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Molybdenum metal coatings punch above their weight

Molybdenum plays an important role in the performance of piston rings used in combustion engines. Applied as a plasma-sprayed coating, it delivers good wear resistance and better overall performance than materials used in the past.

Numerous uses of molybdenum metal contribute to a higher standard of living, yet are not well known. One of these is, undoubtedly, the molybdenum coating applied to piston rings in all modern combustion engines. The amount required per vehicle is measured in grams, but in boxing terms, this 'lightweight' layer of molybdenum packs a 'heavyweight' punch, improving engine efficiency, power, emission performance, and service life.

Challenges

The unassuming piston ring is itself an unsung hero of today's efficient, low-emission, internal-combustion engine. Piston rings must:

- Block combustion gas from escaping down the cylinder wall between the piston and the cylinder, which would deprive the engine of power, release pollutants, and degrade engine oil performance
- Prevent oil from seeping up the cylinder walls into the combustion chamber, which would produce efficiency-sapping detonation and unacceptable hydrocarbon emissions
- Work reliably from temperatures below -20°C for winter starts to operating temperatures above 230°C
- Bear loads imposed by gas compression, combustion, and piston motion during operation, in addition to thermal frictional stresses
- Be inexpensive.

Piston ring functions

Most pistons employ three rings located in separate machined grooves, each with a specific function. The top (compression) ring seals the combustion chamber. Gas pressure during compression and combustion forces the ring down against the bottom of its groove and out against the cylinder wall to form the seal. The middle (second compression) ring backs up the top seal. It also plays an important role in oil control, scraping remnants of oil from the cylinder wall and preventing oil from entering the combustion chamber. The bottom (oil-control) ring removes most of the oil from the cylinder wall. Unlike the top two rings, the oil-control ring is usually made from several pieces – upper and lower scraper rings and a spacer.

Ring materials and early coating technology

Piston rings are usually made of a ferrous alloy. Examples include alloyed or unalloyed grey, malleable, or ductile cast iron with as-cast or heat-treated microstructures. They also might be carbon steel, low-alloy steel, or even stainless steel, depending on their intended application. Cast irons are the most common automotive piston ring materials because they comfortably meet the performance needs of the consumer and are least expensive to manufacture.

However, these piston ring materials are prone to surface wear so they must be coated with a wear-resistant material. For many years, chromium-plated rings

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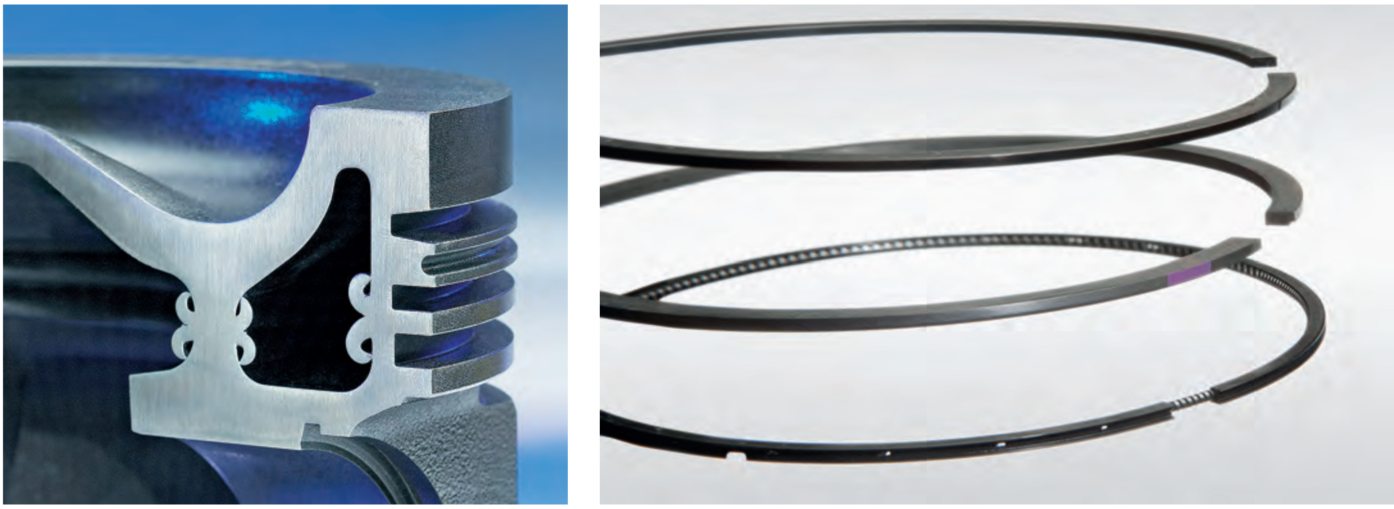
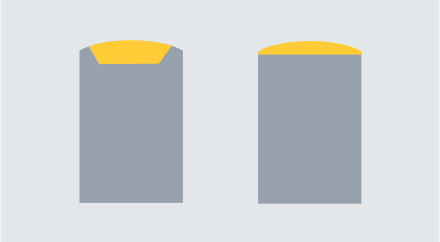


An advanced piston design (left), and a set of modern piston rings (right). © Federal-Mogul Corp.

have served basic engine needs, and they are still available. The plating provides a hard surface to minimize general wear, but it has always suffered from the basic problem of fretting wear, a loss of small particles from the surface.

Flame-sprayed rings coated with molybdenum metal appeared in the 1960s, and delivered improved performance. Flame spraying, one of several deposition techniques in the broad category of thermal spraying, feeds molybdenum wire into a high-temperature flame that melts the wire and forms molybdenum droplets. The combustion gas carries these droplets onto the piston ring surface, creating 'splats' that build up a coating. Oxygen in the combustion gas ends up as an impurity in the molybdenum coating, increasing its hardness and wear resistance. It also forms molybdenum oxides that become part of the coating.

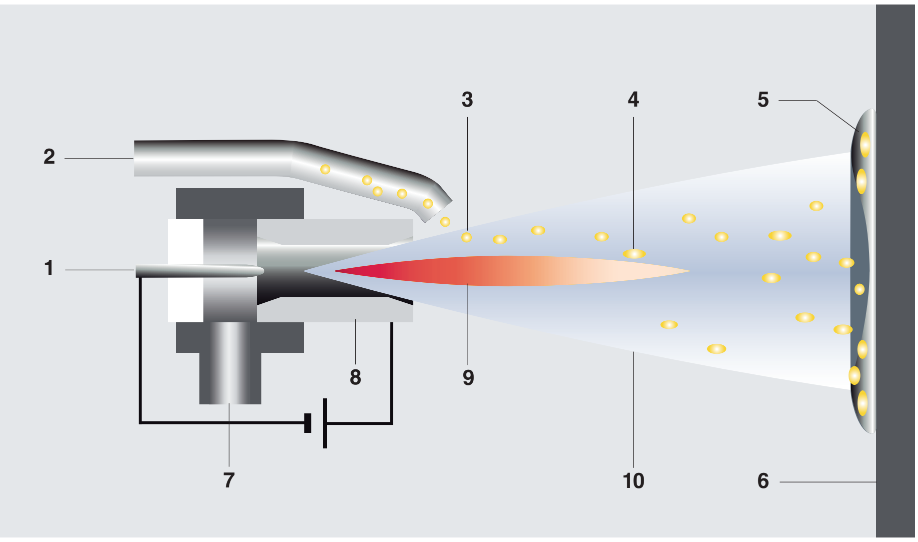
Flame-sprayed molybdenum coatings are hard and rather brittle, so a small channel is machined into the outer diameter of the rings to support the coating, as illustrated in the middle of the page on the left of the schematic showing piston ring cross-sections. In certain high-performance applications, the oxide phase can initiate coating failure even with this support.



Schematic of piston ring cross-sections (grey), showing flame-sprayed (left) and plasma-sprayed (right) molybdenum coatings (yellow).

Plasma-spray coating

Plasma-spray technology, illustrated below, provides an improvement over flame spraying. The inert gas shroud protects the droplets and splats from oxidation, producing a low-oxygen coating free of oxide inclusions. The high temperature of the plasma, exceeding 10,000 K, ensures full melting and significant superheating of even high-melting refractory metals like molybdenum.



Plasma-spray coating: the plasma spray-guns strike an arc between the cathode (1) and the anode (8) of the spray nozzle. A carrier gas (7), usually argon, helium, hydrogen, or a mixture of these, flows through the nozzle and arc at high velocity, forming an extremely hot plasma (9). A powder supply channel (2) feeds the powdered coating material into the high-velocity stream of inert gas and arc (3) where it melts (4). The inert gas stream (10) carries the droplets to the workpiece where they form splats (5) on the substrate (6). Source: Laurens van Lieshaut/ CC-BY-SA-3.0 (http://creativecommons.org/licenses/by-sa/3.0/)

This process produces strong splat-substrate and splat-splat bonding within the coating. The porosity of the coating can be controlled through the process parameters. Optimized porosity enhances the ring's ability to control cylinder-wall lubrication. Because plasma-sprayed molybdenum does not contain as much dissolved oxygen as flame-sprayed molybdenum, it is softer than flame-sprayed molybdenum. It conforms, therefore, to cylinder walls more readily and improves sealing efficiency. The low oxygen content, combined with the high-bond strength of plasma-sprayed coatings, eliminates the need for a grooved ring to support the coating, as illustrated on the right of the schematic of piston ring cross-sections on the previous page. Plasma-sprayed molybdenum-coated rings can provide 150,000-km vehicle life under normal use, a significant improvement over chromium-plated rings. Because the plasma-sprayed coatings are less susceptible to failure caused by oxides, they can be used successfully in more demanding applications, such as the higher efficiency, higher power engines typical of current automotive technology.

Molybdenum-based materials for piston ring and other coating applications

Material composition	Coating process	Applications	Desired properties
Pure Mo	Flame spray HVOF*	Piston rings, synchronizing rings, diesel engine fuel injectors, continuous casting and ingot molds	Lubricity
Mo-3%Mo_2C	Plasma spray	Piston rings, synchronizing rings, pump impeller shafts	Lubricity, wear resistance
Mo-17.7, Ni-4.3, Cr-1.0, Si-1.0, Fe-0.8, B	Plasma spray	Piston rings, synchronizing rings	Lubricity, wear resistance

* High-velocity oxy-fuel, a flame-spray coating process capable of higher temperatures and gas velocities than traditional flame spraying.

Molybdenum alloys for piston ring coatings

Three examples of molybdenum piston ring coating materials are shown in the table above. Pure molybdenum coatings are used where lubricity is required. When greater wear resistance is needed than can be provided by pure molybdenum coatings, alloys with molybdenum carbide and other elements are used.

Summary

Molybdenum metal coatings, while used only in small quantities, provide significant benefits in terms of fuel efficiency, emission control, power output and engine service life. The large benefits derived from these tiny quantities of metal, mean that molybdenum does indeed punch above its weight. (JS)

Molybdenum on point in fencing

A flèche or a lunge are just two of the many attacking moves in fencing that test the cold steel of foils, epees and sabers, subjecting them to brutal bending stresses. These weapons require flexibility and high toughness to ensure the safety of the fencers. The international standard for competition blades is a molybdenum-containing high-strength stainless steel that meets the challenge.

After more than one hundred years of know-how in hot forging of agricultural tools and steel fly-fishing rods, Blaise Frères, a small company from the Loire region of France, has earned highest standing in the fencing world. At the 2012 Summer Olympic Games in London, 95% of the fencers competed with their blades. Molybdenum made a decisive, if not official, contribution to this dominance.

An alloy approved by the International Fencing Federation

In the 1980s, competition injuries arising from failure of carbon steel blades led the International Fencing Federation (FIE) to seek an improved blade material. The primary objective was to guarantee faultless safety. However, it was also important to preserve the characteristic click-clack sound of crossing blades during attacks. This was a criterion of historic importance in this noble sport that harks back to the courts of the Renaissance, and it eliminated composite blades from consideration.

Fencing uses three different blade designs – foil, epee, and sabre. Foils and epees attack solely with the tip,

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which subjects the blades to substantial bending stresses during thrusts and impact loads during parries. Sabers strike primarily on the edge, the flat or the back of the blade, imposing sudden and repeated shocks.

A maraging steel, Z02 NKDT 18 09 05, was chosen and officially approved by the FIE. Maraging steels develop great strength and flexibility through the metallurgical reactions of martensite formation and age hardening. The steel is a low-carbon iron alloyed with 18% nickel, 9% cobalt and about 5% molybdenum. The steel's unique properties optimally balance flexibility and strength so that blades do not twist when bent, which maintains the accuracy of 'hits'. Molybdenum plays a crucial role in blade performance, providing the metallurgical properties required to withstand short and intensive, lightning-like attacks.


A flèche (attack) at the final of the épée world cup tournament in Paris in 2012. Fencing weapons have to be extremely flexible without breaking. © Marie-Lan Nguyen

A completely traditional manufacturing process

Blades begin their life with automatic hot forging of a conical 'mock-up' from a 200–260 mm long bar. The next step is 'free' forging, hot manual shaping of the blade's final profile using a tilt hammer. By the time the blades are forged to their maximum length (870 mm at most), they will have their typical profiles – square or rectangular for foils, V-profile for epees, and Y or V-profile for sabers.

Only the extremities of the blade are machined after forging. The base is threaded to secure the guard to the handle, and the 'tang' (the tip of the blade) is machined to house a micro-switch that registers hits. The switch's signal is transmitted through a 0.6 mm wire running in a groove along the blade. Grinding, polishing, heat treatment and marking give the blades their final appearance and mechanical properties.


Hot forging (left) and cold hammering (right) are performed with the naked eye by experienced craftsmen. © Blaise Frères

During final inspection, tests to verify flexibility and resilience and, sometimes, fatigue and other destructive tests are carried out on equipment calibrated and approved by the FIE. The forging shop ships 70,000 blades around the world each year. High-level fencers, who use some 10 to 15 blades per year, particularly favor its competition models.

A seal of excellence for the manufacturer… and molybdenum

This leader of the high-end blade market depends on the workmanship of its operators, who are capable of checking up to 90% of a blade's precision of shape with the naked eye. The professional skills of its journeymen, the result of a long apprenticeship and experience, earned the company the highly-coveted EPV (Entreprise du Patrimoine Vivant – Living Heritage Enterprise). This seal distinguishes French companies with excellent craftsmanship skills and industrial expertise. Now, molybdenum has become part of this tradition. (TP)

An ever-changing masterpiece

If a building becomes architecture, then it is art. (Arne Jacobson)

London's architect Zaha Hadid, famous for her stunning designs, had a clear vision for the Eli and Edythe Broad Art Museum on the East Lansing campus of Michigan State University. She wanted "…a structure that changes as visitors move past and through it – creating great curiosity…". Her desire to echo the surroundings with a skin made of a series of pleats needed a material that could express her vision. Stainless steel's reflectivity and its ability to be molded and bent to any shape proved to be the perfect solution.

Defining the questions

Designing and constructing a world-class art museum poses many challenges, and requires collaboration and cooperation of many parties, each with different priorities. One of the issues was façade material selection. There were several questions the team had to consider with respect to stainless steel as a candidate. Would it be the right material? Could a stainless steel exterior be built within the available budget? What grade of stainless steel should be used? To help answer these questions the design build team invited Zahner, an architectural fabricator, well versed in the manufacture of stainless steel façades, and other outside consultants to support the project.

Developing the answers

Alloy and surface finish selection – For a stainless steel façade it was important to select the correct grade to ensure low maintenance and a long life. Because the museum would be exposed to East Lansing's road and walkway de-icing salts, the design team chose the molybdenum-containing Type 316L (UNS S31603) grade. With an Angel Hair® finish, this grade also had the desired appearance: a relative gloss several levels lower than other grades, producing a softer, more consistent and more attractive finish.

Feasibility demonstration – The outside consultants argued that stainless steel would be too expensive, could not be welded, and could not develop the design's sharp pleats. They suggested instead a composite structure for the façade. However, the fabricator, who has helped to construct some of the most striking stainless steel buildings in the United States, produced several large-scale stainless-steel mockups of the pleats and welds. These educational and strikingly beautiful mockups demonstrated that stainless steel would fulfill the architect's vision and even exceed everyone's expectations.

The Eli and Edyth Broad Art Museum reflects its surroundings and changes with them. © Justin Maconochie

Other teams produced alternative façade mockups of aluminum composite panels with a silver paint coating and non-welded joints. There simply was no comparison between these and the stainless steel design. The design team recognized that the Type 316L stainless steel, fabricated as proposed by Zahner, would have much greater impact. The stainless steel could be welded and assembled to create sharp angular planes as if the entire building were machined from a block of gleaming metal, making it a beautiful, iconic sculpture on the campus. One additional significant benefit of the choice of 316L was that at the building's end of useful life, the stainless steel could be fully recycled. In contrast, a composite façade could not be completely recycled.

Panel fabrication – The 316L stainless steel pleats were made from 1.5 mm thick sheets that were custom V-cut to create the pleats. The fabricator used a specially designed mill with an accuracy of 0.005 mm to make these cuts.
The formed stainless steel sheets were strong enough that they required no backup support. Each pleat was made of several formed panels, using in total 970 unique panels. The end panels of each pleat were fusion welded using Type 316L wire, argon shielding gas and copper heat sinks to eliminate distortion. These measures kept the weld cleanup and passivation to a minimum.

A breathtaking result

Michigan State University is very pleased. The Eli and Edythe Broad Art Museum is an incredible, iconic building. Thanks to the choice of 316L stainless steel, keeping it stunningly beautiful requires only a fresh water rinse in the spring and autumn. For years to come, passersby will be drawn towards this piece of art. (WZ)

Angel Hair® Trademark of A. Zahner Company

The appearance of the museum transforms as one approaches the building, walks around it, with the weather, the season of the year and with the time of day. It is an ever-changing masterpiece. © Justin Maconochie

Tool steels depend on molybdenum

Many of the best tool steels require molybdenum to increase hardenability and toughness, and to form hard, wear-resistant carbides in the matrix. These attributes make molybdenum-containing tool steels the industry standard.

Most people may not recognize the importance of tool steels in their daily lives, but they are used to manufacture nearly every object in the world. Whether a component is made of metal, plastic or another material, chances are it was formed or shaped by a tool of molybdenum-containing tool steel. The tool steels discussed in this article are found in plastic-molding tools, cold-work tools and high-speed machining tools.

Historical development

The first 'tool steel' (circa 1200 BCE) was probably a simple alloy of iron and carbon. Then as now, military needs drove materials development for swords, battleaxes, and other instruments of war. The famous 'Damascus steel' blades with their layered microstructure date to 540 CE, and similar Japanese blades date to 900 CE. The *crucible process* that used a ceramic crucible to melt and alloy iron appeared in 1740, ushering in the modern era of tool steels. During the 18th and early 19th centuries, metallurgy began to evolve from a branch of alchemy into a science. In 1868, steelmakers learned that tungsten greatly improved the properties of existing tool steels. They introduced vanadium as an alloying element in 1904 and chromium in 1910. Molybdenum, first studied in laboratory experiments in the late 1920s, came into widespread use during World War II due to tungsten's limited wartime availability. These four elements greatly improved steel's wear resistance by forming very hard alloy carbides.

Crucible melting produced steel in heats of only a few hundred kg. The Heroult electric furnace, introduced in 1904, produced steel in heats of more than a thousand kg, fundamentally changing tool-steel economics. However, both processes produced large, slowly solidifying ingots that were finished by traditional rolling and forging techniques.

'Old Heroult No. 1' is now an ASM Historical Monument located in Pittsburgh, PA. © Crucible Industries LLC

The carbides of ingot-based tool steels were coarse and unevenly distributed because of the slow cooling rate, preventing the steels from reaching their ultimate potential. In 1970, atomized tool steel powder was first produced and compacted at high temperature and pressure into larger, fully dense shapes, bringing a substantial improvement to tool-steel performance. Atomization creates a uniform distribution of fine carbides in the steel. The process also tolerates higher carbon contents. These factors produce steels with higher hardness than previously possible. The powder-based process can also make near net shapes, minimizing the machining required to manufacture large die blocks.

Important properties

Tool steels have to be strong and tough to withstand the cutting and forming forces without chipping or breaking on impact. They derive their strength primarily from *martensite*, a hard phase that forms upon rapid quenching from high temperature. Martensite's strength and hardness increase as carbon content increases as illustrated in the figure below; so most tool steels are high in carbon. To regain some toughness

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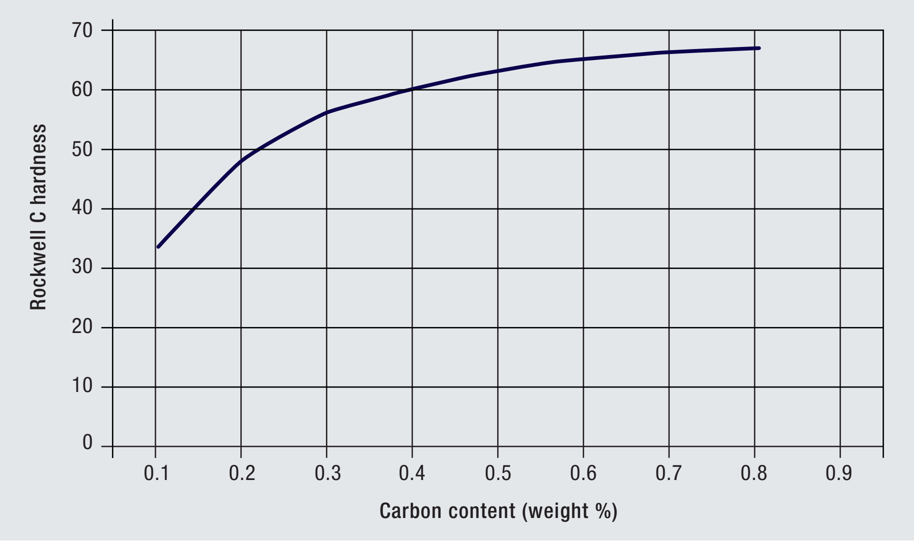
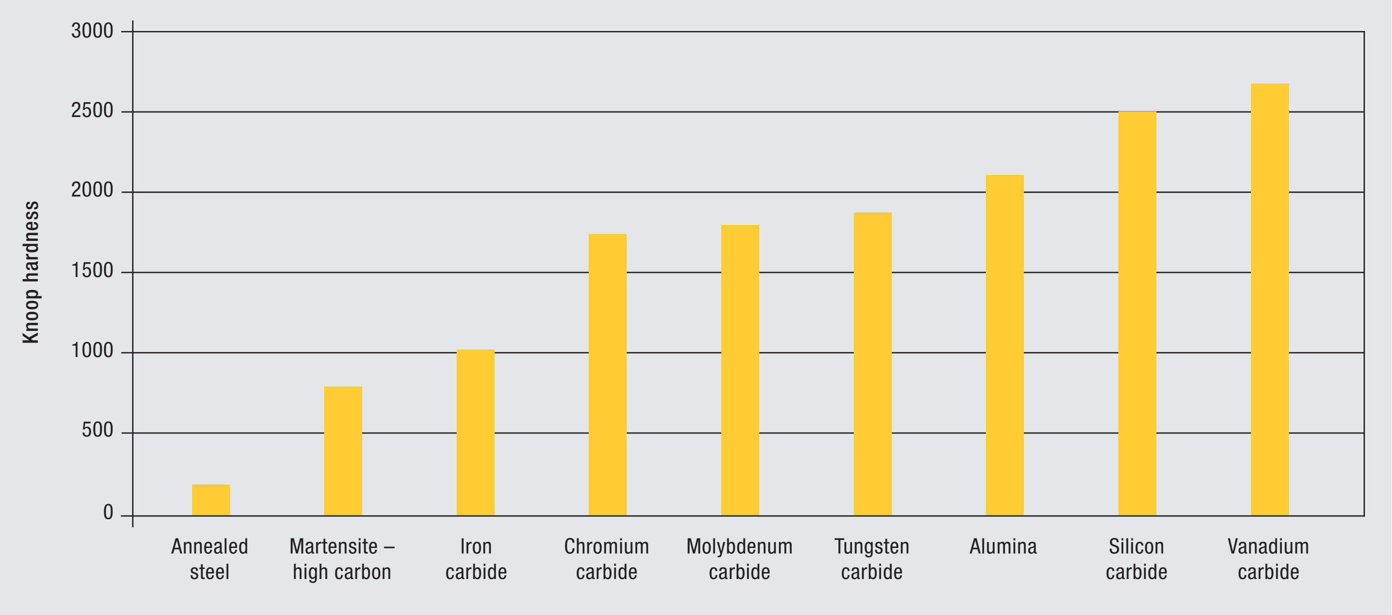
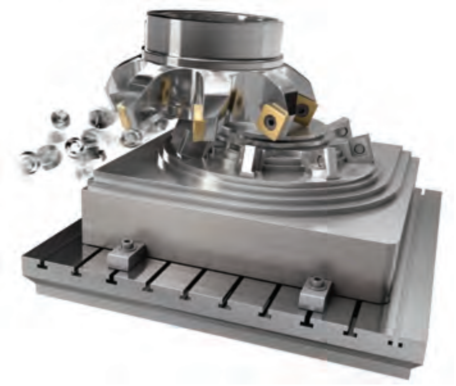


The hardness of martensite increases with increasing carbon content.



Different alloy carbides and alumina are much harder than steels.



This milling tool is made of a molybdenum-containing tool holder steel, the cutting edges are inserts of a different material. © Uddeholm

martensite has to be tempered after quenching. Depending on the tempering temperature, this can reduce hardness and strength slightly, but through the precipitation of additional fine alloy carbides, it improves wear resistance. Wear resistance is the third important property of tool steels, because it determines the length of tool life before it needs replacement.

The best tool steels incorporate a large number of fine, hard carbides in the martensite matrix. Molybdenum, tungsten, and vanadium all produce very hard carbides as shown in the figure above. However, no element increases *hardenability* (the ability to be hardened in thick sections, where quenching is slow) of these steels better than molybdenum and also increases the strength and toughness after tempering. As a result, many tool steels contain molybdenum, some grades in amounts up to 11% by weight.

During high-speed machining of metals, tools become very hot. The most highly alloyed tool steels are known as high-speed steels (HSS) because their carbides are very stable at the high temperatures encountered in high-speed machining and the matrix is temper resistant, enabling HSS tools to retain superior cutting ability.

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The dishwasher interior was cold formed with tools of molybdenum-containing tool steel. © Uddeholm

Selected AISI tool steel categories with nominal composition ranges

AISI category/grade group	AISI grade designations	Carbon	Chromium	Molybdenum	Tungsten	Vanadium	Cobalt
Cold working/air-hardening, medium alloy	A2–A10	0.70–2.25	1.00–5.25	1.00–1.40	0.00–1.25	0.00–4.75	–
Cold working/high-carbon, high-chromium	D2–D7	1.50–2.35	12.00	1.00	–	0.00–4.00	–
Plastic mold	P2–P21	0.07–0.35	0.60–5.00	0.20–0.75	–	–	–
High-speed/tungsten base	T1–T15	0.75–1.50	4.00–4.50	–	12.00–20.00	1.00–5.00	5.00–12.00
High-speed/molybdenum base (standard)	M1–M36	0.80–1.30	4.00	4.50–9.50	1.50–6.00	1.00–4.00	0.00–12.00
High-speed/molybdenum base (ultrahard)	M41–M62	1.10–1.35	3.75–4.50	3.75–11.00	1.50–10.50	1.15–3.25	5.00–12.00

Classification

The widely used AISI method of tool steel classification contains eleven grade groups designated by letters. Most of these grade groups contain molybdenum-alloyed steels. The following briefly summarizes the grade groups used for cold-forming, plastic-molding, and machining tools. The table above shows their composition ranges.

Cold-work tool steels (A and D grades) bend or shape other materials at and near ambient temperature. Tool-steel dies produce a wide array of products, including auto-body and home-appliance panels, stainless-steel sinks, electronic components, battery cases, and heart pacemaker cases. Cost is very important in cold-working operations, so these grades contain low alloy content to minimize tooling costs. Nevertheless, some 3,400 metric tons of molybdenum were used for these steels in 2012, providing as an example, the hardenability required in large dies for components such as auto-body panels.

Mold steels (P grades) form and mold plastic parts. These parts vary widely in size, and include items such as Lego® bricks, gears, mobile phone cases, baskets, buckets, automotive and aircraft interior panels, and automotive bumpers. Some 5,300 metric tons of molybdenum were used for this application in 2012, again mostly in large molds to ensure through-hardening.

High-speed steels (M grades) are used for machining tools for drilling, turning and milling. They retain their strength, hardness, and wear resistance at high temperatures produced by very high cutting speeds. For example, high-speed lathe-turning may produce surface speeds resulting in temperatures of approximately 500°C at the interface of the tool and workpiece. With 14,000 metric tons in 2012, HSS use the most molybdenum.

Alternatives to high-speed tool steels

Molybdenum-containing HSS face strong competition from alternative tool materials such as cemented tungsten carbides and ceramics. These materials are much harder than HSS, potentially resulting in longer tool life. However, they are also brittle and more expensive. They require large, heavy and rigid machinery to be effective. The choice is therefore dictated by the demands of the job and variables such as vibration, cutting forces, dimensional tolerances and surface finish requirements. High vibrational loads, cutting forces, and impact loading are likely to cause chipping or fracture of a brittle cemented carbide or ceramic cutting edge. HSS tooling can also be given a much sharper cutting edge than cemented carbide or ceramic tooling, allowing shallower depths of cut and tighter finished-part tolerances. Thus, each of these cutting tool materials has its proper place in the machining world, defined by the specifics of the individual job.

Summary

Molybdenum greatly enhances the performance of the tool steels that are essential in any kind of manufacturing industry. The tool steels discussed here represent about 7% of total molybdenum use. The cost and versatility of molybdenum-alloyed tool steels makes them effective competitors to tool materials such as tungsten carbides and ceramics. The high productivity and high recycle content of molybdenum-containing tooling portend that molybdenum will continue to play a major role in the shaping of manufactured parts. (CK)

Wireline for downhole tools

Wireline is cable used to lower oil- and gas-well tools and measuring equipment downhole. Wireline must be strong, dependable and resistant to the increasingly corrosive conditions encountered in today's deeper wells. Molybdenum imparts the required corrosion resistance to the stainless steel and nickel alloys used in this application.

Drilling for oil and gas is not as simple a task as might be imagined. Boring the hole is only the beginning of a producing well. When the hole is complete, and at many points during boring, drillers must install components that help to control the flow of oil once production starts. They must do it in a manner analogous to building a ship-in-a-bottle, except that the bottle's neck length is measured in kilometers instead of millimeters.

In addition to these production-related needs, oil and gas geologists and drill-rig personnel need to know the nature and characteristics of the geological formations they encounter as they drill. To obtain this vital information, they stop drilling periodically and lower measuring, or 'logging', tools into the well. These tools measure the chemical and physical properties of the downhole rock, and capture the data for evaluation. Logging tools are packed with sophisticated and very expensive analytical equipment; some can even reach out and grab small samples of surrounding rock.

These production components and logging instruments are lowered into place using wireline, special cabling designed for the purpose and made from molybdenum-containing alloys that can bear the load and withstand the high temperatures and corrosive environments of deep wells.

The wireline

Drillers use two kinds of wireline: 'slick' line and 'electric' wireline. Slick line is typically 1.83–4.06-mm solid wire, used to handle valves and other essential production equipment that controls the flow of oil once the well is producing. Operators also use it to retrieve downhole equipment that is no longer needed, and to fish out broken components that block the well bore. Electric wireline is a more complex product, consisting of a braided-wire sheath that encloses insulated signal wires. Electric wireline lowers instruments into position for well-logging tests. The braided sheath supports the weight of the instruments and protects the signal wires, while the signal wires transmit data from the logging tool to the surface.

The function and importance of electric wireline cannot be overstated. Modern logging equipment employs a variety of active and passive instruments to extract information about the rock formations surrounding the bore. Simple tools such as calipers and electrical probes provide information about the integrity of the rock, the identity of contained fluids and the fluids' corrosion potential. Highly sophisticated tools that probe the surrounding rock's response to sonic waves and neutrons provide data about porosity and rock composition. Gamma ray detectors monitor the natural radiation emitted by the rock, allowing geophysicists to differentiate sandstone from shale. The data transmitted by the instruments paint an accurate and detailed picture of what is present in the rock along the entire length of the borehole, helping geophysicists determine where the well is most likely to yield oil and gas. Wireline is a key part of the technology needed to make good drilling decisions.

Logging tools that are ready to be lowered into the well with wireline. © Downunderphoto–Fotolia.com

Wireline performance requirements

Wireline integrity is critical to the success of drilling and operating a well, and molybdenum helps to ensure wireline performance. Both slick line and electric wireline must be very strong to support the weight of both the instrument or tool and of the wireline itself. The weight of the wireline can be significantly greater than the weight of the instruments and tools, because of the need to lower them to great depth. In many regions of the world, the easily extracted oil and gas, located relatively near the surface, have already been exploited. Newer wells are often drilled thousands of meters deep to find commercially viable pay zones. Wireline with uniform mechanical and physical properties is required in corresponding lengths.

Wireline must also tolerate the high temperatures, high pressures, and hostile chemicals such as chlorides and hydrogen sulphide that characterize the downhole ❯

The crew is preparing to lower wireline equipment downhole for logging on an offshore oil rig. © Ingvar Tjostheim/shutterstock.com environment. These extreme conditions can promote catastrophic failure, so wireline must be highly corrosion resistant as well as strong.

Wireline materials utilize molybdenum

Molybdenum-containing stainless steels and nickel-chromium alloys are the materials of choice for wireline. A variety of grades and alloys offer a range of performance and cost. The alloy choice depends on the strength and corrosion-resistance requirements of each individual well. Type 316 stainless steel is the basic material for sweet wells with moderate conditions. In medium sour wells without H_2S, the stronger 2205 duplex stainless steel is a candidate. As depth increases, temperatures increase and the conditions become highly corrosive; especially for sour wells with H_2S, catastrophic failure becomes likely in many materials. Only the highly molybdenum-alloyed super austenitic stainless steels or nickel-based alloys will do the job in this case. These alloys are effective because they can be cold worked to high strength while retaining resistance to hydrogen. At the same time, they are highly corrosion-resistant thanks to their chromium and molybdenum content.

Nominal compositions of some wireline alloys

Alloy	% Mo	% Cr	% Ni	% Cu	% C	% N	% Co
S31600	2–3	17	10.5	–	0.05	–	–
S32205	2.5–3.5	22	5	–	<0.02	0.17	–
N08028	3.5	27	27	1.2	<0.015	0.05	–
N08936	5.4	27	34	–	<0.02	0.4	–
N08031	6.5	27	31	1.2	<0.015	0.2	–
N08926	6.5	20	25	0.9	<0.02	0.2	–
S31277	6.5–8	20.5	27	–	<0.02	0.3	–
R30035	9–10.5	20	35	–	<0.02	–	35

According to a 2012 market study, about 50% of wireline is Type 316 stainless steel, some 30% is duplex stainless steel and 10% is the nickel-based alloy 28 with the rest being the other grades. The annual demand for slick lines and electric lines is some 2,500 metric tons and the average molybdenum content is estimated to be 3.4%.

Summary

Oil and gas are essential to our modern way of life. A seemingly simple product – wireline – is an important part of oil and gas production technology. Molybdenum-containing alloys are indispensible materials for wireline, thanks to their excellent strength and corrosion resistance. They enable us to exploit oil and gas reserves that might otherwise be inaccessible. (FS)

3D printing – future of manufacturing?

3D printing is a manufacturing process that has great potential because it can produce complex parts without expensive tooling. The technology is stimulating strong interest from the aerospace industry, where there are many opportunities to use molybdenum.

People have manufactured things since the beginning of civilization, and revolutionary changes in how things are made have dramatically changed the course of society’s development. Examples include the first use of tools, shifts in materials from stone to bronze to iron, the introduction of the printing press and mass production. Today is an exciting period with the advent of 3D printing, enabling the printing of things in addition to words.

What is 3D printing?

3D printing, or additive manufacturing (AM), is a method to manufacture three-dimensional objects using a computer-controlled ‘printer’. It has been used to make products as diverse as biomedical tissue and rocket parts. Using a digital file, for example a CAD (Computer Aided Design) drawing, the printer builds up individual parts layer upon layer, allowing drying or solidification time between layers, thus the term ‘additive manufacturing’. This is unlike machining, for example, a technique that removes layers (‘subtractive manufacturing’) from a larger block of material. 3D printers can use a variety of materials including metals (e.g. stainless steels, nickel alloys, aluminum, and titanium), plastics, ceramics, and even living tissue.

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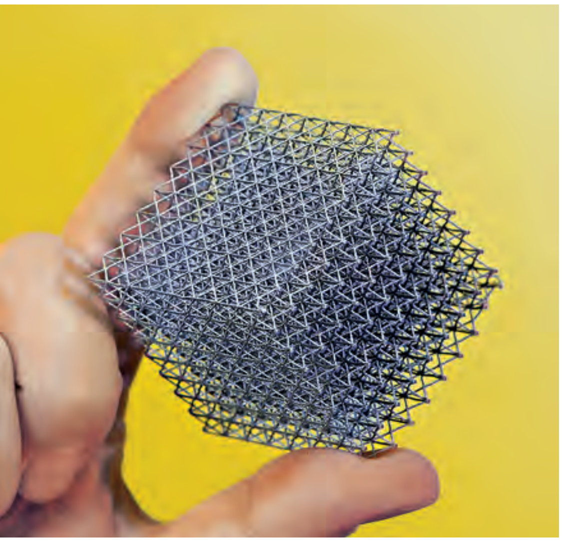

This intricate object has been produced out of powdered metal using a laser melting process – a technique that can quickly manufacture even very complex parts. © www.siemens.com/press

3D printers have been under development since the mid 1980s, working at first mostly with plastic products but also with metal sintering. Early on, the method was mostly used for one-off parts such as prototypes during product development. Throughout the ensuing decades, engineers developed the technology to manufacture actual production parts. Some industrial metal applications began to reach commercial scale over the last few years. Today, it is estimated that more than 20% of 3D-printer output is final product, and some predict this number will rise to 50% by 2020.

3D printing makes it unnecessary to produce thousands of parts in order to cover the fixed costs of tooling and storage, thereby reducing cost and lead-time. If spare parts for an old washing machine can be printed when needed, as an example, the management of spare part inventories can be greatly simplified and warehouse space reduced. It enables a great deal of product customization, and allows production of complex parts that cannot be made in any other way. These factors have the potential to change the whole concept of mass manufacturing. Some see customers in the future downloading an electronic file for a product, as they do now for music or movies, to print the product at home or at a local 3D production center. While this may be a faraway dream for the mass market, it is already happening for some enthusiasts. A new industrial revolution may be on the way that reduces risk, lead-time and cost.

Metal 3D printing

Metal 3D printing uses, among other processes, focused laser or electron beams to melt fine metal powders. The powder is added to the process chamber in dimensionally controlled layers and melted to build the part in an inert atmosphere to minimize oxidation. Layers are added until the finished part is complete. Each individual layer is between 20 and 100 microns thick, so it is an easily modelled building block. Unused loose powder that remains can be collected, screened, and used again.

Depending on the material and the process, the properties of the final part can be similar to as-cast material or better. For many applications this is sufficient, though there are some high-end applications (e.g. turbine blades), where the resulting properties are not yet good enough to replace traditional manufacturing techniques.

Molybdenum is playing a very important role in metal 3D printing as can be seen from the alloys supplied by EOS, one of the leading companies in this field. The powders include Type 316 stainless steel with a minimum of 2.25% molybdenum, maraging steel with 4.5% molybdenum, cobalt-chromium alloys with 5% molybdenum and nickel- based alloys such as UNS N06002 (Hastelloy®-X) or UNS N06625 (Inconel® alloy 625), both with at least 8% molybdenum. Key industries that are already using metal 3D printing routinely, include medical and dental, tool making and aerospace.

Design and applications for metal parts

3D printing's advantage over conventional manufacturing is its ability to make virtually any shape and internal complexity without subassemblies. This allows designers to think far beyond the design limitations of subtractive manufacturing, a huge advantage when it comes to high-tech metal parts. These are parts normally built from multiple subcomponents using expensive alloys, which are difficult and costly to manufacture by conventional methods. It allows designers to optimize the weight of a part, omitting any material that is not strictly necessary for its function. This way extreme lightweighting with weight savings of up to 80% is possible. In the future, it will also be possible to print a part wherever there is a suitable

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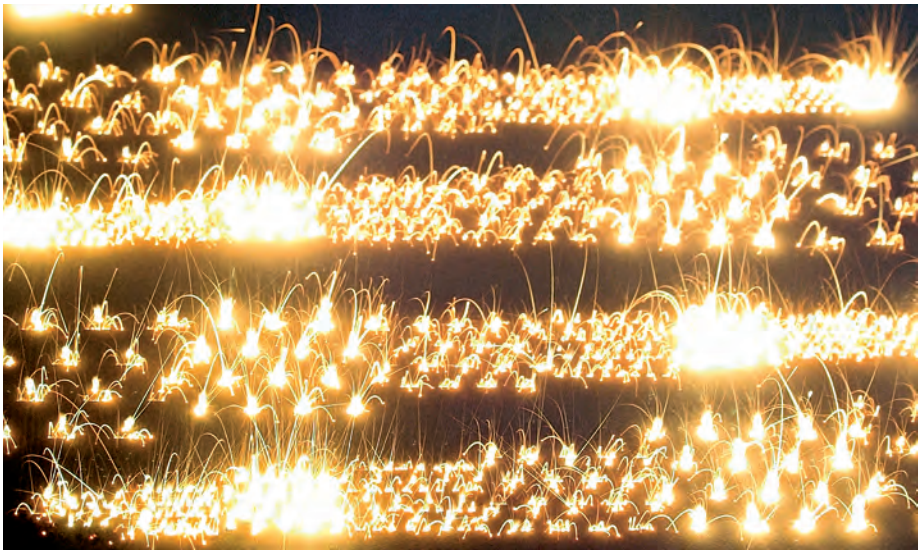

Lasers fuse metal powder during 3D printing. © www.siemens.com/press

3D printed cobalt-chromium can be used to make a complicated fuel nozzle in one part instead of 20… © GE Aviation

…and to make the metal part of very intricate partial dentures. The production stages from left to right: partial denture directly after 3D printing on its support structure, support structure removed and polished and after completion. © EOS

3D printer, allowing the printing of spare parts on site or at local centers instead of waiting for replacement parts to be shipped from a different continent. Engineers even dream of taking 3D printers on space missions to produce the parts necessary for any repairs right on board.

The aerospace and gas turbine industries are understandably enthusiastic about 3D printing. Weight and material costs play an important role here, as turbine parts are usually machined from solid input stock of very expensive super alloys. In some cases, 90% of the input material is machined away. The left over chips and turnings must be sent back to the alloy producer for remelting. In contrast, 3D printing can recycle surplus powder, and the parts may use as little as 10% of the raw material required in conventional processes. Researchers also envision parts made from new alloys and ceramics that cannot be produced by traditional technologies.

All the major gas turbine and jet engine manufacturers are actively developing 3D printed components. Siemens is using 3D printing to make a complex multi-element gas turbine component in a single piece, which can only be achieved by AM. They are also using the technology in the repair of gas turbine burners. 3D printing the new Hastelloy X tip onto the old burner, allows them to cut the repair time from 44 weeks to only 4 weeks and to upgrade the part to the latest design. GE is building the world's first dedicated 3D printing facility for jet engine parts, where they plan to produce fuel nozzles for the CFM LEAP engine starting in 2015. Over 6,000 of these engines are already on order, each requiring 19 cobalt-chromium nozzles. The current nozzle has twenty separate parts whereas the 3D printed nozzle, five times more durable and 25% lighter, is made in only one. Cobalt-chromium alloys with 5% molybdenum have been used for years for dental implants and replacements joints. Today, millions of crowns and bridges are produced through AM every year.

GE is also a leader in reaching beyond its corporate borders to spur development of 3D printing by sponsoring challenge grant projects. Their interest in refractory metals is underscored in the 3D Printing Production Quest. This program challenges participants to produce complex high-precision parts from refractory metals for the X-ray based medical imaging arena. 3D printing can produce complicated geometries in almost any metal, even a high melting-point metal like molybdenum. IMOA member company Plansee has recently announced that they have perfected the AM process for tungsten and molybdenum products over the last few years.

This new technology faces many challenges. It is comparatively slow, so it lends itself mostly to prototypes and smaller production runs. Surfaces tend to be rough and require polishing or other finishing for high-flow applications. It is also limited in the size of parts that it can produce. The largest metal component produced as of this writing using 3D printing, an aluminum gear part, measures 474 x 367 x 480 mm. These numbers will continue to grow in the foreseeable future.

What will the future bring?

The future of 3D printing looks bright. The technology can reduce development time and cost for complex parts, make optimized designs possible that cannot be manufactured with conventional means, and may reduce lead time and cost for small production runs and spare parts. The process offers the world a new manufacturing method that will supplement present technologies and help stimulate economic growth. It will make the dream of spare parts on demand anywhere in the world possible.

The potential for metals, molybdenum included, is very high. Much of the research work on 3D printing is focused on high-value, high-performance, difficult-to-machine alloys and pure metals. Molybdenum is frequently an important component of such materials, and thus is likely to play an important role in existing material needs as well as in new alloy development focused specifically on 3D printing. (AK)

IMOA news

OECD endorses IMOA dataset

The technical quality of IMOA's dataset about molybdate effects in the environment and on human health has been recognised by the OECD's Cooperative Chemicals Assessment Programme (COCAM) with the award of Mutual Acceptance of Data (MAD) status. The molybdate dataset will now be used as the key reference point for the development or review of any environmental or human health legislation concerning molybdenum in all 34 OECD member states and many other countries around the world. Applications for this data include risk assessment, regulatory compliance, environmental quality standard setting and mine development impact assessments.

First developed to register molybdenum substances under the EU's REACH Regulation that seeks to achieve safer management and handling of chemicals (including metals), the dataset uses highly soluble molybdenum compounds to generate and assess molybdate effects. High solubility is a worst-case scenario that generates precautionary results. Precautionary data is the calibre most acceptable to the regulatory community which is a major user of this type of data.

Sandra Carey of IMOA's Health, Safety and Environment Committee said: "The COCAM process is effectively an independent scientific audit. We are very pleased to have achieved MAD status, not only because it is a data quality endorsement, but also because it significantly enhances the global relevance and utility of the dataset. IMOA is the first metal commodity association to secure MAD status for its REACH-submitted dataset."

The data is now publicly available on the OECD website. The OECD download is called a SIAP (SIDS Initial Assessment Profile), which is a 15-page overview document containing the key data and hazard conclusions in the molybdate effects dataset. (http://tinyurl.com/molyoecd)

IMOA duplex shop sheets

IMOA has updated and re-issued its popular duplex stainless steel fabrication shop sheets. There are five shop sheets covering topics such as hot and cold working, heat treating, machining and welding. Each is held in a concise format, providing tables with key processing parameters for different duplex stainless steels. The new shop sheets can be downloaded from the IMOA website at http://tinyurl.com/duplexss

Dissimilar metal welds and weld joint design for duplex stainless steels

Welding parameters for duplex stainless steels

Further case studies published

IMOA has published four further case studies demonstrating the valuable contribution that molybdenum makes to sustainable development. The first study looks at how molybdenum-containing stainless steel greatly increases resistance to corrosion in desalination plants. The second study explores the benefits of correcting molybdenum deficiencies in soil to increase agricultural productivity. The third study examines how high-strength steel reduces vehicle weight and fuel consumption. The final study looks at how molybdenum helps to increase thermal efficiency in fossil fuel power stations, thus delivering significant reductions in CO_2 emissions.

All case studies are available for free from the sustainability section of the IMOA website at http://tinyurl.com/imoascs.