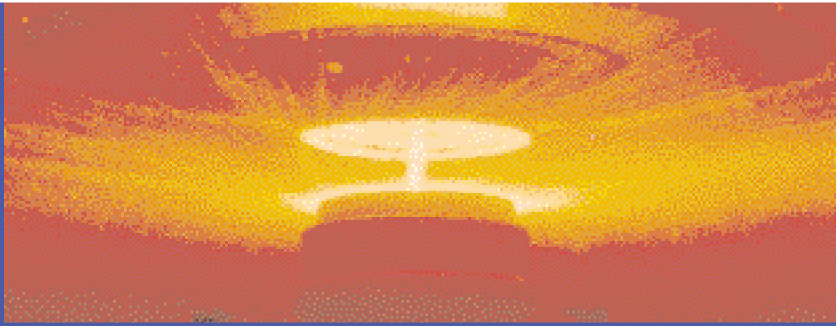

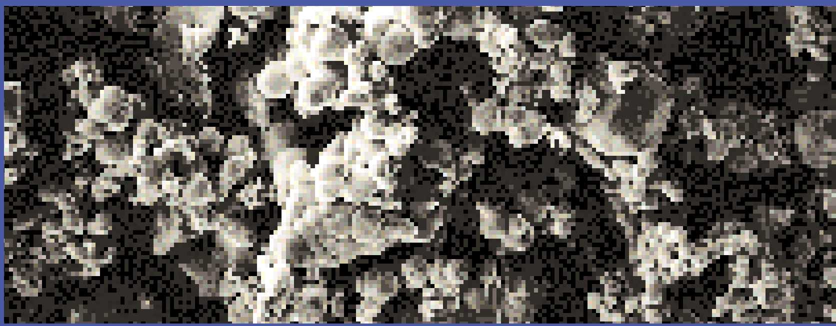

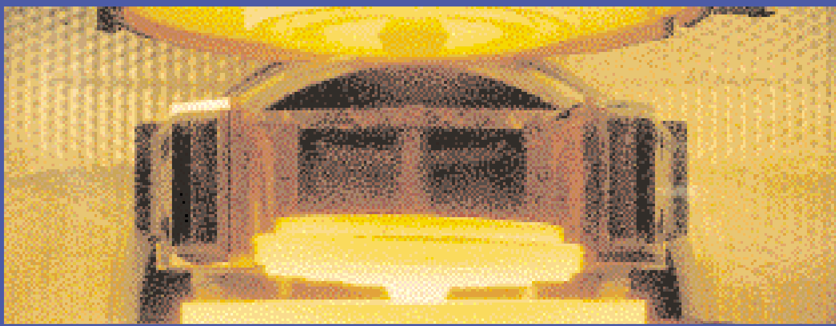

APPLICATIONS OF MO METAL AND ITS ALLOYS

WRITTEN FOR IMOA BY DR. JOHN SHIELDS, JR, FAFM, OF
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IMOA

INTRODUCTION

Molybdenum metal and its alloys are used in a variety of markets including electrical and electronic devices, materials processing, glass manufacturing, high temperature furnaces and equipment, and aerospace & defense applications. The properties that make molybdenum metal and its alloys the materials of choice in these markets include thermal and electrical conductivity, thermal expansion, high-temperature strength, vapor pressure, environmental stability, and resistance to abrasion and wear. This report attempts to provide the reader with an understanding of just why this unique material is used in its many applications. A short primer on techniques for fabricating and working with molybdenum follows the applications discussion.

ELECTRICAL AND ELECTRONIC DEVICES

This market is probably the largest for molybdenum and its alloys. It includes applications such as mandrel wire for manufacturing lamp filaments, wire leads and support structures for lighting and electronic tube manufacture, powders for specially formulated circuit inks and the tooling used to apply them to multi-layer circuit boards, internal components for microwave devices, high-performance electronic packaging, and heat sinks for solid state power devices. A subset of this market is comprised of electrical and electronic equipment used in the medical industry. Many of the internal components of X-ray tubes, from the target itself to support structures and heat shields, are manufactured from molybdenum and molybdenum metal alloys. Molybdenum also finds its way into X-ray detectors, where sheet with precisely controlled gauge is used.

Figure I (taken after Zweben[1]), shows various levels of solid state electronic packaging present in modern components. Examples of components typical of each level are shown in Table I, while Table II summarizes the technical requirements of the various levels.

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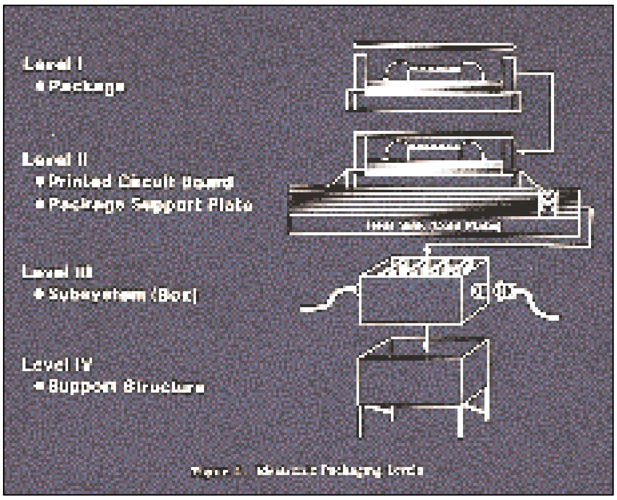


TABLE I. PACKAGING COMPONENTS

Level I

Chip carriers
Electronic packages
Microwave packages
Photonics packages
Laser diode packages

Level II

Printed circuit boards
PCB heat sinks
Package mounting plates

Level III

Enclosures
Covers

Level IV

Support structures

TABLE II. MATERIAL REQUIREMENTS

Level I

Heat dissipation (High thermal conductivity)
Low thermal stresses (Thermal exp. match)
Hermeticity
Electromagnetic shielding

Level II

Heat dissipation
Low thermal stresses
Minimal vibration (High stiffness and strength)
Light weight

Level III

Heat dissipation
Minimal vibration
Electromagnetic shielding
Light weight

Level IV

Minimal vibration
Light weight

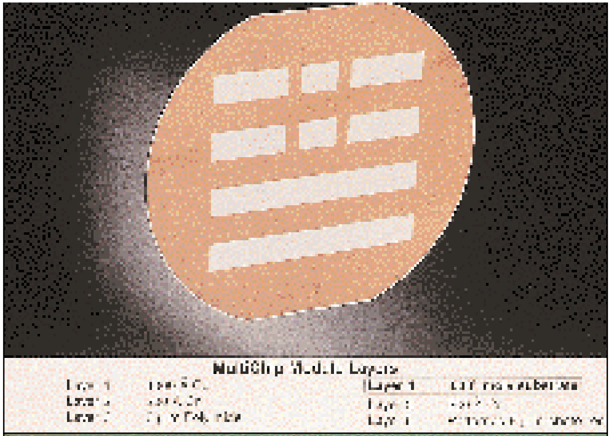
Molybdenum is typically used in Level I and II components, where thermal expansion matching, thermal conductivity, and to a lesser extent stiffness, are important issues. Table III lists some physical properties of a variety of materials commonly used in electronic packaging. The first group is device materials, whose properties and performance characteristics drive the selection of other materials in electronic packages. The second group of materials consists of non-metallic substrates and circuit board materials. The third group contains several metals in common use for electronic packages.

The heat created by the device must be removed to ensure reliable operation. In addition, the thermal expansion created by the heating must be prevented from causing excessive stresses that could develop from mismatches between packaging materials. In military devices, minimum weight and high stiffness are added requirements. The advantages conferred by molybdenum and molybdenum-containing composites such as Cu/Mo/Cu are clearly shown in the table. The last two columns are specific properties, normalized by the specific gravity (r/r H_2O) of each material. The high modulus and conductivity of molybdenum more than compensate for its density, with the result that it still enjoys significant advantage in specific properties.

TABLE III.
PHYSICAL PROPERTIES OF ELECTRONIC PACKAGING MATERIALS

Material	CTE, 10^{-6} K^{-1}	k, W/m·K	E, GPa	r, g/cm^3	$k_{spec.}$, W/m·K	$E_{spec.}$, GPa
Si	4.1	135	113	2.3	59	0
GaAs	5.8	39	85	5.3	7	0
Al_2O_3	6.5	20	380	3.9	5	97
BeO	6.7	250	330	2.9	86	114
AlN	4.5	250	330	3.2	78	103
Epoxy	60	0.3	3	1.2	0	3
Al (1100)	23	221	69	2.7	82	26
Cu	17	400	117	8.9	45	13
Mo	5	140	324	10.2	14	32
Kovar®	5.9	17	131	8.3	2	16
Cu/Invar®/Cu (20/60/20)	5.2	176* 53**	138	8.4	21* 6**	16
Cu/Mo/Cu (13/74/13)	5.7	208* 170**	269	10.0	21* 17**	27
Cu/Mo/Cu (33/33/33)	8.6	311* 251**	186	9.7	32* 26**	19
Mo 15 Cu (infiltrated powder composite)	7.0	160	280	10.01	16	28
Mo 30 Cu (rolled powder composite)	7.5*	176*	240*	9.64	18*	25*
W 10 Cu (infiltrated powder composite)	6.5	180	330	17.0	11	19

**In-plane   **Through-thickness*



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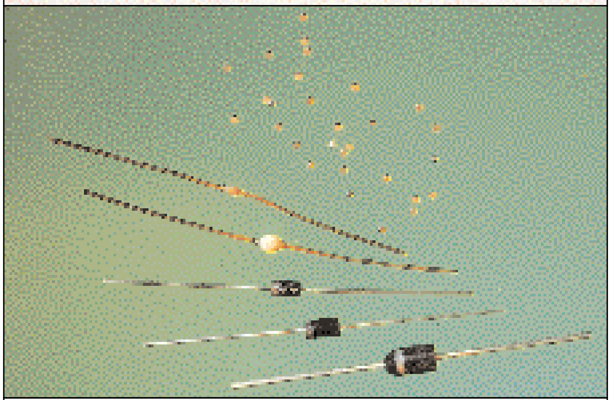

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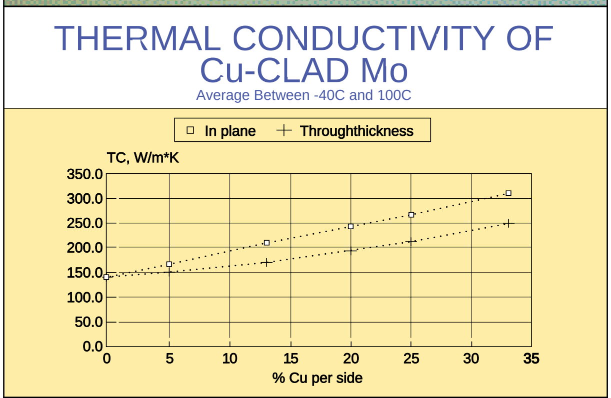

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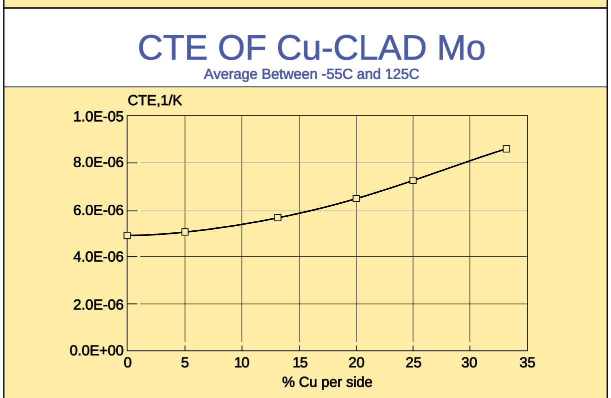

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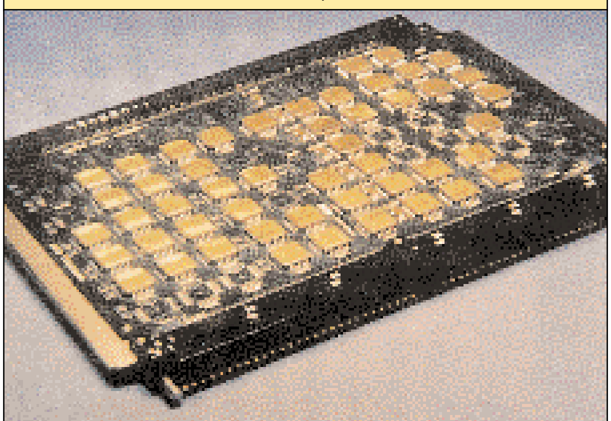

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Molybdenum finds application as a buffer between the relatively low-expansion materials used in integrated circuit (IC) packages and the copper normally used to supply electrical power to the devices and to remove heat from them as well. It is even finding application as a replacement for the silicon substrates used in some devices. ***Figure 2*** illustrates a multichip module application where molybdenum has displaced silicon as the device substrate. This particular application uses thin film technology to apply the various layers which make up the device. Power rectifiers use large quantities of molybdenum sheet that is stamped and plated with nickel, copper, or rhodium to provide both thermal expansion control and heat management. These devices find application in diesel-electric and electric railroad engines and industrial motor power supplies and controls. Pressed and sintered heat sinks for small electrical devices ***(Figure 3)*** are ubiquitous in the consumer goods arena.

Cladding molybdenum with copper results in a material (Cu/Mo/Cu, or CMC)whose properties can be tailored to the application at hand. ***Figure 4*** illustrates the effect of copper cladding thickness on thermal conductivity of CMC. The copper also increases the thermal expansion coefficient of the composite as illustrated in ***Figure 5***, allowing a good match with ceramic substrate materials such as alumina (Al_2O_3) and beryllia (BeO). ***Figure 6*** illustrates a CMC application in military electronics. The high-density surface mount avionics board shown in the figure employs a CMC constraining core to modify the expansion of the epoxy resin board so that it is compatible with the alumina chip carriers that are mounted directly on the board. The ability to employ surface mounting allows designers to employ higher density circuitry and reduce the overall volume of the components. CMC brings the added benefit of high elastic modulus to the assembly, resulting in reduced susceptibility to vibration-induced failures.

Several groups have also worked on molybdenum-copper analogues to the tungsten-copper powder composites that have been long available[2,3]. These materials are available commercially in various compositions and shapes. Powder composites offer the potential advantage of isotropic properties and less hysteresis in thermal expansion, probably due to the greater triaxiality of the internal stress distribution[1]. They also offer greater flexibility in tailoring thermal properties because varying powder blends is significantly less cumbersome than manufacturing different cladding ratios on rolled sheet.

Hot Work Tooling

High-temperature strength and resistance to deformation play an important role in this segment. Aerospace forgers employ tooling made of molybdenum alloys to forge engine materials at high temperature. Extrusion houses have found molybdenum alloys to be ideal for certain applications in the brass industry. Molybdenum - tungsten alloys are used in the handling of molten zinc, due to their chemical compatibility with that material. The processing of many electronic components, whether it be by sintering the ceramic material used in high-performance circuit boards or the metallization of silicon wafers, requires molybdenum metal components.

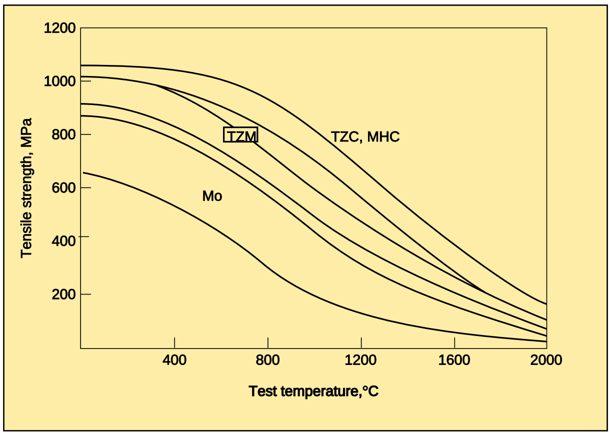
Table IV lists a variety of molybdenum alloy compositions that are commercially available, along with the approximate one-hour recrystallization temperature for the alloy. The precise recrystallization temperature will depend also upon the manufacturing history of the particular product form being considered (a large forging with 60-65% reduction will recrystallize at a higher temperature than wire with 99.9%+ reduction in cross-section). There are three broad classes of molybdenum alloys: those strengthened by reactive metal carbides, those strengthened by substitutional elements, and those stabilized by a mechanically dispersed second phase. Alloys designed to take advantage of a combination of these different approaches also can be found.

TABLE IV.
COMMERCIALLY AVAILABLE MOLYBDENUM ALLOYS

Alloy	Nominal Composition, Wt. %	$T_{Recryst.}$, C
Pure Mo	100 Mo	1100
Carbide-Strengthened		
TZM	0.5 Ti, 0.08 Zr, 0.03 C	1400
TZC	1.2 Ti, 0.3 Zr, 0.1 C	1550
MHC	1.2 Hf, 0.05 C	1550
ZHM	0.4 Zr, 1.2 Hf, 0.12 C	1550
HWM-25 (Combination)	25 W, 1.0 Hf, 0.07 C	1650
Substitutional		
25 W	25 W	1200
30 W	30 W	1200
5 Re	5 Re	1200
41 Re	41 Re	1300
50 Re	47.5 Re	1300
Dispersed-Phase		
PSZ	0.5 vol % ZrO_2	1250
MH	150 ppm K, 300 ppm Si	1800
KW	200 ppm K, 300 ppm Si, 100 ppm AL	1800
MLR	0.7 La_2O_3	1800
MY	0.55 yttrium mixed oxide	1300

The carbide-strengthened alloys are normally employed where high-temperature strength is required. ***Figure 7*** is a composite plot of the strength of several of these alloys as a function of test temperature[4], with a similar plot for pure molybdenum. The scatter bands on the figure were derived from a variety of points determined for samples having differing processing histories, and are typical of the range of properties available in commercially available materials.

The high strength at elevated temperatures combined with high thermal diffusivity inherent in molybdenum make the carbide-strengthened alloys attractive for hot-work tooling applications. ***Figure 8*** illustrates the use of TZM tolling in the Gatorizing®, or isothermal forging, process used to forge superalloy engine discs. In this process, the tooling and workpiece are both heated to the forging temperature, and the disc is formed superplastically. The entire tooling stack and workpiece are contained in a vacuum chamber, in order to avoid formation of volatile oxides of molybdenum. This technique is capable of producing highly defined disc forgings that require much less machining than those produced by conventional techniques. This practice has produced integrally bladed discs on an experimental basis.



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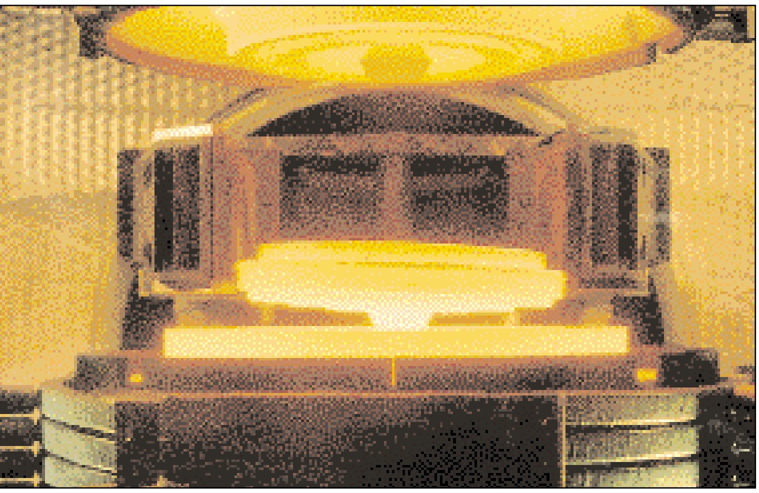

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These alloys also find application in conventional hot work tooling as well. A primary reason for this is their resistance to thermal shock and cracking. One way to illustrate the advantage inherent in molybdenum in such applications is by the use of a parameter developed for thermal fatigue. The thermal fatigue resistance parameter is given by:

$$P = \frac{s_y \times k}{E \times CTE}$$

where s_y = Yield Strength
k = Thermal Conductivity
E = Elastic Modulus
CTE = Coefficient of Thermal Expansion

High yield strength (resistance to plastic deformation) and thermal conductivity (dissipation of thermal gradients and stresses), or low modulus and coefficient of thermal expansion (both related to the degree of thermal stress developed), give high values for P (a desirable result). Table V summarizes the values of P obtained for iron-base, nickel-base, and molybdenum tooling materials using room temperature values for the formula's components. While the steel has a distinct advantage in strength, and both the steel and nickel alloys have advantage in modulus, the high thermal conductivity and low coefficient of expansion for molybdenum make it the preferred material for thermal shock applications. TZM and MHC alloys both find application in the extrusion of copper and copper alloys. The die design requirements are somewhat different from those normally used by tool designers, primarily because of molybdenum's low coefficient of thermal expansion. Significantly more shrink fit is required for molybdenum than for steel or nickel alloy dies in nickel alloy cases, so that the die does not loosen as the assembly heats up to its normal operating temperature. Once this is accounted for, the molybdenum dies perform very well.

TABLE V. VALUES OF THE THERMAL FATIGUE PARAMETER FOR SEVERAL MATERIALS

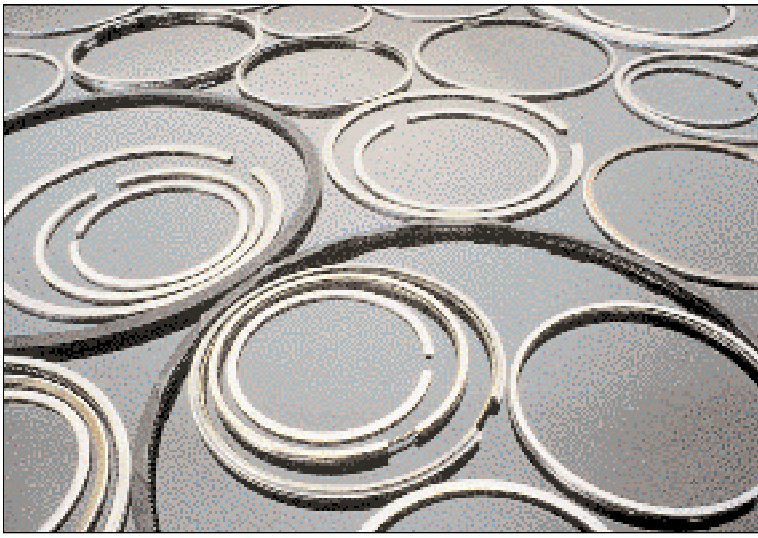
Material	s_y, MPa	k, W/m·K	E, GPa	CTE, 10^{-6} C^{-1}	P
H-13	1227	28	215	12	.013
Ni-base	500	10-20	200	10-12	.002-.005
Mo	620	140	324	5	.054

Molten Metal Processing

Aluminum die casters use molybdenum to solve thermal checking and cracking problems that otherwise cannot be eliminated. In this case, TZM inserts, cores and pins are used in areas prone to hot checking. Molybdenum's cost makes the cost of tooling quite high in comparison to steel if the entire tool is manufactured from moly. Rapid solidification equipment using rotating disc and rotating drum technology benefits from the use of TZM and MHC alloys. Here again, the high-temperature strength of these materials and their resistance to thermal shock failures permits the processing of higher melting point materials by this technique than would be otherwise possible. ***Figure 9*** illustrates this application in the melting of highly reactive metal powders. Another unique application for molybdenum alloys is in the handling of molten zinc. At one point in time, tungsten was thought to be the only material resistant to corrosion by molten zinc. Alloying molybdenum with tungsten resulted in an equally resistant material at a greatly reduced cost. The Mo-25% and Mo-30% tungsten alloys evolved from this work, and are widely used for impellers, pump components, and piping that handle molten zinc.

Thermal Spray Processing

A significant amount of molybdenum powder is consumed by thermal spray applications. In this technology, molybdenum metal powder is blended with binders rich in chromium and nickel, then plasma-sprayed on piston rings and other moving parts where wear is a critical performance issue. The older wire spray process still accounts for the majority of molybdenum consumed in the market. In both cases, the material to be sprayed is fed through a high temperature gas jet. This jet may be generated by a plasma torch or a high velocity gas torch. The feed material is melted in the flame, and droplets are carried by the jet to the surface of a substrate, where they impact the surface and freeze rapidly[5]. With time, a coating is built up on the substrate's surface. Composite or graded coatings can be produced by controlling the composition of the feed material to the jet.



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Piston rings ***(Figure 10)*** are coated with pure molybdenum, or alloy powder blends. The paper and pulp industry also employs the coatings for wear and corrosion resistance. A variety of compositions is possible by blending with other powder components. The most common alloy blends contain varying amounts of Ni, Cr, B, and Si. The powders used in spray applications are markedly different from those used to

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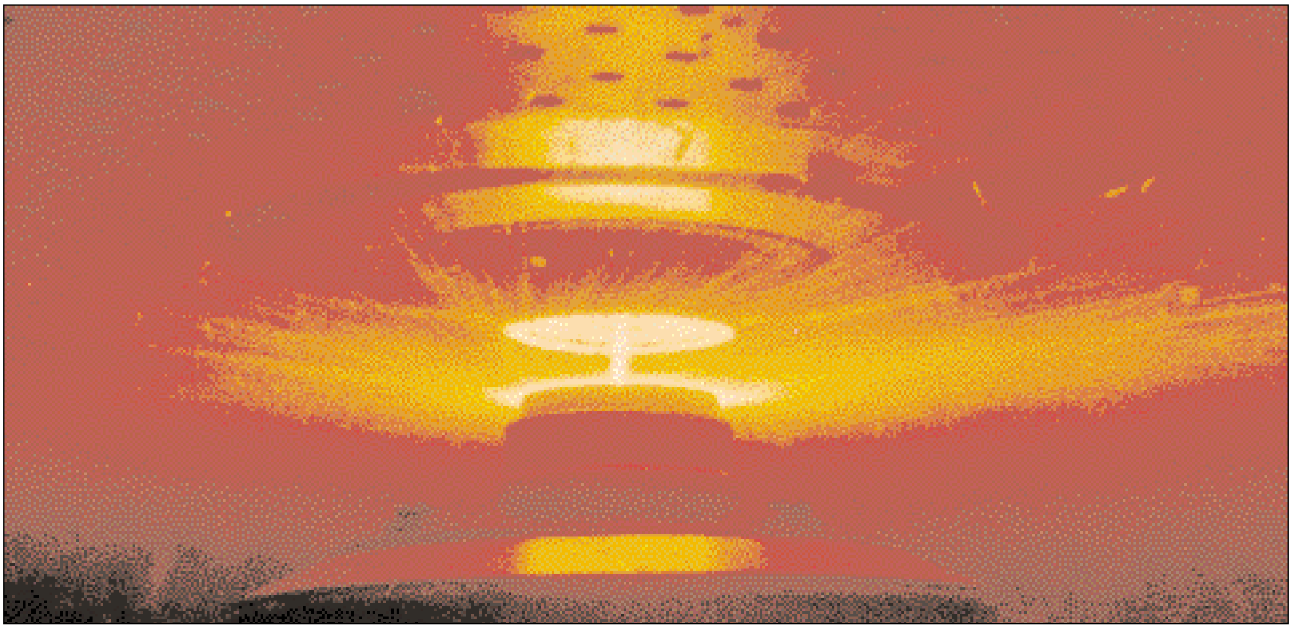
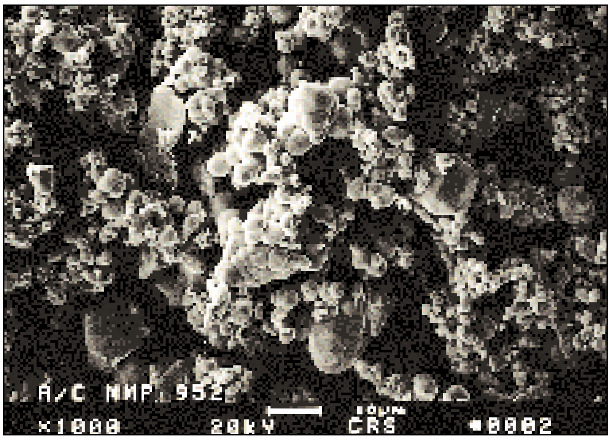


produce mill products. Because most mill products start as pressed and sintered billets, great attention is paid to producing a powder that will press to high density and produce green billets that have strength enough to be handled in industrial operations. This means that the powders that work best for mill products tend to be agglomerates of fine particles that provide easy mechanical interlocking. Spray applications require just the opposite characteristic—good flowability. Thermal spray powders are generally processed by spray drying to produce spherical or nearly spherical powders that flow easily through spray equipment. Note the difference in powder particle morphology of the pressing-grade powder of ***Figure 11*** and the spray powder grade shown in ***Figure 12***.

Table VI summarizes qualitatively several powders available for thermal spray applications[6]. The table shows the typical practice used to manufacture the powder, the spray process (plasma or high-velocity oxy-fuel) used to deposit the coating, maximum use temperatures, and typical Vickers hardnesses is attained by the coatings. In addition to these powders, prealloyed powder grades are also available, in which the molybdenum and alloy blend powders are themselves densified together in a plasma jet. These powders have been reported to give improved wear resistance in laboratory evaluations[7], and are useful where corrosion is a concern.



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12.

Chemical Processing

Although tantalum is by far the most widely used of the refractory metals to impart corrosion resistance to chemical process vessels and components, there are some applications where molybdenum has been used to great success. Molybdenum support structures have replaced graphite in the processing of high-purity alcohols. Molybdenum-rhenium alloys, first developed because of their vastly improved ductility at low temperatures and in the recrystallized condition, have been employed as vessel linings and piping components for the manufacture of Freon® replacements.[8,9,10]

TABLE VI.
POWDERS FOR THERMAL SPRAY APPLICATIONS

Material	Production Process	Spray Process	T_{Max}, C	HV
Mo	Spheroidized	Flame/Plasma	340	200-700
Mo	Agglomerated	Plasma	340	400-600
Mo	Sintered	Plasma/HVOF	340	900
Mo/3-4% O	Agglomerated, sintered	HVOF	340	900
Mo/NiCrBSi 70/30	Blended	Plasma/HVOF	340	600-800
Mo/NiCrBSi 75/25	Blended	Plasma/HVOF	340	600-800
Mo/NiCrBSi 30/70	Blended	Plasma/HVOF	340	600-800

GLASS MANUFACTURING

Because of its compatibility with many molten glass compositions, molybdenum has found application in handling equipment, tooling, and furnace construction. The most common use for molybdenum is as electrodes for the melting of glass. Because glasses are electrically conductive when molten, molybdenum electrodes can be used to increase the energy input in conventionally fired furnaces and thereby increase the throughput of the furnaces. There are as many electrode designs as there are design firms, but all immerse the molybdenum electrode into the furnace where it is protected from oxidation by the glass itself. *Figure 13* illustrates a common type of design, wherein the electrodes are introduced through the side of the glass furnace[11]. This necessitates protection of the portion of the electrode exposed to the atmosphere from oxidation. This can be done by internal or external cooling by the use of protective atmospheres or by protective coatings based on molybdenum silicides[12]. The advantage of this design is that, as the electrode wears in the furnace, it can be replaced by adding on to its external end, and pushing the newly extended electrode into the bath.

Molybdenum is not the only potential electrode material. Table VII summarizes the advantages and disadvantages of several materials that are in use or have been in used in the past. Molybdenum's advantages in creep resistance, glass compatibility, and resistance to thermal shock all outweigh the increased cost with respect to most of the other materials.

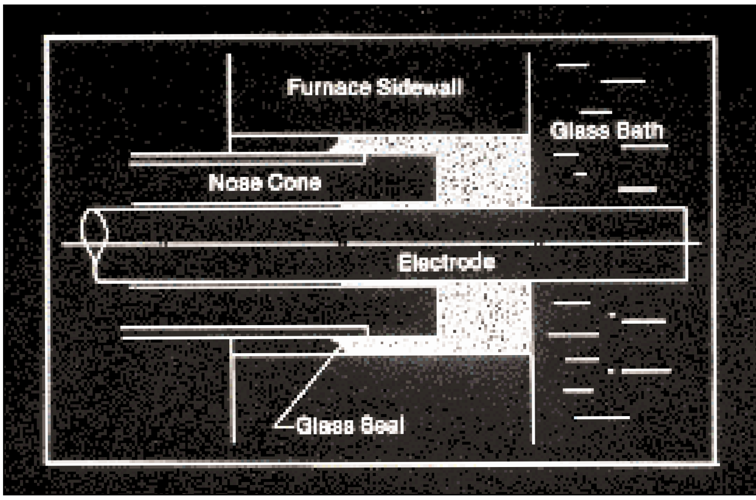

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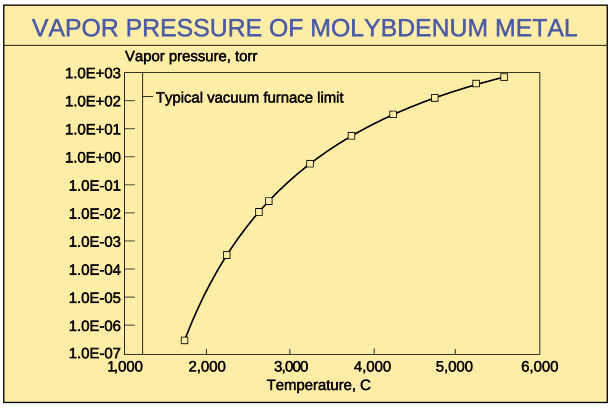
TABLE VII. GLASS MELTING ELECTRODE MATERIALS

Advantages	Disadvantages	Advantages	Disadvantages
Molybdenum		**Inconel 600**	
High current density	Oxidation	Corrosion resistant	1200 C maximum
Excellent strength	Incompatible with lead glass	Moderate cost	Low strength above 1200 C
Thermal shock resistance	Moderately high material cost	Moderate strength	Poor sag resistance
1700 C capability			
Excellent total cost			
Carbon		**Platinum**	
Very low cost	Requires reducing conditions	Extraordinarily stable	Extremely expensive
2000 C capability	Low current densities	1400 C capability	Poor in reducing conditions
	Bubble formation		High frequencies (10 khz)
Iron		**Tin Oxide**	
Low cost	Colors glass	No coloration	Oxidation
	Oxidation	1350 C capability	Low shock resistance



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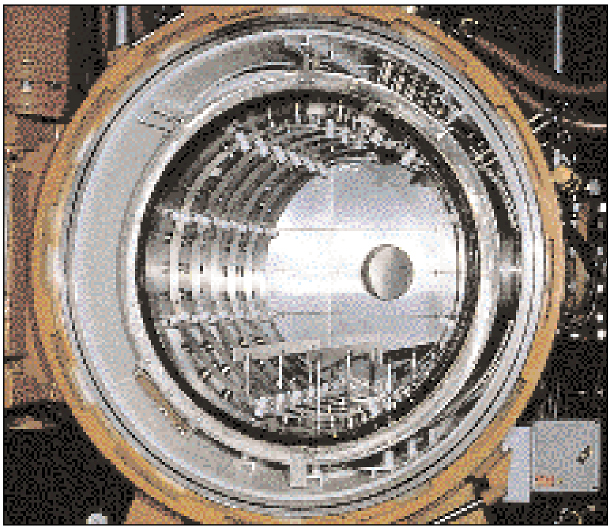

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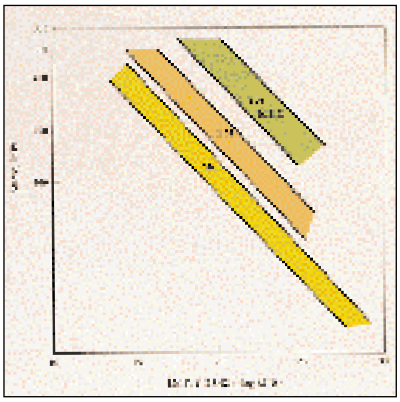

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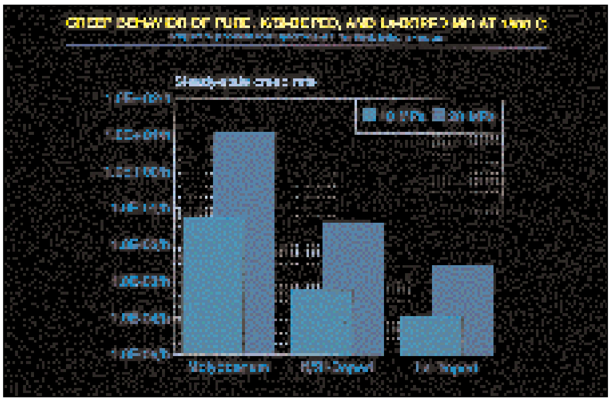

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HIGH-TEMPERATURE FURNACES AND EQUIPMENT

Molybdenum's strength and stability at elevated temperature make it an attractive material for construction of high-temperature furnaces and the fixtures and tooling associated with them. ***Figure 14*** shows the vapor pressure of molybdenum as a function of temperature[13]. Molybdenum's high melting point means that at typical operating temperatures for vacuum furnaces, volatilization of internal components made from molybdenum or molybdenum alloys will be negligible. ***Figure 15*** illustrates an all-metal hot zone employed in a modern vacuum furnace. Metal hot zones offer the utmost in vacuum cleanliness for those heat treating applications that cannot tolerate carbon or oxygen contamination. (Titanium, niobium, and tantalum are all metals that require environments free of oxygen and carbon.) The increasing use of hot isostatic pressing (HIP) to consolidate powder materials and improve the integrity of cast metals has also boosted the need for molybdenum products. Molybdenum and its alloys are widely used as materials of construction for HIP vessels, being found in their heating elements, mantles, and support structures .

The ceramic processing industry also makes extensive use of molybdenum components for fixtures and sintering boats. Molybdenum and its alloys are the materials of choice for sintering ceramic nuclear fuels, while the oxide ceramics processed by the electronics industry are nearly universally sintered in hydrogen on molybdenum carriers.

In these applications, the long-term mechanical stability of components is important. ***Figure 16*** shows the stress-rupture behavior of molybdenum and the carbide-strengthened alloys[4]. The strength advantage and resistance to recrystallization conferred to these alloys is reflected in their greater creep resistance at moderate temperatures (<1500 C). Above these temperatures, especially for longer times, the microstructures of these materials recrystallize and they lose their strength. For applications requiring creep resistance at 1500 C and above, the dispersion-strengthened alloys are superior. ***Figure 17*** illustrates this in a dramatic way, showing the creep rates measured on pure molybdenum, potassium/silicon doped molybdenum, and lanthanum-doped molybdenum at 1800 C[14]. Note that the scale is logarithmic, and not linear. The doped alloys are several orders of magnitude better than pure molybdenum under these conditions. These materials are typically employed in applications such as sintering boats and trays for nuclear fuels and ceramics.

AEROSPACE AND DEFENCE APPLICATIONS

Compatibility with hot gases and strength at temperature are the typical properties that result in molybdenum being used in this market area. Molybdenum's poor oxidation resistance prevents it from being used in a wider variety of applications that could use its high strength, but in rocket and reactive gas valves, where high performance is required for a relatively short time, it finds application. For certain of these components, the metal injection molding process is being developed because of its potential for significant material and machining savings. Molybdenum is also being employed in munitions applications, a relatively new application.

MANUFACTURING CONSIDERATIONS

Molybdenum alloys, like all materials, are seldom used in their applications as they are produced by the mill or the raw materials manufacturer. They must be formed, joined to other components, machined, and otherwise changed into an engineered component. This section briefly summarizes a few of the more important points regarding the use of these materials in manufactured components.

Machining

Molybdenum metal and its alloys are machinable by all the common metal removal processes. Many shops around the world have manufactured a wide variety of parts in a range of sizes from all the molybdenum alloys The materials are capable of being machined with excellent surface finishes and to exacting tolerances.

Several points must be borne in mind when preparing to machine molybdenum or any of its alloys. While molybdenum retains its strength to high temperatures, it is not particularly strong at ambient temperatures. Neither is its ductility as great as carbon steel or brass. Furthermore, its (relatively speaking) high ductile-brittle transition temperature 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. Close attention should be paid to tool sharpness. Dull tools can tear the material instead of cutting it cleanly, and create microcracks that limit the life of the component being machined. High speed tools are generally adequate, as long as they are kept sharp. Carbide grades perform well, particularly where problems arise due to the abrasiveness of chips and dust. The tendency for molybdenum to form discontinuous chips and abrasive dust is one reason why inexperienced shops sometimes are over-optimistic about their ability to machine these materials economically. Carbide tools also prove their economic worth in jobs where long uninterrupted cuts are required, due to their better life between regrinds.

Much heavy machining, such as ingot scalping and rough turning, is accomplished without lubrication. For best finishing work, lubrication flushes dust away from the tool/workpiece interface and provides cooling as well. Chlorinated solvents were once the coolant of choice for fine finish machining of molybdenum and its alloys, but environmental and health concerns with the use of such coolants has reduced their use to near zero levels.

Table VIII (see over page) summarizes the results of an extensive research program funded by the U. S Air Force into the appropriate techniques for machining molybdenum and its alloys[15]. The parameters in the table 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.

Other machining processes such as grinding, photo-etching, and electrical discharge machining are also commonly performed on molybdenum and its alloys. Care must be exercised when EDMing molybdenum and its alloys because the surface zone frequently contains a recast layer. This structure is susceptible to microcracking and should be removed by mechanical or chemical polishing prior to placing the part in service. Grinding also has the potential to cause overheating and surface cracking in these materials if sufficient amounts of coolant are not employed. Manufacturers of grinding wheels and abrasives have a variety of wheel compositions that are designed to be employed for a range of applications. They can be a valuable source of information and technical assistance in choosing wheel compositions and grinding practices.

TABLE VIII. SUGGESTED PARAMETERS FOR SOME COMMON MACHINING OPERATIONS

Operation	Tool Material	Tool Geometry	Tool Used	Depth of Cut, in.	Width of Cut, in.	Feed	Cutting Speed, ft/min
Turning	C-2 Carbide	BR: 0° SCEA 15° SR: 20° ECEA: 15° relief: 5° NR 1/32"	5/8 in. Sq 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. diam 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°	3/4 in. diam four-tooth 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 Angle: 7°	0.250 in. diam drill, $2\frac{1}{2}$ in. long	$\frac{1}{2}$ Through Hole	—	0.005 in./rev	150
Reaming	M-2 HSS	Helix Angle: 0° CA: 45° Clearance: 10°	0.272 in. diam six-flute chucking reamer		0.010 depth on hole radius	0.015 in./rev	60
Tapping	M-10 HSS	Four-flute plug 75% Thread	5/16-24 NF tap		—	—	70

Forming and Metalworking

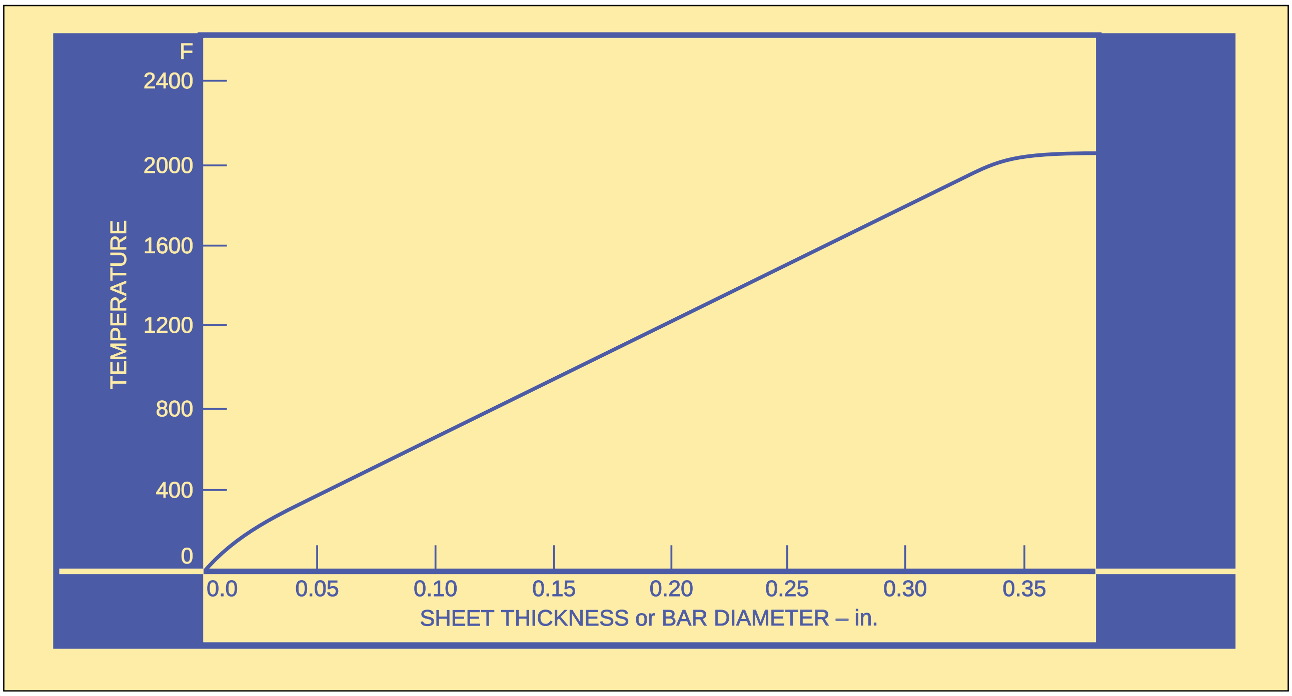
Molybdenum and its alloys can be formed by all common metalworking practices such as bending, punching, stamping, drawing, and spinning. As in the case of the machining practices discussed above, consideration must be given to the mechanical behavior of the materials. The ductile-brittle transition temperature of molybdenum and its alloys is increased by such factors as increased strain rate and triaxiality of applied stresses. The ability to work the material successfully will thus depend upon the surface condition of the material, the size of the section being formed, and the speed of the deformation. In bending operations, this means that the bend radius which can be successfully bent without cracking will be a function of the sheet thickness. Thicker sections may require heating above room temperature to remain in the ductile regime, due to the greater triaxiality of stress present during the forming operation. In addition, molybdenum and its alloys are typically anisotropic in their ductility properties, unless special processing has been employed to equalize the directionality of deformation in the material. When bending sheet, for example, orienting the bend axis of a blank perpendicular to the dominant rolling direction will result in better performance, as measured by the propensity to crack on bending and the minimum bend radius which can be successfully produced. ***Figure 18***[16] shows recommended temperatures to be used when forming molybdenum metal of varying section thicknesses. Forming temperatures for the carbide-strengthened alloys are 50-100 C higher for any section thickness, due to their greater sensitivity to embrittling factors.

Operations that employ shearing, such as stamping, punching, and blank shearing, are particularly sensitive to the formation of planar cracks in the sheet being formed. These defects are commonly called *delaminations*; they are in fact intergranular cracks which propagate along the planar grain boundaries which develop during the rolling of sheet and plate. Tool clearances and edge condition are the major contributors to this phenomenon[17]. Dull and damaged tool blades are invitations to delamination. Clearances between blades, or between punch and die in stamping operations, should be in the range of 5-8% per side to minimize delamination. Sheet up to 0.5 mm thick can be successfully sheared at ambient temperature. Preheat temperatures of 65-95 C are recommended for sheet between 0.5 and 1.2 mm thick. In the range of 1.5 mm-3.2 mm, the preheat temperature should be increased to about 350 C, and 600 C preheat is necessary to shear plate of 6.3 mm thick. The method of heating is limited only by the creativity of the operator. Linear gas burners, infra-red lights, air furnaces, hand-held torches, and hot plates have all been successfully employed as heat sources for shearing operations.

Joining

Molybdenum and its alloys can be successfully welded and brazed, but welding is normally employed only for applications not subjected to great stress. The weld and surrounding recrystallized zone in the base metal have significantly lower strength, and a much higher ductile-brittle transition temperature than the surrounding material which is unaffected by the welding process. This tends to concentrate the deformation in the weld

18.



zone, and the triaxial stresses produced by the constraint of the base metal can result in brittle fracture. There are applications where welded structures perform quite well, and all common welding techniques have been employed to join molybdenum and its alloys. Generally speaking, the lower the heat input required, the more reliable the weld. Electron-beam welds, with their narrow weld and heat-affected zones, are less susceptible to failure than GTA welds which require large amounts of heat input.

Oxygen is also a bad actor in welded components. It tends to segregate to grain boundaries, further reducing ductility. For this reason, the arc-cast alloys which generally contain higher carbon levels, are somewhat more readily welded than the powder metallurgy analogues. The carbide-strengthened alloys are also more forgiving than pure molybdenum for the same reason. Most welding of molybdenum components is performed inside high purity inert gas chambers to minimize oxygen pickup.[18]

The doped alloys generally do not weld as successfully as the other alloys, because the volatile alloy elements in the materials produce gassy welds. Rhenium alloys are quite weldable. The well-known rhenium ductilizing effect[19] renders these alloys ductile at cryogenic temperatures even in the as-solidified or recrystallized condition. As noted earlier, this property has been utilized to design and fabricate large chemical pressure vessels by weld cladding Mo-Re to inexpensive plate steel alloys[8-10].

Brazing is also in common use for joining molybdenum and its alloys. Commercial brazing alloys are available that have flow points ranging from 630 C through 1400 C. Compositions vary widely, with most containing precious metals. Nickel-base alloys are also available. This is another area where manufacturers of brazing compounds and equipment can provide excellent technical assistance. In most cases, it will be desired that the brazing temperature be below the recrystallization temperature of the alloy to be brazed. In this manner, the improvement in strength and ductile-brittle transition behavior which accrues with mechanical working can be retained.

SUMMARY

- *Molybdenum and its alloys are used in a broad spectrum of markets, in applications that vary from traditional "smokestack industry" uses through cutting edge electronic device design and manufacturing.*
- *The properties that have made these materials 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 in the future to be required in demanding applications.*
- *A considerable base of fabrication knowledge and manufacturing organizations also exists, permitting these materials to be fabricated into useful components so that new applications can be readily brought to market.*
- *Because of these factors, it is expected that the demand for molybdenum and its alloys will continue to be strong, and that growth will occur as new applications and alloys come into production.*

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Figure List

THE INTERNATIONAL MOLYBDENUM ASSOCIATION (IMOA) was set up in 1989 and it has quickly earned its reputation as the focal point of reference for the molybdenum industry. There are member companies from every sector of the Western world's industry and China is also now represented. Although IMOA is registered under Belgian law, its secretariat is based in London.

The Association's activities centre around:

- the promotion of molybdenum as a competitively priced and abundant material, which gives to the products in which it is used maximum performance at minimum cost;
- molybdenum in relation to health, safety and the environment. With the increasing amount of legislation on metals, IMOA provides a central service which saves individual companies time and money;
- the collection of statistics on the molybdenum market. Production, consumption and inventory data is collected and summarised both regularly and confidentially;
- the organisation of regular meetings and conferences at which the industry can meet to exchange views, make new business contacts and learn about the latest technical innovations;
- preparation of guidelines on sampling and assaying procedures.

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