MOLYREVIEW

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INTERNATIONAL MOLYBDENUM ASSOCIATION

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Moly takes off on Super Jumbo

Photo: AIRBUS S.A.S. 2007 by e^{x}m company/H. Goussé.

The latest-generation Jumbo plane, the A380, is jumbo in more than just size and weight. It carries more passengers farther, with greater comfort, safety, and economy, than previous jumbo jets. These features demand parts that are stronger, lighter and more reliable than ever before. Molybdenum is an essential component in the alloys that enable the A380 to accomplish these goals.

Bigger, but with lighter components: an "impossible" contradiction that the designers of this flagship of European aeronautics had to balance, resulting in intense competition between composite materials, which account for 25% of the aircraft's structure, and metallic alloys in which molybdenum plays an important role.

In the weight loss race, aluminium claims the lion's share, about 60% of the total weight of the plane. It is found in many traditional structural applications: wings, airframe, and stub wings, for example. The requirement for stronger, lighter components means that material density is less important than the strength-to-density ratio. When this is considered, aluminium alloys have fierce competition from titanium alloys for highly stressed parts, particularly for the critical parts like the engines. Titanium and nickel-based superalloys are widely used in these parts that operate at elevated temperature. Molybdenum increases the strength, the high-temperature stability and in some cases the corrosion resistance of these materials.

However, as emphasised by a metallurgical engineer of one of the major suppliers of forged parts for the aeronautics industry: "The A380 is a 'classic' plane. Compared to the rest of the Airbus range, in terms of alloys, it's just a larger version of a smaller plane!" In other words, many of the alloys used in its construction (several of them molybdenum-containing) have proven their worth, both on the existing Airbus range and, earlier, on the Concorde.

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Blast furnace stoves get second wind with moly-grade steel

Smelting iron to make steel is a high-temperature, high-pressure, high-corrosion process. Moly-grade steel, with its increased high temperature strength and resistance to nitrate stress corrosion, has replaced carbon steel in the outer shells of three hot air stoves in this blast furnace renovation.

Trend towards moly-grade steel
Blast furnaces for iron smelting, the initial step in the steelmaking process, use significant amounts of moly-grade steel in their construction. For example, the heat resistant pressure vessel steel 16Mo3, containing 0.25 to 0.35% molybdenum for added high temperature strength, is being used more and more to manufacture and maintain blast furnace stoves. Blast furnaces are pressure chambers in which iron ore, fuel (usually coke), and flux (limestone and slag) are mixed together with air (sometimes enriched with oxygen), which is pre-heated in the blast furnace stoves. In the resultant reaction, iron ore is chemically reduced and separated into molten iron and carbon dioxide. The slag and limestone combine with coke ash to form a protective layer that also refines impurities in the melt. Waste gases exit through a flue pipe, leaving behind molten metal and slag.

Blast furnaces have been around for a long time, and while the chemical reactions occurring in them have remained unchanged, engineers have radically transformed furnace design to attain ever-greater efficiency. The hot gases exiting modern blast furnaces are recovered and used to preheat the blast air, saving large amounts of energy. A modern blast furnace produces around 80,000 tonnes of iron a week, an enormous increase over its eighteenth-century counterpart, which could manage only 360 tonnes a year.

Wise material choice is an important factor in increasing efficiency. The stoves that supply hot air to the furnace used to be made of carbon steel boilerplate, but in the last ten to fifteen years, 16Mo3 has been taking over.

Case study
Recently, Australian steelmaker BlueScope Steel needed to overhaul the No. 5 Blast Furnace at its Port Kembla Steelworks. The furnace, commissioned in 1978, required remedial work to keep operating at its designed efficiency. Replacement dome plate covers, which serve as the new outer shells of each of the three stoves supplying the blast furnace with hot air, were fabricated from 16Mo3 steel. BlueScope believes this will provide another 15 to 20 years of useful working life for the furnace.

“The stoves are crucial pressure vessels that are subjected to enormous thermal stresses over several cycles around the clock each day,” BlueScope Steel project manager Peter Roberts explained. Stress corrosion is another problem, he adds.

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Content

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Hot rolled plate chemical composition of 16Mo3 (WNr. 1.5415) in mass% according to DIN EN 10028-2:

C	Si	Mn	P	S	Cu	Cr	Ni	Mo
0.12 – 0.20	0.35 max.	0.40 – 0.90	0.025 max.	0.010 max.	0.30 max.	0.30 max.	0.30 max.	0.25 – 0.35

“Nitrogen oxide gases that are formed inside the stove above 1,350°C condense on the surface and create corrosive nitrates. This attacks areas of high residual stress on the inside of the shell plate and affects the microstructures of the steel, which in turn leads to stress corrosion.”

The fabricator used BlueScope Steel’s own creep-resistant 16Mo3 grade XLERPLATE® for the dome shells. “Its molybdenum content makes it ideal for use in such severe applications,” explained Mr Roberts. “More than 100 tonnes will go into the fabrication of each dome.”

Creep resistance

This application required creep-resistant steel, as the domes experience temperatures of 100–250°C over a lifetime of 15 to 30 years. Molybdenum increases the steel’s strength and creep resistance at these slightly elevated temperatures, so the choice of 16Mo3 was natural.

The sections of the dome plate covers were fabricated in plate thicknesses ranging from 20–55 mm. These fabricated sections were shipped to Port Kembla for blasting and coating before installation 40 metres above the furnace base. The project presented a challenge for the fabricator, as the moly steel’s mechanical properties are very different from those of traditional carbon steels.

“One of the main challenges was hot forming 55 mm plate to a complex double knuckle,” Peter Roberts explained (see photos). “A knuckle is a transition in the stove shell plate structure where the vertical straight cylindrical section, which is 11 metres in diameter and 30 metres tall, meets the 12-metre diameter spherical dome. The transition is a curved plate section that is also on an 11-metre diameter. So the sections of plate required had to be curved in the shape of an extended ‘s’ (or double knuckle) and also curved to match the diameter of the dome and cylindrical section in what is called a knuckle joint. This involved heating the steel up to 900°C and welding the two subsections of the double knuckle. The finished segment was then normalised.”

“The thinner sections were cold formed,” the fabricator said. “Each individual ring was trial-assembled prior to delivery. Completing the fabricated sections for the first dome went slowly because we had to calculate and then closely observe every procedure as we progressed.”

The result met everyone’s expectations, showing that even existing structures made from conventional materials benefit from modern alloys when being retrofitted.

Sources: www.bluescopesteel.com.au and communication from Peter Roberts of BlueScope Steel.

Project summary

Location	Port Kembla, New South Wales, Australia
Client	BlueScope Steel
Engineer	John Holland Group
Fabricator	Wenco Pty Ltd
Product used	XLERPLATE® 16Mo3 steel from BlueScope Steel

Pre-assembly of the knuckle ring at BlueScope Steel’s Port Kembla Steelworks. Photo: BlueScope Steel.

Installation of the knuckle ring. Photo: BlueScope Steel.

Duplex rebar restores resistance to waves

The Hassan II Mosque began to show structural deterioration shortly after its inauguration: the concrete walls, which were built into the Atlantic Ocean, started to crumble under the steady attack of the saltwater waves. After a spectacular reconstruction, replacing large parts of the original structure and reinforcing it with 1,300 metric tonnes of moly-grade duplex stainless steel, the mosque is ready to withstand the elements for decades to come.

The Hassan II Mosque in Casablanca, Morocco, is one of the largest in the world. Its unique location partially extending over the Atlantic Ocean requires special protection against the aggressive saltwater environment. Photo: Jerzy Strzelecki.

An architectural jewel

The Hassan II Mosque in Casablanca, Morocco, is one of the largest mosques in the world. Exceptional in its vastness and luxury, it was designed by the French architect Michel Pinseau and inaugurated in 1993 after seven years and 50 million hours of construction work by 35,000 workers and craftsmen. It has been built on reclaimed land, so that almost half of the surface of the mosque lies over the Atlantic Ocean.

The mosque's prayer room measures 200 x 100 m and can accommodate 25,000 worshippers. It has a movable, 60 m high, 3,400 m² large roof, which can be opened in five minutes through a rolling chain mechanism. Part of its floor is made of glass, so that worshippers can kneel directly over the sea. This feature was reportedly inspired by the Qur'an verse: "The throne of God was built on water."The front square can host an additional 80,000 worshippers. The minaret, standing 210 m high, is the tallest in the world.

Chemical composition of 2205 duplex stainless steel (EN 1.4462/UNS S32205):

	C	Si	Mn	Ni	Cr	Mo	N
Min.				4.5	21	2.5	0.11
Max.	0.03	1	2	6.5	23	3.5	0.22

A highly aggressive environment

The mosque extends over the Atlantic Ocean and is partially in direct contact with seawater. As waves beat against the concrete walls, saltwater migrated into the porous concrete. When it reached the carbon steel rebar inside, the rebar started to rust. As rust forms on the rebar, it expands and presses against the concrete from inside the structure, leading eventually to cracking and loosening of the concrete and further penetration of the saltwater into the structure. Only ten years after its inauguration, this part of the mosque had deteriorated badly because of the corrosion of the rebar.

A reconstruction aimed to last 100 years

To remedy the problem, a major restoration project was launched in April 2005. Given the building's importance, the authorities specified that the repaired structure should last 100 years. Three years of testing, study and review went into the design developed to meet the challenge. To meet the long-life requirement, the designers recommended the use of moly-grade stainless steel rebar combined with a concrete highly resistant to chloride penetration.

The rehabilitation work was performed in four phases over a four-year period:

- A watertight dike surrounding the mosque was first constructed to create a "dry" work site located 5 m below the highest water level.
- A portion of the voids under the prayer room was filled with concrete.
- Structural slabs and pillars surrounding the building on the ocean side were demolished.
- Identical replacements for these components were constructed using a high-performance concrete reinforced with 2205 duplex stainless steel (UNS S32205, EN 1.4462). This steel contains 3% molybdenum, which provides excellent resistance to corrosion in saltwater.

"Unlike traditional projects, the renovation of the ocean-exposed portions of the Hassan II Mosque, whose durability is vital, was planned with exceptional design and construction conditions, upon request from the Moroccan government," explains Pierre Bessières, Construction Manager.

After the structural design had been modified to address the impact of wave penetration and their absorption under the building, tests were carried out on a scale model in a wave basin. The quality of all materials to be used on the project had to be exceptional and traceability of all material production steps was required.

It is not always possible during the design process to foresee all the work necessary to meet design goals. The Hassan II Mosque project was no exception. During construction, it was discovered that 100 external pillars (referred to as “combs” because of their wave-breaking effect) exposed to the ocean and supporting the peripheral slabs also needed replacement. Here again, high-performance concrete reinforced with 2205 duplex stainless steel rebar was chosen. This work required installation of an additional peripheral watertight curtain in the existing dike.

Duplex stainless steel guarantees durability

“For us, the project to repair the portions of the Hassan II Mosque in Casablanca exposed to the ocean represented the supply of 1,300 tonnes of stainless steel cut to length for the customer according to their drawings and delivered by number of parts and not by weight,” indicates Bernard Demelin, Marketing Manager for Ugitech SA. “The use of stainless steel… in construction applications helps save both energy and resources,” he adds. Indeed, stainless steel offers not only a longer life and improved corrosion resistance in buildings and structures, but also requires less maintenance in the long term. Additionally, stainless steel is 100% recyclable and new stainless steel generally contains some 60% recycled scrap material.

Type 316/316L stainless steel with 2% molybdenum is a grade that is often used for rebar with maritime exposure. However, because of the size, location and importance of this project, 2205 duplex stainless steel was recommended instead. Its corrosion resistance is much higher than that of Type 316/316L, and its price was lower given the cost of raw materials at the time of construction.

The maritime environment had taken a toll on the mosque’s ocean-front portions, leading to deterioration of the pillars under the prayer room. Photo: Ugitech.

Installation practices for the duplex grade are identical to those for traditional stainless steel, with the exception of a requirement for approximately 25% higher machine power due to the duplex steel’s higher strength. The 8–20 mm bars used in the Hassan II Mosque project have a yield strength of roughly 850 N/mm², while the 25–32 mm bars have a yield strength of roughly 650 N/mm². This compares to typical yield strength values of 500 N/mm² for similar Type 316/316L bars. The higher strength of the duplex alloy compared to Type 316/316L and other steels means that smaller bar diameters provide the same level of reinforcement as larger bars of lower-strength steel, another source of cost savings.

Source: Ugitech S.A.

Key reconstruction figures

- 200,000 m³ of dike material (rock fill and pit run gravel)
- Demolition of 8000 m³ of concrete
- 100,000 m³ of containment concrete (non-reinforced bulk concrete)
- 10,000 m³ of high-performance concrete
- 1,300 tonnes of stainless steel rebar, containing almost 40 tonnes of Mo
- 100 pillars poured
- Cost of work: roughly 50 million Euros

100 external “combs” supporting the peripheral slabs were rebuilt with high-performance concrete-reinforced stainless steel rebars (2205 duplex) to ensure a long lifespan for the sacred building. Photo: Ugitech.

Continued from page 1

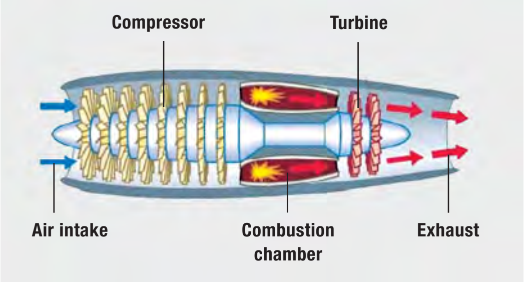
Moly takes off on Super Jumbo

Super requirements for superalloys

The engines, which must propel the aircraft and up to 800 passengers over 15,000 kilometres (the non-stop distance from New York to Hong Kong), must operate reliably throughout a huge temperature range. The air inlet of the compressor fan experiences temperatures of -50°C at cruise altitude, while the turbine's fixed and moving parts reach 600°C, and the combustion chamber must withstand 1,000°C.

The engine's compressor blades are made from the iron-based, high-temperature austenitic alloy 286, containing 1.25% molybdenum (table), and the disks supporting them are made from a titanium alloy that contains 3% molybdenum. Molybdenum gives strength at temperature and corrosion resistance to these alloys, minimising the weight of the components.

In the turbine section of the engine, nickel-based superalloys containing 3–10% molybdenum are the materials of choice. Molybdenum improves high-temperature strength and creep resistance in these alloys. Alloy 718, an austenitic nickel-based alloy containing chrome and iron, and hardened with molybdenum (3%), niobium and titanium, offers very high strength up to 700°C with excellent weldability. It is also found in the vanes and disks of compressors. More than a third of the alloys used in modern turbine engines are nickel-based superalloys containing molybdenum.



Molybdenum is an essential component of alloys used in aircraft propulsion systems. It imparts high-temperature strength and creep resistance, making it an essential constituent of alloys for rotating parts (turbine blades, compressor vanes, and the disks that support them).

Nickel-based alloy 625, containing 9% molybdenum, with its high corrosion and heat resistance, is used for the small-diameter fuel tubing that must endure high temperatures near the hot parts of the engine. For hydraulic systems not subjected to very high temperatures (landing gear actuation, braking system, flight controls), conventional 2% molybdenum Type 316L stainless steel is widely used.

The many hot bearings supporting the compressor and turbine shafts withstand very severe conditions. They must resist fatigue at temperatures up to 300°C, so they are made from a heat-resistant Cr-Mo-V steel that contains 4.25% molybdenum, the most widely used alloy in the world for this type of engine part.

No less important, the many rivets, bolts and attachments near hot engine parts must have high strength, corrosion resistance, and high-temperature stability. Austenitic alloy 286 is used for these applications.

Molybdenum plays a critical role in the engine beyond that of an alloy addition – lubrication. Molybdenum disulfide (MoS_2) provides robust lubrication of the engine's rotating parts, forming a strongly adherent film with high lubricity that resists other lubricants and protects surfaces against corrosion. →

The inlet fan diameter of the engine is about 3 m. Four of these engines are required to propel the A380 through the sky. Airbus A380 customers have a choice between two engines with similar characteristics and whose respective market is nearly equivalent: the Trent 900 produced by Rolls-Royce and the GP7200 manufactured by Engine Alliance, a consortium uniting two American companies, General Electric and Pratt & Whitney, with the participation of the French company, Snecma. Photo: Engine Alliance.

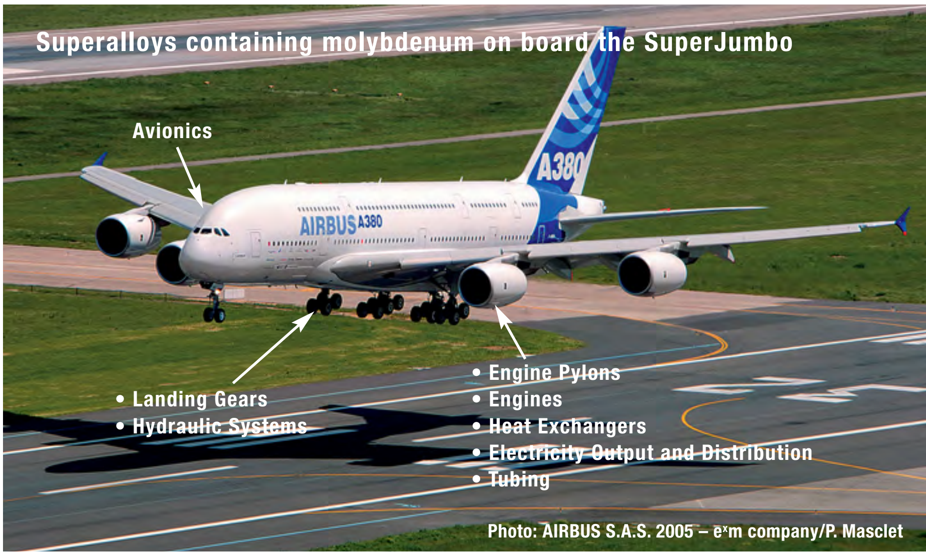
Producing electricity in flight

More than just a propulsion system, engines supply the plane with the electrical energy needed for internal operations: avionics, lighting, pressurisation, heating, control and hydraulic systems, for example. Over 600 kW of power are required to operate all these systems. To accomplish this task, a heat exchanger/power generator turbine unit is associated with each engine. Because they are exposed to hot gases from the engine, the heat exchangers use alloy 718 or corrosion-resistant alloy 625. The generator rotors and stators are made from soft magnetic iron-cobalt alloys containing 0.5% molybdenum. These alloys are more expensive than conventional iron-silicon alloys that fulfill the same function in cars and refrigerators, but at equal strength, they offer a 25% weight savings, a decisive criterion for the “giant of the skies”!

Moly for an easy landing

The enormous forged landing gear of the A380 must bear the shock loads that occur when the nearly 386-tonne aircraft lands. This is where alloy 300M, with 0.4% molybdenum takes the spotlight. The alloy’s molybdenum content reduces the sensitivity of forged parts to annealing during their heat treatment, thereby preserving their strength and impact resistance. Alloy 300M has replaced aluminium in the A380 landing gear boxes, one of the largest parts ever forged (over 7 tonnes), because of its higher strength and stiffness combined with lower cost. →

When it lands, the A380 absorbs the shock of a total mass of nearly 386 tonnes travelling at 300 km/h. The landing gear (or leg), is made of alloy 300M, containing 0.4% molybdenum. Manufactured by Aubert & Duval, this is a critical forged part that responds to the extreme constraints of landing with surprising smoothness for the greater comfort of the 500 to 800 passengers. Photo: Florian Lindner.



Superalloys containing molybdenum on board the SuperJumbo

Photo: AIRBUS S.A.S. 2005 – e^x^m company/P. Masclet

System	Component	Material	Nominal composition[1], w-%	Mo, w-%	UNS number
Engines	Fan compressor	A 286	Fe-26Ni-15Cr-2Ti-1.25Mo-2Ti-Al	1–1.5	S66286
	Compressor disks	Ti6-3-2	Ti-6Al-3Mo-2Cr	3	NL[2]
	Turbine vanes and disks	Alloy 718	Ni-19Cr-18.5Fe-5.1Nb-3Mo-Ti-Al	2.8–3.3	N07718
	Compressor and turbine bearings	M50	Fe-4.3Mo-4Cr-1V-Si-Mn	4–4.5	T11350
	Fuel tubing	Alloy 625	Ni-21.5Cr-9Mo-2.5Fe-2.6Nb	9	N06625
	Lubricants	MoS_2	$100MoS_2$	60	NL[2]
	Fasteners (rivets, bolts)	A 286	Fe-26Ni-15Cr-2Ti-1.25Mo-2Ti-Al	1–1.5	S66286
Hydraulic systems	Landing gear, braking, flight control tubing	Type 316 SS	Fe-18Cr-12Ni-2.5Mo-Mn-Si	2–3	S31600
Power generation	Heat exchangers	Alloy 718	Ni-21.5Cr-9Mo-2.5Fe-2.6Nb	2.8–3.3	N07718
		Alloy 625	Fe-25Co-Mo	9	N06625
Avionics/electronics	Generators rotors and	25 Co	Fe-50Co-Mo	0.5	NL[2]
	stators	50 Co	Fe-80Ni-4.2Mo	0,5	NL[2]
	Shielding	A753 Alloy 4	Fe-25Co-Mo	4.2	N14080
	Displays	Mo	99.95Mo min	100	NL[2]
Landing gear	Landing gear boxes	300 M	Fe-1.8Ni-1.67Si-0.8Cr-0.8Mn-Mo-V	0.3–0.65	K44220
	Potential new alloy	X1CrNiMoAlTi 12-11-12	Fe-12Cr-11Ni-2Mo-1.5Al-Ti	2	NL[2]

[1] Alloying elements with less than 1 weight per cent are listed by name only
[2] Not listed

Hundreds of thousands of passengers carried by the airlines annually present other problems for designers. In seat components, strength and fatigue resistance are required, and liquid spills and cleaning solutions can cause corrosion problems. For these reasons, some airlines choose a titanium alloy containing molybdenum for the upper part of the seat slides.

Molybdenum makes it happen

Molybdenum plays an important role in the materials used to build and operate the record-setting A380, boosting the performance of metal alloys across a wide spectrum including steels, nickel-based superalloys, titanium, and specialty electronic and magnetic alloys. Wherever one looks in the aircraft molybdenum is present, increasing strength and corrosion resistance, reducing friction, generating power, and assuring the stability and safety of control systems.

A new alloy taking flight?

Aircraft designers must balance complex and often conflicting technical and economic demands. They strive to limit aircraft weight to maximize fuel economy and reduce maintenance costs. To make matters worse, materials like alloy 300M require chromium plating for corrosion resistance, and may be rendered obsolete by environmental regulations. In this rapidly evolving area where engineering, economics, and regulation overlap, a new alloy offers great promise. Alloy MLX17, a precipitation hardening martensitic steel containing 2% Mo to provide intrinsic corrosion resistance, is a stainless steel par excellence. Surface treatments harmful to the environment are unnecessary for this alloy, making it an interesting material choice for new projects. Alloy MLX17 represents a likely alternative for aerospace projects currently in development like the Airbus A350, the Boeing 787 Dreamliner and the 747-8 (the improved version of Boeing’s large airliner).

The A380’s avionics: a heavily shielded civil aircraft

“Fly-by-wire” control systems use soft magnetic shielding alloys against electromagnetic interferences, while molybdenum metal is an important part of the displays that keep the crew informed about the aircraft. Photo: AIRBUS S.A.S. 2007, by e^{x}m company/H. Goussé.

Severe or even violent weather conditions such as cumulus-nimbus clouds, thunderstorms and lightning may often add to an already cluttered magnetic environment (radio communications, “fly-by-wire” control systems, etc.) in the cockpit. Shielding of all related sensitive equipment of the aircraft is achieved through specific materials with significant molybdenum content.

A modern plane is nothing without quality avionics. “Fly-by-wire” control systems combined with computers use full-electrical control circuits. They have replaced most of the mechanical and hydro-mechanical systems using cables, cranks, wires, pulleys, etc. Airbus A380 “fly-by-wire” control systems feature a state-of-the art cockpit equipped with interactive flat screens, an embedded information system and integrated modular avionics systems connected via a large-capacity Ethernet network. This requires hundreds of metres of electric cables, actuators, rectifiers and miniaturised electronic power components that have more stringent shielding requirements than their ground-based equivalents. All this equipment must be shielded from energy conversion and transmission devices to avoid electromagnetic interference with aircraft controls, which can lead to dramatic consequences… The aircraft’s gyroscopes, crucial instruments for constantly maintaining the stability (or “trim”) of the aircraft, must also be protected from geomagnetic fields that could interfere with their operation.

Shielding requires specific materials that offer high permeability, low loss level and low coercive force. This is where the use of soft magnetic iron-nickel alloys containing about 5% molybdenum comes into play. These alloys shield the circuit breaker relays, magnetic sensors such as read/recording heads and other electronic components. They are also used to produce magnetic cores in measuring instruments, differential circuit breakers and line transformers used in modems.

The cockpit displays, which present all the A380’s information to the pilots, use pure molybdenum thin films. They are applied atom-by-atom to the glass to operate the individual pixels and protect the display circuit elements. Molybdenum contributes to increased system performance and reliability in the cockpit. Thus it helps provide the pilot, the most important part of the control system, with the information needed to make critical flight decisions.

Moly provides key to tropical rainforest growth

What processes stimulate the wild growth of the tropical rainforests? The question has assumed some urgency in view of global warming and the capacity of tropical forests to absorb CO_2. Scientists have been working on this problem for some time, among them a team of scientists from Princeton University who recently carried out research in Panama. There they made an unexpected find: molybdenum plays a greater role in supporting this growth than was previously suspected.

A team of researchers led by Princeton University scientists has discovered that tropical rainforests, a vital part of the Earth's ecosystem, rely on the trace element molybdenum to capture the nitrogen needed to support their growth. Most of the nitrogen that supports the rapid, lush growth of rainforests comes from tiny bacteria that can turn nitrogen in the air into fertiliser in the soil.

Until now, scientists had thought that phosphorus was the key element supporting the prodigious expansion of rainforests, according to Lars Hedin, a professor of ecology and evolutionary biology at Princeton University who led the research. But an experiment testing the effects of various elements on test plots in lowland rainforests on the Gigante Peninsula in the Barro Colorado Nature Monument in Panama showed that areas treated with molybdenum fixed (or absorbed) more nitrogen from the atmosphere than areas treated with other elements.

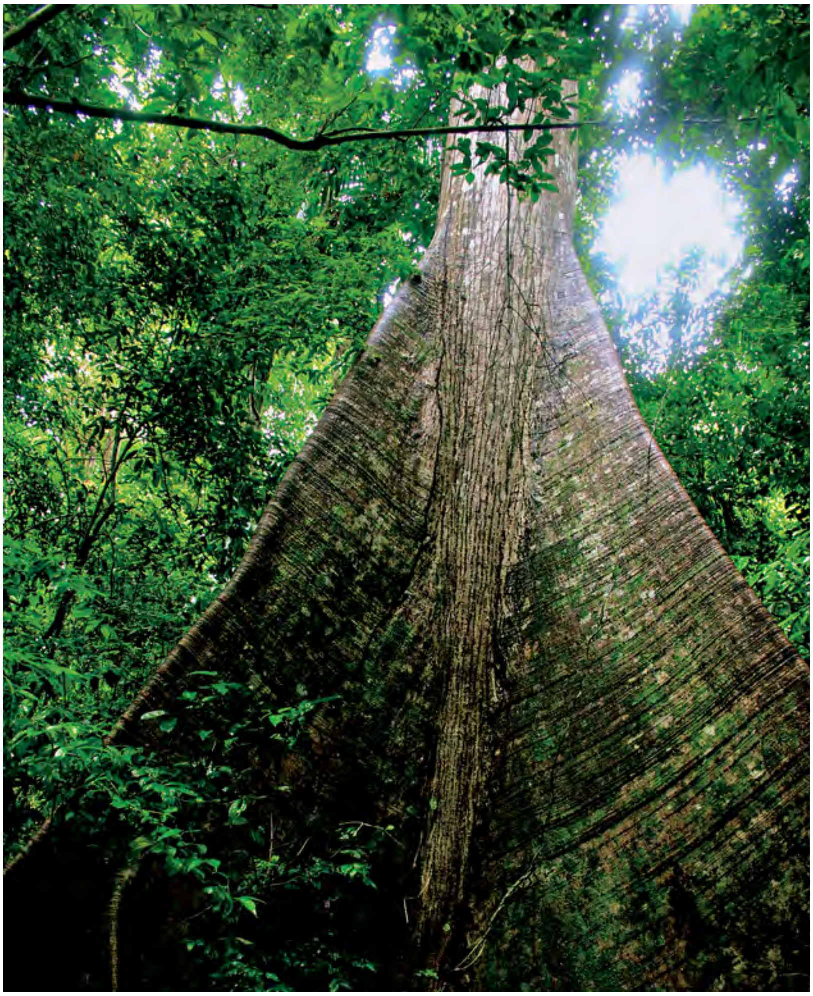
"It was not what we were expecting," said Professor Hedin. "We carried out various experiments with different kinds of fertilisers: nitrogen, phosphorus and some micronutrients such as molybdenum and others. The role we discovered molybdenum was playing came as a surprise; it was serendipity."

Plant growth is stimulated by nitrogen. Nitrogen from the air is taken up and converted to a form which can be used by the plant (a process called "nitrogen fixation") by the enzyme nitrogenase. Since molybdenum is an essential component of nitrogenase, molybdenum plays an important role in the fixation process. Professor Hedin's team has confirmed that molybdenum is the essential element for controlling the biological conversion of nitrogen in tropical rainforests. "Just as trace amounts of vitamins are essential for human health, this trace metal [molybdenum] is indispensable for the vital function of tropical rainforests in the larger Earth system," Hedin said. Molybdenum is 10,000 times less abundant than phosphorus and other major nutrients in these ecosystems.

Professor Hedin's team observed fixation where phosphorus is present, a well-known phenomenon. "But we also saw that in plots where micronutrients were added, we found a similar response," Hedin explains. "So we started wondering if it was the phosphorus or the micronutrients or both that were causing the fixation. Then one day Alex Barron [the lead author on the paper, which was published in the December 2008 issue of Nature Geoscience – ed.] called me and revealed an interesting fact: when phosphorus fertiliser is made, there are normally traces of molybdenum present. So we added pure, molybdenum-free phosphorus and found there was no fertilising effect."

The discovery that phosphorus on its own cannot stimulate growth in tropical rainforests whereas molybdenum can, may have implications for our understanding of CO_2 absorption. Molybdenum is essential for nitrogen uptake and so for forest growth. If molybdenum is, indirectly, the controlling factor in the biochemical processes involved in the uptake of carbon dioxide, then the availability of molybdenum may limit how much carbon tropical rainforests can absorb.

Based on a text provided by Kitta MacPherson of the Princeton University Office of Communications and an interview with Professor Lars Hedin.



The rainforest of Panama. From the cover of Nature Geoscience (December 2008), reprinted with permission.

Jogging and jumping again with new joints

Prostheses improve the lives of millions of people young and old. The growing worldwide demand in the hip and knee prosthesis market is met by the development of increasingly reliable, robust and durable devices. Molybdenum plays an important role in the metallic materials used to make them.

Growing demand

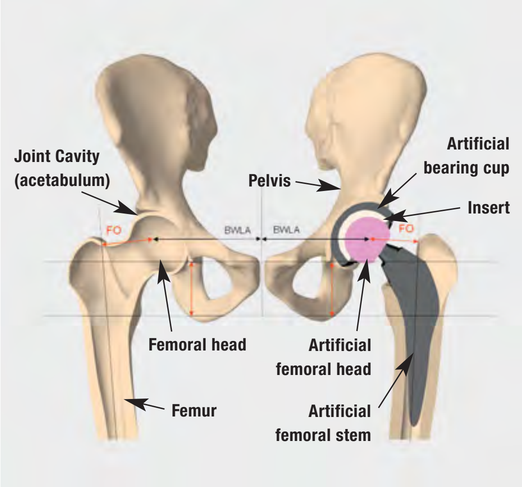
Molybdenum is widely used in building construction because it gives hardness, strength, and corrosion resistance to structural materials, in particular alloy and stainless steels. It confers these same properties to the alloys used in human body reconstruction, as an alloying element in orthopaedic implants.

It is estimated that each year nearly 1.5 million hip and several hundred thousand knee replacements (arthroplasties) are performed throughout the world. The number of replacements is growing, driven by age-related causes like arthritis, and the growing needs of an active younger population, often sports enthusiasts, whose joints are worn by heavy exercise.

When joints are replaced, the prosthesis must remain in good condition for a long time to assure the patient's comfort and quality of life. Even normal daily activities (walking, standing, climbing stairs) impose significant stresses and frictional effects on the prostheses, which present a challenge to joint-replacement technologies.

A Co-Cr-Mo porous coated hip stem supports a Co-Cr-Mo femoral head, pivoting against a high-density polyethylene insert in a porous titanium-coated cup. Photo: iStock.

Photo: Symbios.



The hip: a ball and socket joint. Photo: Symbios.

The hip, a ball pivot as fragile as it is essential

The hip is the ball-and-socket joint formed by the femoral head at the upper end of the femur freely rotating in the cup-like cavity called the acetabulum at the edge (ilium) of the pelvis (see illustration). A deficient hip undermines the body's dynamic and static balance and can be extremely painful. There are many possible causes for hip replacements: osteoarthritis (wear of the cartilage), necrosis of the femoral head (death of bone tissue due to temporary or permanent loss of blood supply to the femoral head), a rheumatic disease, a congenital (present at birth) malfunction, or the fracture of the neck of the femur, which cannot be repaired in a different way, especially in elderly people. In most of these cases a total hip replacement is the solution to the problem.

Total hip replacement means a complete replacement of the joint linking the femur to the pelvis with artificial components.

The anatomy of the cantilever-like femur presents a risk of breakage (the infamous femoral neck fracture) and requires a robust femoral stem design that can only be obtained by using metal, which is strong and tough. To attain a strong bond between the metallic femoral stem and the femur two techniques are used: One is to cement the stem in place, while the other is to apply a double coating, a coat of porous titanium followed by a coat of hydroxyapatite (a pure bone crystal comparable to coral), which stimulates bone cell growth into micro-pores in the titanium.

The rotation of the head of the femur in the acetabulum produces the hip's motion. In a prosthesis, this function is replicated by rotation of the

➔

implant's head in the artificial bearing cup which is fixed in the acetabulum by means of the double coating technique or by screwing. Friction in this ball/cup joint must be as low as possible so that the patient's hip can recover its original range of motion. The prosthetic system also operates in a sea of body fluids, and must not corrode or interact with the body in harmful ways. The prosthesis materials and mechanical design must satisfy all these, sometimes conflicting, requirements.

The head of the femur, and the bearing cup, constitute the most complex part of the prosthesis. The successful operation of this pair of components determines the operation of the joint itself.

The importance of reducing friction

There are four possible material combinations for the bearing cup and femoral head in hip prostheses (Table 1). Often the pair uses a metal head (Co-Cr28-Mo6 (ISO 5832-4) with 6% molybdenum or stainless steel) in contact with a polyethylene insert to minimise friction. The insert is housed in the metal bearing cup fixed in the acetabulum. To reduce polyethylene wear that may produce debris in the joint, thus influencing the durability of the implant (risk of loosening), ceramic (alumina) is sometimes used for the head instead of metal (alumina causes less erosion of the polyethylene than metal). This approach is not suitable for patients who engage in extreme sports like sky diving or mountain bike freeriding; the impacts related to these sports could overstress the more brittle ceramic head. The highly wear-resistant alumina is also difficult to machine, which raises the cost of the head. Nonetheless, ceramic-ceramic pairs (alumina head in a bearing cup equipped with an alumina insert) are finding wider acceptance for some applications.

Metal-to-metal combinations fell out of favour because of friction and wear problems, but they are now returning thanks to advances in the understanding of tribology (the study of friction and wear), improvements in machining precision, and more frequent use of high-carbon alloys (see below). A metal-to-metal combination using a cobalt-chromium-molybdenum (CoCrMo) alloy pair is particularly suitable for implanting large diameter femoral heads (40–56 mm) that help to avoid joint dislocation in highly active patients. Well suited to the static and dynamic balance of these patients, large diameter heads are also less affected by wear-related damage caused by debris around the femoral head.

Biocompatibility and standardisation
Biomaterials (also called biocompatible materials) used for implant technologies (metals, ceramics and polymer) are subject to a strict standard in Europe. They are covered by directive 93/42/CEE, relating to non-living materials used in a medical device designed to interact with biological systems.

Recent improvements in machining and alloys have led to renewed interest in metal-metal bearings. The CoCrMo femoral head is housed in a CoCroMo bearing coated with porous titanium and hydroxyapatite, a pure bone crystal comparable to coral. Photo: Symbios.

CoCrMo: a winning combination

Each component of the prosthesis has unique requirements. The hip stem must be strong, not fail because of fatigue or overload, and not corrode; the femoral head must have ultra-low surface roughness and resist scratching and corrosion that can degrade joint performance. To meet these demands, high-performance biomedical materials are essential, as they offer the best possible compromise between strength, wear resistance and corrosion resistance.

The high hardness of the cobalt-chromium-molybdenum alloy Co-Cr28-Mo6 makes it particularly suitable for the femoral head application. Molybdenum contributes strength and corrosion resistance to this alloy. The alloy has a very low coefficient of friction when paired with either a bearing cup of the same material (metal-to-metal) or one having a polyethylene insert (metal-polymer pair). ➔

Table 1. Hip protheses: joint cavity (acetabulum) / femoral head friction pairs

	Metal-polymer	Metal-metal	Ceramic-polymer	Ceramic-ceramic
Acetabulum (bearing cup)	PEHD Insert + titanium alloy bearing cup (Outside coating) porous titanium + hydroxyapatite)	CoCrMo alloy bearing cup (Outside coating) porous titanium + hydroxyapatite)	PEHD Insert + titanium alloy bearing cup (Outside coating) porous titanium + hydroxyapatite)	Alumina Insert + titanium alloy bearing cup (Outside coating) porous titanium + hydroxyapatite)
Femoral head	CrNi stainless steel Titanium alloy CoCrMo alloy	CoCrMo alloy	Alumina	Alumina

The alloy is generally delivered in bars 8–60 mm in diameter and either forged or machined on a digital lathe. The need for hard, wear-resistant surfaces dictates the choice of material. High-carbon (0.20–0.25% C) CoCrMo alloys are here preferred over low-carbon (0.05–0.08% C) variants.

Other alloys for cemented hip prostheses (femoral stems and bearing cups) may include austenitic stainless steels and titanium alloys (see box "Materials for differentiated uses").

Cemented femoral hip stem in stainless M30NW alloy with a 2–3% Mo content. Photo: Symbios.

Materials for differentiated uses

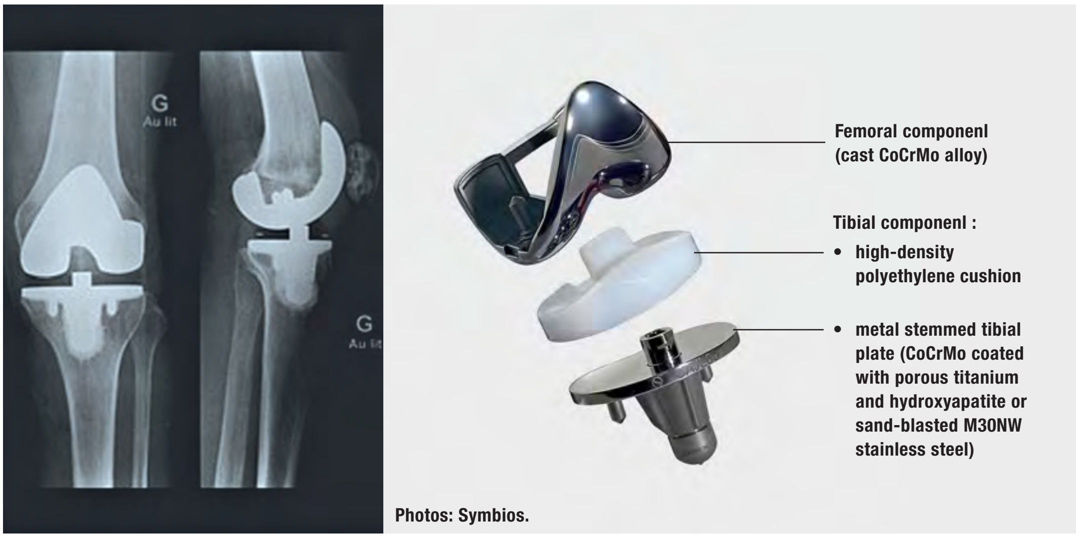
- Cobalt-chromium-molybdenum alloys are particularly interesting. In addition to their strength, toughness and resistance to wear, their elasticity is closer to that of bone than the elasticity of other alloys. CoCrMo alloy is mainly used for the femoral head and the bearing cup. It is also used sometimes for femoral stems.
- Cemented and screwed hip prostheses (femoral stems and bearing cups) generally use austenitic stainless steels for their corrosion resistance and strength. This can be M30NW (Cr21-Ni9-Mn4-Mo2.2-N0.4) or other grades: AISI 316L, ASTM F-55 or F-138 (Cr17–20%, Ni13–15%, Mo2–3%).
- Cementless hip prostheses (femoral stems and bearing cups), which simultaneously require strength and good adherence to bone, use titanium alloys (Ti6Al4V) coated with porous titanium and hydroxyapatite (HA).
- Ceramics (such as alumina (Al2O3) are used in hip prostheses for their low coefficient of friction as femoral heads and as inserts in the bearing cups.
- High-density polyethylene (HDPE) is used as an insert in the bearing cups of hip prostheses and as a tibial component (cushion) supporting the femoral implant in the knee.

The knee, a highly complex hinge

With many muscular points of attachment and a complex anatomy, the knee has stimulated many innovations in prosthesis design. The knee joint is much more delicate than the hip. It is composed of two separate joints: one between the femur and the tibia and the other between the femur and the patella, or kneecap. These joints are controlled by a complicated system of lateral and crossed ligaments that can apply considerable stress on the joint itself. To distribute these stresses evenly designers are creating prostheses that minimise friction while supporting significant mechanical loads (up to eight times the weight of the body when jumping, for example).

For Jean Plé, CEO of Symbios, a Swiss company specialising in hip and knee prostheses, the design and manufacturing of knee prostheses differs from hip prostheses because the geometry of the joint imposes more constraints: "The complex surface of the femoral component of the implant requires very costly and hard-to-perform machining. Hence, the solution of lost wax casting an alloy to give it its definitive form directly. The choice of CoCrMo, suitable for this technique, gives the implant the required mechanical qualities." The alloy offers the femoral component significant hardness and strength (it is more resistant to fatigue than titanium) and a low coefficient of friction. Pivoting on the base formed by the tibial component made of high-density polyethylene, it allows the repaired joint to recover all its rotation and extension capabilities.

The fact that wearers of prosthetic knees or hips now frequently practice sports proves that implant technology is truly robust. The materials used in implants provide the required mechanical, frictional and corrosion properties to allow implants to operate reliably for long times. Molybdenum, because of its beneficial effects on strength, fatigue resistance, hardness and corrosion resistance, plays an important role in this technology.



Photos: Symbios.