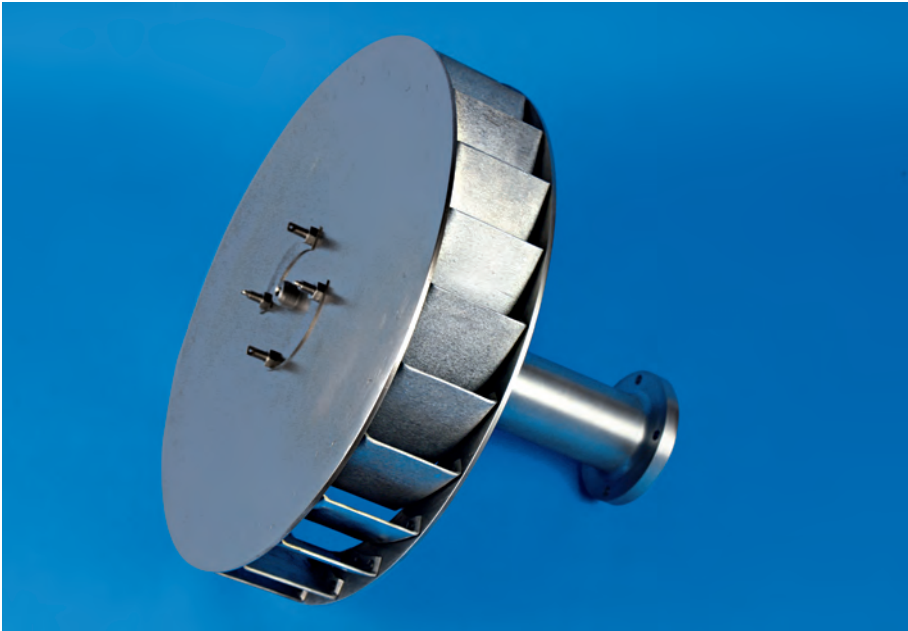
37

Figure 56. Machined and formed TZM and Molybdenum components assembled into a rotor.
© Elmet Technologies

Clearances between blades, or between punch and die in stamping operations, should be in the range of 5−8% of the sheet thickness to minimize this problem. Figure 56 shows a rotor assembly that required stamping, punching, bending, machining, and riveting operations to make the finished product.

Joining

Molybdenum and its alloys can be welded, but normally only for non-structural joints. The weld and surrounding recrystallized zone in the base metal are significantly less strong, and have a much higher ductile-brittle transition temperature, than the base material itself. This strength disparity concentrates deformation in the weld zone[46], and the triaxial stresses produced by base metal constraint can initiate fracture. Welded structures perform well in some applications, and all common welding techniques have been employed to join molybdenum and its alloys. The lower the heat input used to make the weld, the less fragile it is.

Electron-beam welds, with their narrow weld and heat-affected zones, are less susceptible to failure than gas tungsten arc (GTA) welds that deposit large amounts of heat to the workpiece.

Oxygen contamination is a problem in some welds because oxygen segregates to grain boundaries and reduces ductility beyond that of the effect of the weld microstructure. Arc-cast molybdenum, which contains higher carbon than PM molybdenum, is somewhat more weldable than PM molybdenum. TZM is more forgiving than pure molybdenum because

the alloy's reactive metals titanium and zirconium react with oxygen to form fine oxides during welding. Molybdenum is often welded inside high-purity inert gas chambers to minimize oxygen contamination[46].

Potassium-doped alloys generally do not weld as successfully as other molybdenum alloys because the volatile elements in the materials produce gassy welds. Rhenium alloys are quite weldable. The well-known rhenium ductilizing effect[47] renders these alloys ductile at cryogenic temperatures even in the as-solidified or recrystallized condition. The oxide-dispersion strengthened alloys can be welded because the oxides do not evaporate like potassium. While welding changes the unique grain structure of these alloys dramatically, the weld and heat-affected zone (HAZ) grain size is finer than that seen in welds of pure molybdenum. This tends to ameliorate welding's negative consequences in these alloys. Figures 57 and 58 compare the transition between HAZ and base metal in a TIG-welded ODS molybdenum component with that of a TIG-welded pure molybdenum component. The oxide dispersion in the ODS alloy produces a desirable structure of long, interlaced grains in the HAZ, compared to the undesirable recrystallized equiaxed grains in the pure molybdenum component[48].

Figure 57. Transition between HAZ (right) and base metal (left) in TIG-welded ODS Mo-La alloy.
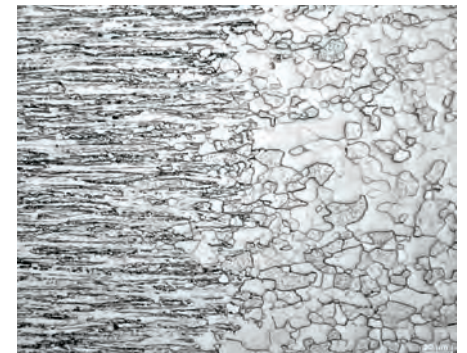© Rhenium Alloys

Figure 58. Transition between HAZ (right) and base metal (left) in TIG-welded pure Mo component.
© Rhenium Alloys.

Figure 59 Illustrates a common use of welding for molybdenum components, to seal crevices in formed and riveted sintering boats.

Brazing is commonly used to join molybdenum and its alloys. Commercial brazing alloys are available with flow points ranging from 630°C through 1400°C. Compositions vary widely; most contain precious metals, but nickel-base alloys are also available. Manufacturers of brazing compounds and equipment can provide technical assistance in this area. The brazing temperature should be below the recrystallization temperature of the molybdenum alloy, so that minimum loss in strength occurs during the process.
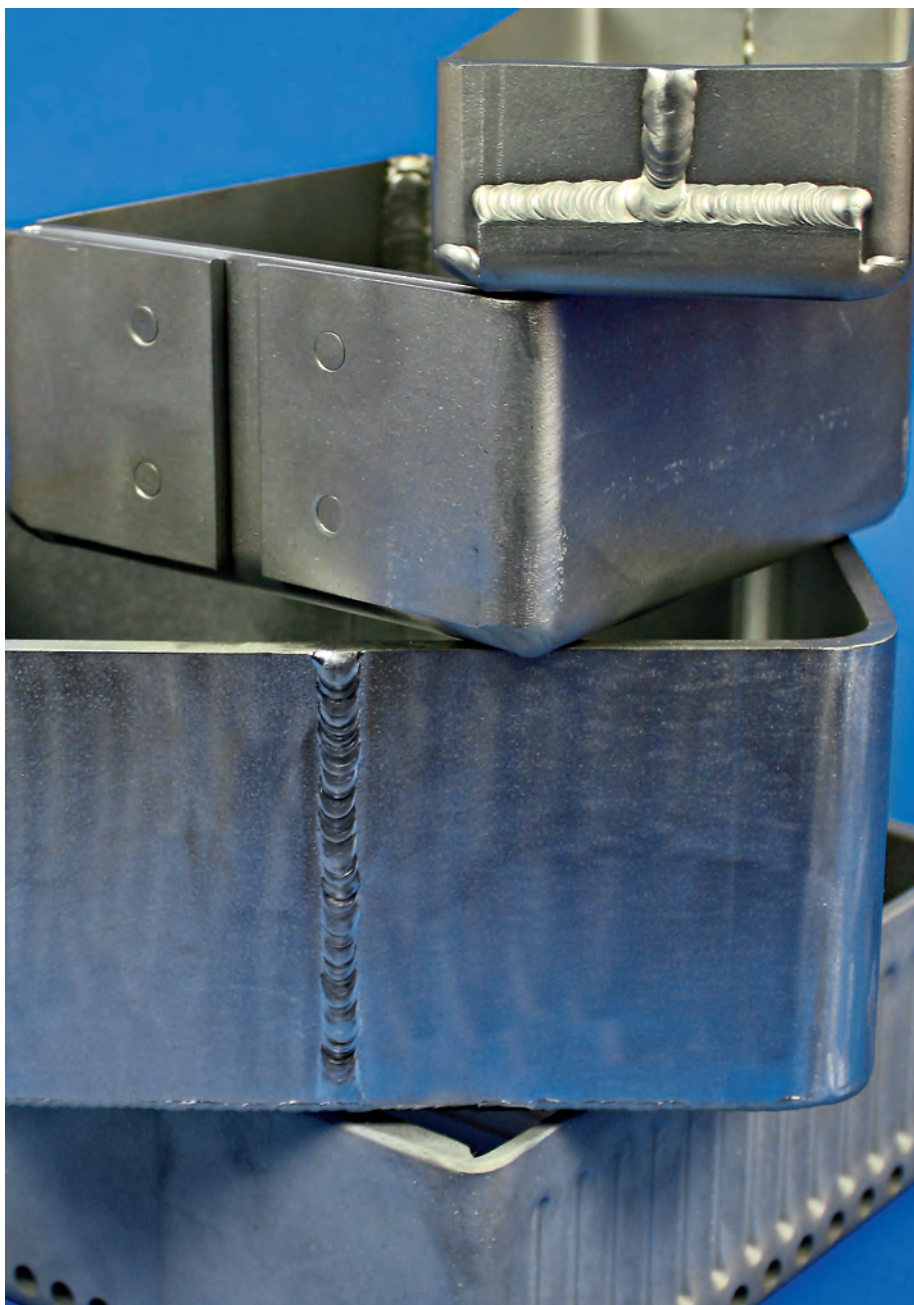

Figure 59. Molybdenum boats, illustrating both basic forming and fabrication techniques and GTA welding to seal crevices at joints. © Elmet Technologies

Summary

Molybdenum and its alloys are used in a broad spectrum of markets, for applications in traditional "smokestack industry" technologies, cutting-edge electronic devices and their manufacture, and emerging "green" technologies such as LED lighting and high-efficiency thin-film solar cells. The properties that originally made molybdenum metal so attractive – strength at high temperature, high stiffness, excellent thermal conductivity, low coefficient of thermal expansion, and chemical compatibility with a variety of environments – will continue to be important in future demanding applications. A considerable manufacturing knowledge base exists, along with numerous organizations able to employ that knowledge. Because of these factors, we expect that applications in existing and emerging markets will continue to arise. The technological infrastructure exists to support new applications with new materials and processes, so the use of molybdenum metal should contiue to grow in the future.

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