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:

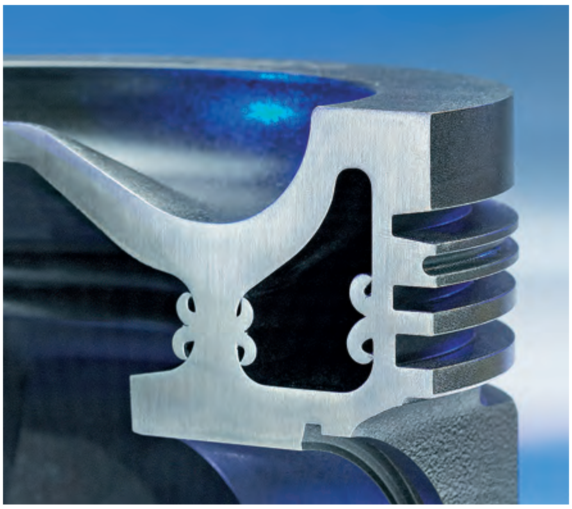
- Block combustion gas from escaping down the cylinder wall between the piston and the cylinder, which would deprive the engine of power, release pollutants, and degrade engine oil performance
- Prevent oil from seeping up the cylinder walls into the combustion chamber, which would produce efficiency-sapping 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.

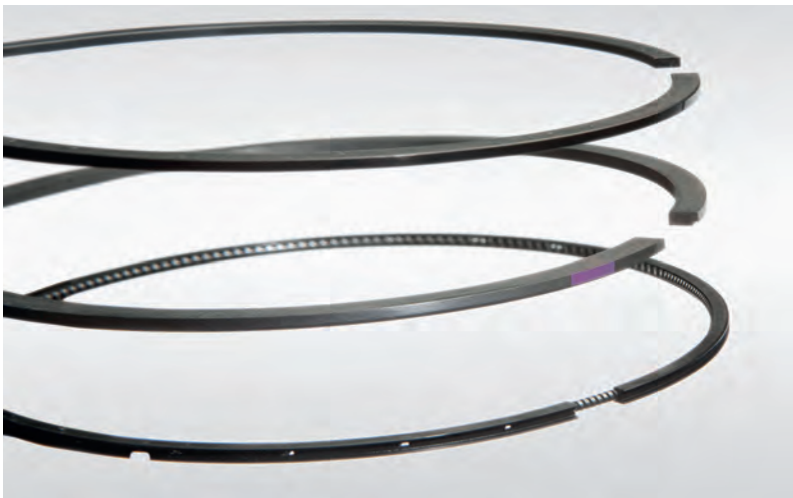
Piston ring functions

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 ›





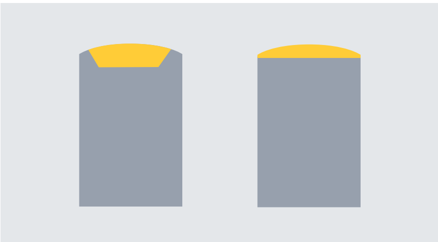
An advanced piston design (left), and a set of modern piston rings (right). © Federal-Mogul Corp.

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.

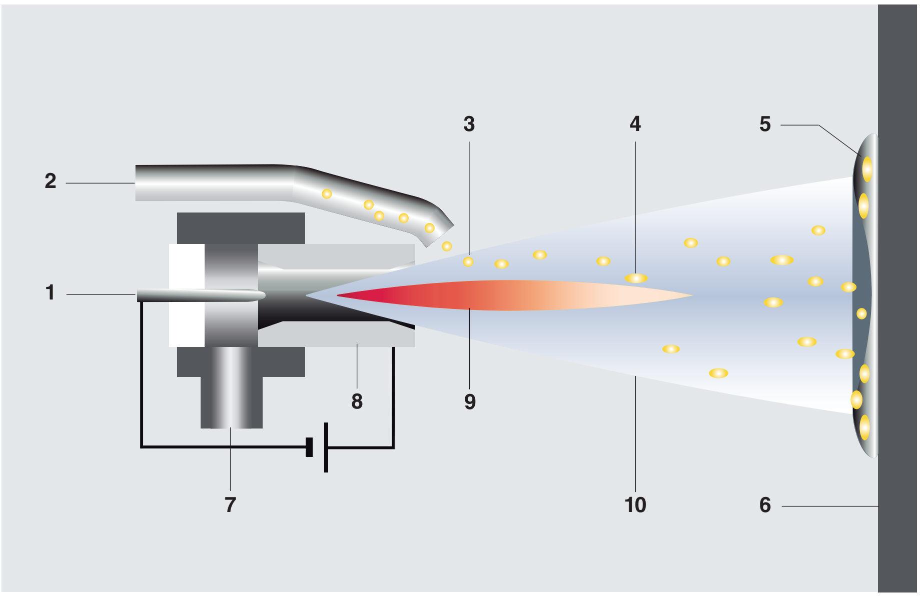
However, these piston ring materials are prone to surface wear so they must be coated with a wear-resistant material. For many years, chromium-plated rings have served basic engine needs, and they are still available. The plating provides a hard surface to minimize general wear, but it has always suffered 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 below 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: 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/)

Plasma-spray coating

Plasma-spray technology, illustrated above, 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.

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.

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Molybdenum alloys for piston ring coatings

Three examples of molybdenum piston ring coating materials are shown in the table. 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. (John Shields)

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.