

Technology for Applying Solid Lubricant to the Piston Skirt of Internal Combustion Engine and Its Effects

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ABSTRACT

A molybdenum disulfide piston coating technique was developed using the Wonder Process Craft (WPC) processing method to apply high-purity molybdenum disulfide onto the sliding surface of the piston skirt for an internal combustion engine. This technique is a world first, and the pistons manufactured using this process gained the full effect of durability while also achieving significant reduction in sliding resistance at a low cost because the coating process does not require use of a binder. The technique is also noteworthy for making manufacturing easier, since it does not alter the dimensions, shape, or surface roughness of the base material. In addition, this piston manufacturing process uses compressed air and molybdenum disulfide powder. The molybdenum disulfide discharged from the process can also be recycled. Thus the process realizes zero waste and addresses the current need for environmentally friendlier technology.

1. Introduction

Improving fuel efficiency in automobile engines is one effective way to pursue goals for more efficient energy resource usage, environmental preservation, and cleaner emissions. Reducing sliding resistance within internal combustion engines can offer significant improvements to fuel efficiency and the industry has seen many such developments, including the improvement of lubricating oil and the coating or plating of sliding surfaces with solid lubricants. On the other hand, methods that involve coating parts with a thin film of solid lubricant present certain difficulties, including the potential alteration of part dimensions and the diminishment of inherent lubricating performance due to binder materials added to the solid lubricant.

2. WPC Processing

The surface treatment method described in this report is based on the surface treatment method known as WPC ("Wonder Process Craft"), which is an application of shot peening technology. The WPC treatment uses a stream of compressed air to shoot fine particles (200 μm or smaller) of a material with desired qualities at high speeds (over 100 m/sec.) at the surface of the object being treated, thereby raising its surface temperature above the A3 transformation point (for ferrous metals) or above the recrystallization point (for nonferrous metals). This causes the outer surface layer of the treated object to melt momentarily and then recrystallize, resulting in modified surface properties. This type of surface heat-treat technology can be used to improve certain mechanical characteristics of the treated object, including sliding resistance.

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3. Reducing Sliding Resistance Using Molybdenum Disulfide

As shown in Fig. 1, various types of surface treatment were experimentally applied to several piston skirts and these were then bench tested to compare the resulting levels of motoring friction among them. The results of this comparison suggested that a process to apply a layer of the solid lubricant molybdenum disulfide to the piston's sliding surface and its outermost layer would be the most effective way of modifying the surface to improve its sliding characteristics, and thus it was in this direction that we took our research and development efforts.

Our development of this new surface treatment technology focused on the following:

- (1) Achieve a binderless treatment process (to take full advantage of reducing sliding resistance.)
- (2) Suppress or prevent changes in the shape and/or dimensions of the objects treated
- (3) Complete recyclability of wastes discharged from the process
- (4) Sufficient repeatability
- (5) Easy application to mass production
- (6) Low cost

Further, pistons manufactured using this technology are named and described as "molybdenum disulfide shot pistons."

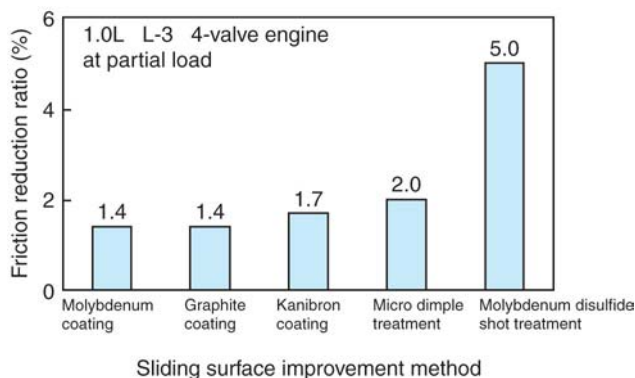


Fig. 1 Characteristics of surface treatment method and friction reduction ratio

4. Characteristics of Molybdenum Disulfide Shot Peening

Because the process used involves no added binder material, and relies instead on the formation of a high-purity solid lubricant layer embedded in the outermost layer of the treated object's surface, it is particularly effective toward reducing sliding resistance. Also, since WPC treatment involves thermal diffusion of a portion of the solid lubricant during application, the shape or dimensions of the treated object remain unchanged, ensuring that the process lends itself easily to mass production activities. Further, because the treated surface is very durable and highly resistant to peeling and frictional wear, the reduction of sliding resistance effects are long-lasting and sustained. Another advantage is that its only waste products are broken powder of molybdenum disulfide and air because the process uses only compressed air and molybdenum disulfide. Since the broken molybdenum disulfide grains are not altered except for being made smaller, they can be separated and sorted by size using a specially designed cyclone separator. Grains of uniform size can be collected, with no risk of introducing foreign matter, and either fed back into the process or reused in other applications. Therefore, the process is both environmentally friendly (since it generates no unusable waste) and useful toward reducing equipment cost (since no waste processing is required).

5. Measuring Molybdenum Disulfide Grain Size

An electrical sensing zone method particle size distribution analyzer (coulter counter) is used to measure the size of the scale-shaped or amorphous molybdenum disulfide grains. To summarize the measurement principle used by this analyzer, a particle passing through a fine pore causes a change in electrical resistance depending on its volume, and this change is converted into particle spherical diameter. Compared to laser Doppler and other two-dimensional techniques, this type of three-dimensional measurement technique yields values that are much closer to true values. The median diameter of the volume distribution determined by this method is used as the indicator of molybdenum disulfide grain size. (Molybdenum disulfide grain sizes listed hereafter are expressed using this volume distribution median diameter).

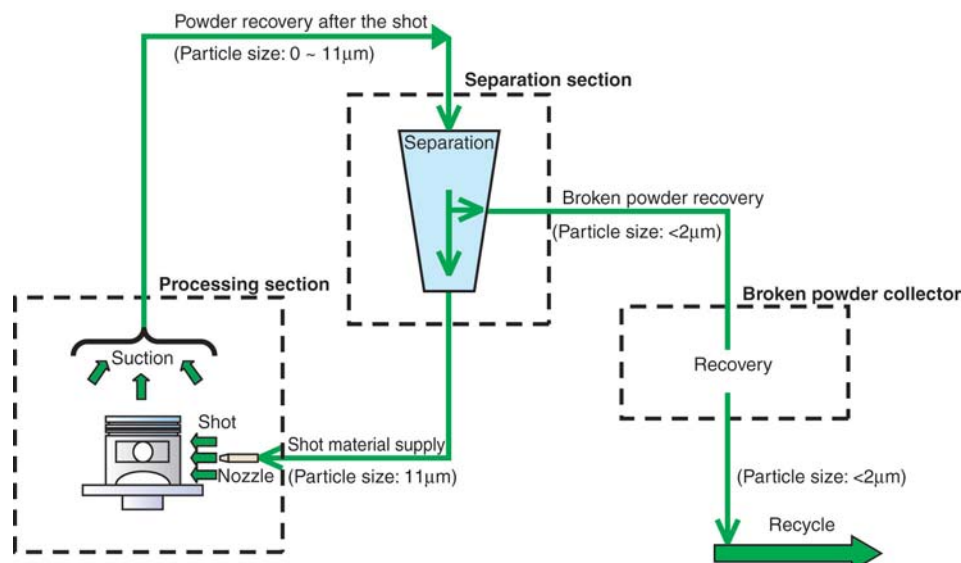


Fig. 2 Shot material supply process

6. Outline of Processing Facilities

As shown in Fig. 2, the processing facilities are comprised of three main sections: a separation section, a processing section, and a broken powder collection section. After being used for blasting in the processing section, the remaining molybdenum disulfide shot powder will be a mixture of grains that fractured after a single use and grains that did not fracture and remain whole. These are separated using a specially designed and built cyclone separator. Fractured molybdenum disulfide grains less than about $2\ \mu\text{m}$ in size are sent to a collection device. Unfractured grains, or grains that have fractured but are still of a usable size, pass through the separator and are returned to the shot nozzle for re-use. Grains continue to be recycled in this way until they are finally fractured into an unusable size and are removed from the process by the separator.

Details of the process are shown in Fig. 3. Compressed air is used to shoot the molybdenum disulfide shot powder against the skirt of the piston. The piston itself is positioned on a turntable that rotates and the shot nozzle moves up and down, thereby ensuring that the spray of molybdenum disulfide powder is distributed evenly over the entire surface of the skirt.

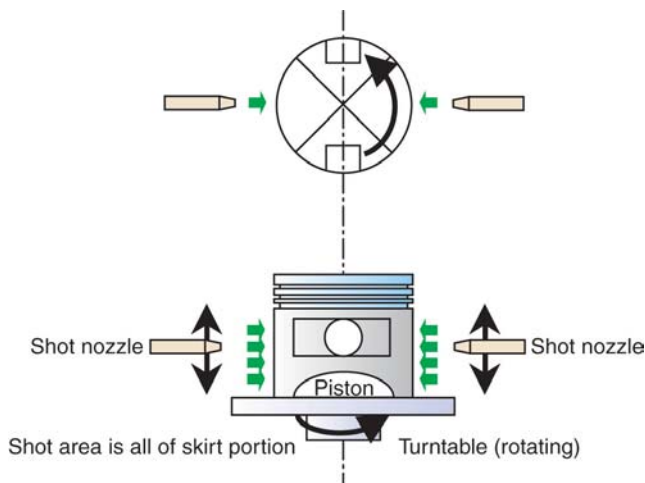


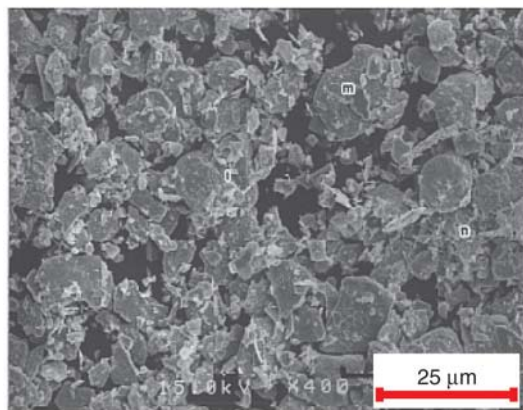
Fig. 3 Processing section outline

7. Establishing Optimum Blasting Conditions

Conditional parameters for air blasting include a variety of factors such as pressure, time, the quality, properties and grain size of the blasting medium, the mixture of blasting medium and compressed air, distance, and others. In some cases varying even one of these parameters can cause changes in the resulting surface properties, while in other cases varying even several parameters will result in no changes to the result. There are also opposite cases in which changing multiple parameters did link to changes in the resulting surface properties. In other words, determining optimum blasting conditions for such a process can be quite difficult under any circumstances. Our particular development attempted to use the WPC process to shoot molybdenum disulfide into a base metal material that was the first attempt of its kind, and the lack of precedent made it difficult to determine optimum blasting conditions. The parameters we eventually found to be particularly effective for use in molybdenum disulfide blasting are described below.

7.1 Optimum Blasting Medium Specifications

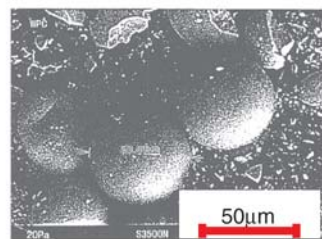
Figure 4 shows the fine molybdenum disulfide powder used in the air blasting process. In order to take sufficient advantage of molybdenum disulfide's inherent properties as a solid lubricant, we used powdered molybdenum disulfide of at least 98.5% purity, containing no binder additives, and of the largest available grain size ($11\ \mu\text{m}$). This larger grain size was chosen to maximize the energy of the molybdenum disulfide for optimum penetration of the target surface. The results of experiments determined that smaller-sized particles could not penetrate deeply enough. Specially made larger-sized particles not generally available on the market also were found to be unsuitable since, with their larger size, they proved to fragment too quickly and completely under repeated use, also resulting in insufficient penetration. Eventually, considering various factors including molybdenum disulfide penetration depth and blast medium consumption rate due to grain fragmentation, it was determined that there exists an optimum size of $11\ \mu\text{m}$ for the molybdenum disulfide shot grains, and this size was adopted for application in mass production.



Molybdenum disulfide powder SEM image

Purity	98.5% over
Particle size	$11\ \mu\text{m}$
Moisture	0.01%
Oil	0.03%

※ Particle size is mean of sensing zone method volume distribution



※ Reference: Ceramic beads for MD treatment

Fig. 4 Molybdenum disulfide powder for shot material

7.2 Optimum Blasting Pressure

To determine optimum blasting pressure, we referred to the parameters used in MD (micro-dimple) air blasting⁽¹⁾, which uses an air pressure of 0.34 MPa [3.5 kg/cm^2] to project roughly spherical ceramic beads having a hardness of HV 500–600 (Mohs 6–7), a specific gravity of 2.3–2.5, and an average grain diameter of $\phi 50 \mu\text{m}$. To project scale-shaped molybdenum disulfide grains having a hardness of Mohs 1 and a specific gravity of 4.8 onto the target object, with considering such factors as units-per-hour requirements for piston production and shot material consumption through fragmentation, an optimum blasting pressure of 0.902 MPa [9.2 kg/cm^2] was established. This high pressure is generated using a special compressor. This blasting pressure is also closely linked to blasting time, and is a significant factor in determining the depth of molybdenum disulfide penetration.

7.3 Optimum Blasting Time

Experiments on optimum blasting pressure revealed that blasting time per unit area is closely linked to molybdenum disulfide penetration depth. Blasting time was established based on this and also such factors as production- and cost-related requirements. With blasting pressure set at a relatively moderate level, we thereafter were able to deepen the molybdenum disulfide penetration by setting longer continuous blasting times per unit area of the base metal. As shown in Fig. 5, intermittent blasting resulted in shallower penetration even when total blasting time was the same. We surmise that this happens because during intermittent blasting, the temperature of the heated base metal is allowed to drop again, while the process is momentarily stopped and waiting for the next blast, and that such repeated rises and falls in temperature result in a relatively lower temperature increase compared to that of continuous blasting. The temperature increase caused by continuous blasting is greater than that caused by intermittent blasting. It is thought that continuous blasting therefore produces deeper molybdenum

disulfide penetration.

In reference to temperature increase, maximum increases of over 1,500 K have been reported based on the results of model calculations.⁽²⁾

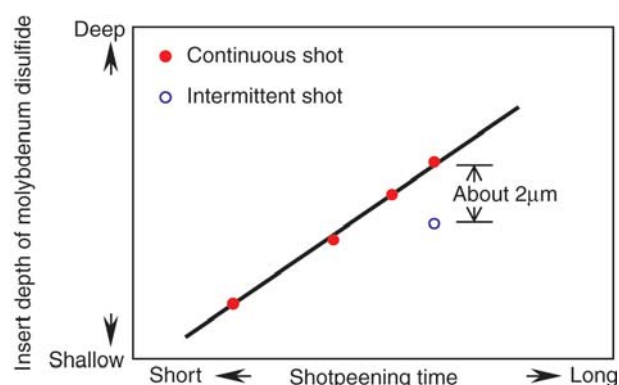


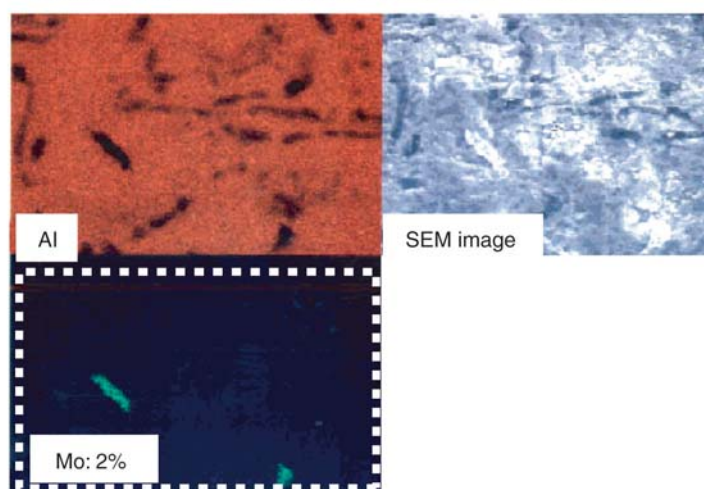
Fig. 5 Characteristics of insert depth of molybdenum disulfide and shotpeening time

7.4 Classification of Used Blasting Medium

The conditions mentioned above were established to minimize blasting medium grain fragmentation, as such fragmentation is unavoidable. Consequently, we developed a special cyclone separator component that ensures only grains about $11 \mu\text{m}$ in size are returned to the blasting process to be used again. This not only helps standardize penetration depth for more stable product quality, it also greatly reduces blasting medium consumption and contributes significantly to reduced production costs.

Depth	Surface	1 μm	2 μm	3 μm
Molybdenum area ratio (%)	64	4	2	0

Color mapping results and molybdenum area ratio of each depth



FE-SEM/EDX surface analysis (Magnification: $\times 2000$ observation area: $60\mu\text{m} \times 45\mu\text{m}$)

Fig. 6 Measurement of molybdenum disulfide area ratio by image processing

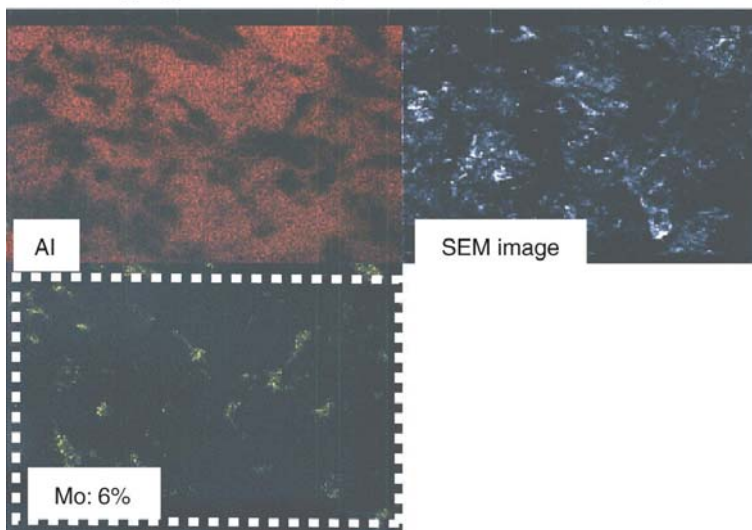
8. Quantifying Molybdenum Disulfide Penetration Depth

Base metal penetration with molybdenum disulfide is a more complex structure than the uniformly thick membranes typical of coated or plated surfaces. In order to measure actual molybdenum disulfide penetration depth, we had to define what is meant by “penetration depth.” First, we used ion milling (to avoid process-related heat effects, contamination and damage) to mill by 1 μm intervals into the sliding surface of a piston freshly treated with the molybdenum disulfide shot process. As shown in Fig. 6, each of the exposed surfaces was color-mapped using FE-SEM/EDX (Field Emission Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy), indicating only the elemental molybdenum, followed then by segmentation image processing of the displayed surface and calculation of the molybdenum area ratio.

Based on the results of analysis using the method described above, and measurements of motoring friction, it became clear that if a surface with a molybdenum area ratio of greater than 2% exists at a depth of more than 2 μm from the initial sliding surface, then the sliding resistance reduction effect and the sustainability of this effect will be sufficient. Based on this we defined penetration depth as the deepest depth at which a molybdenum area ratio of 2% is found, and we set a depth of 2 μm or greater as the standard for molybdenum disulfide penetration.

Depth	Surface	1 μm	2 μm	3 μm	4 μm
Molybdenum area ratio(%)	6	1	1	1	0.3

Color mapping results and molybdenum area ratio of each depth



FE-SEM/EDX surface analysis
(Magnification: $\times 2000$ observation area: $60\mu\text{m} \times 45\mu\text{m}$)

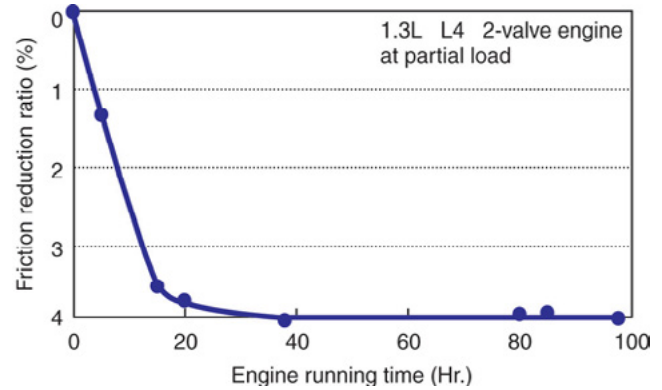
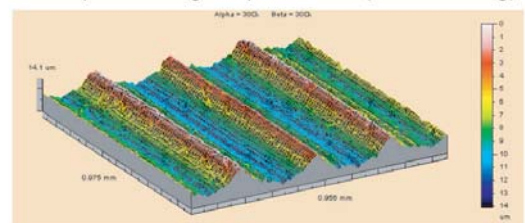


Fig. 7 Engine beak-in time and friction reduction ratio

9. Remaining Molybdenum Disulfide & Sustainability of Effect After Friction Wear of the Sliding Surface

As shown in Fig. 7, a piston treated with molybdenum disulfide to a depth of 2 μm was bench run for 100 hours. Partial-load motoring friction stabilized after 40 hours of operation, and the resulting level continued to remain stable even after 100 hours, with a 4% reduction in friction compared to that at starting time. Further, after the 100-hour mark, we examined the remaining presence of molybdenum disulfide on the friction-worn piston skirt striation tops (the

Development image of piston skirt (Before sliding)



Development image of piston skirt (After sliding)

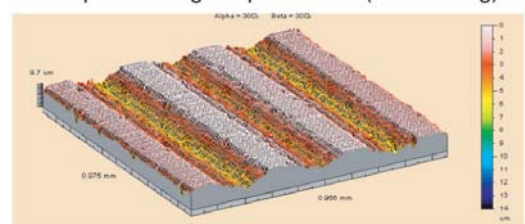


Fig. 8 Molybdenum disulfide residual on piston skirt surface after long period of running engine

actual sliding surface), using FE-SEM/EDX surface analysis color-mapping. As shown in Fig. 8, the results confirmed a molybdenum disulfide area ratio of 6%, as well as a 0.3–1% area ratio to a depth of 4 μm from the surface. The amount of reduction by friction to the striation tops after 100 hours was observed to be 2–4.9 μm in areas of high wear. The fact that we were able to confirm the remaining presence of molybdenum disulfide deeper than the initial penetration depth after longterm operation may be attributed to the transfer of molybdenum disulfide effected of high-purity molybdenum disulfide containing no binder material.

This is easy enough to imagine considering the crystalline structure of molybdenum disulfide. A molecule of molybdenum disulfide is comprised of one molybdenum atom and two sulfur atoms, with the molybdenum atom positioned diagonally below the sulphur atoms in a triangular prism $2H_6$ formation (hexagonal laminate). The Mo-S bond within the layers is a covalent bond, including a fairly strong binding energy and an interatomic distance of only about 1.5 Å. In contrast, between the layers the only binding force is a van der Waals force binding the sulfur atoms at an interatomic distance of about 3 Å. This van der Waals force is inversely proportionate by a power of 7 to interatomic distance, meaning that the binding energy between the layers is considerably weaker than that within the layers. Consequently, because of the covalent bonds within its layers, molybdenum disulfide is relatively strong against perpendicularly oriented forces but, because the van der Waals forces between the layers are weak against forces acting horizontally, inter-layer sliding is exhibited. However, for this inter-layer sliding to occur, intervals between the layers must exist, and there exists a minimum laminal unit. Cross-sectional high-resolution electron microscope examination of the friction area of the molybdenum disulfide, from one time of the sliding portion, 4 layers of molybdenum disulfide have been observed.⁽³⁾ In other words, it is hypothesized that if the molybdenum disulfide is in 4-molecule layers comprised of 3 nm-thick particles, self-cleavage will manifest and give rise to lubrication performance. Manifesting even greater friction reduction in the friction area requires orienting the layers parallel to the

Insert depth of MoS ₂	Friction reduction
1 μm	2.1% (Results may be vary)
2 μm	4.3%
3 μm	3.9%
4 μm	4.1%
12 μm	4.3%

Fig. 9 Characteristics of insert depth of molybdenum disulfide and friction reduction ratio

sliding direction (crystalline orientation) and perpendicular to the load orientation. It is thought this crystalline orientation is accomplished by adding load and sliding the particles, it is accompanied by crystal breakage and rotation that accelerates the transfer of the cleaved particles to separate areas.⁽⁴⁾ The sliding experienced in an internal combustion engine piston is a sliding that receives the explosive force of the piston being pushed through the cylinder, and the surface pressure being received from this is clearly sufficient for such orientation. From the fact that stable friction reduction had appeared by the end of the continuous operation shakedown run, we surmise that the molybdenum disulfide completes its orientation through repeated crystal breakage and transfer early in the shakedown run, becoming one cause of a stabilized friction coefficient. These observations lead us to think that the friction reduction effects of molybdenum disulfide depend largely on its crystal structure. From this we can infer that the sliding resistance reduction properties of molybdenum disulfide do not necessarily increase with greater permeation depth, and that instead high sliding resistance reduction will still be achieved as long as permeation is below a certain specific depth. In bench tests measuring the motoring friction of actual pistons embedded with molybdenum disulfide to depths of 1, 2, 3, 4 and 12 μm , as shown in Fig. 9, all offered roughly similar sliding resistance reduction.

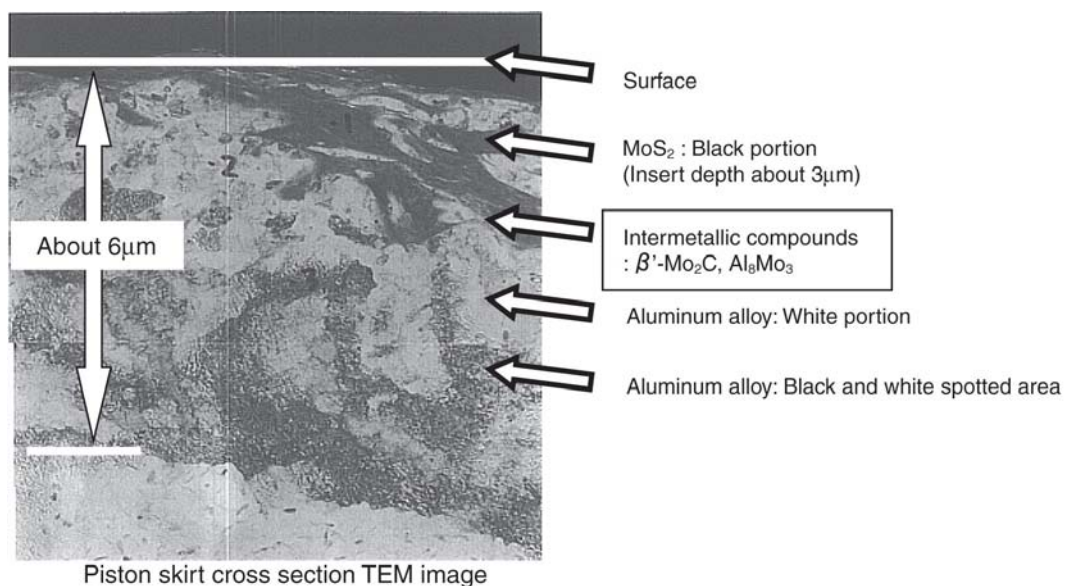


Fig. 10 Molybdenum disulfide insert condition

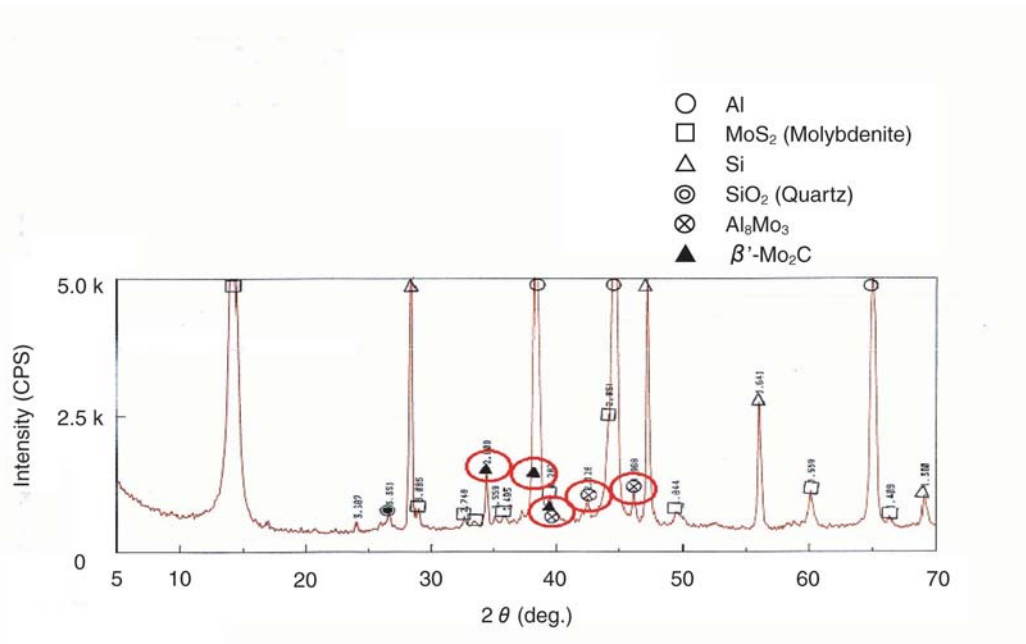


Fig. 11 X- ray diffraction measurement result

10. Observations of the Condition of Molybdenum Disulfide Penetration

Fig. 10 shows the results of TEM (Transmission Electron Microscope) examination of the penetration of molybdenum disulfide into the aluminum alloy base metal. Identification of those elements found by X-ray diffraction are shown in Fig. 11. These results give evidence that WPC treatment is in fact a surface improved heat treatment method, since two intermetallic compounds — β' -Mo₂C and Al₈Mo₃, created only when aluminum alloys and molybdenum are present and subjected to temperature rises of at least several hundred degrees — are detected at the interface between the base metal and the embedded molybdenum disulfide. It has also been reported, in the model calculation results mentioned earlier, that the extreme temperature rises occurring over such tiny ranges in the course of this process is an extremely fast phenomenon on the order of μ secs.⁽²⁾ Such temperature rises are thought to result from multiple continuously occurring phenomenon, including the conversion of the kinetic energy of the shot material into heat upon impact, as well as the shot particle size is on the micron order, most of it does not impact the surface of the base metal, but is instead carried by the

pressurized air current to graze its surface, thereby generating heat by the friction of abrasion.

11. Intermetallic Compounds

The projected molybdenum disulfide becomes enmeshed in the upper layer of the aluminum alloy base metal, which has been melted by an extreme temperature increase, and at the same time, intermetallic compounds are formed in some areas, likely due to thermal diffusion. Since the two intermetallic compounds formed in this case, β' -Mo₂C and Al₈Mo₃, are not corrosion-causing chlorides, fluorides or sulfides, we determined that their presence would not be problematic in terms of the required functioning in an internal combustion engine piston. Further, the aluminum alloy in the piston base metal and the molybdenum disulfide are not only simply in contact, they are actually adhered to one another by these intermetallic compounds, which may be viewed as a type of binder. Compared to cases in which such intermetallic compounds do not exist, we think that the presence of the bond actually helps to make the molybdenum disulfide more resistant to peeling and flaking.

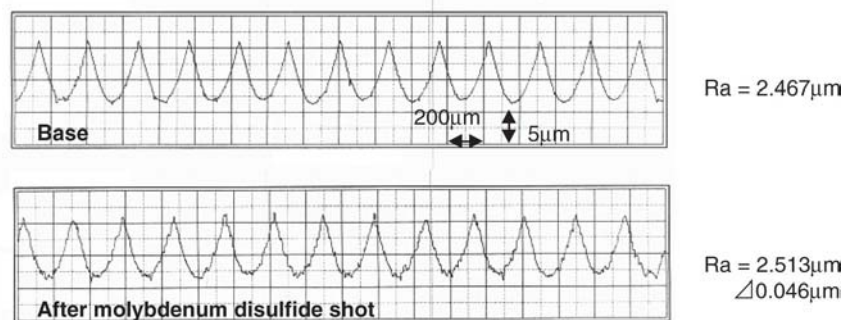


Fig. 12 Shot surface roughness

12. Surface Properties After Treatment

Examining the cross-sectional roughness curves for two different piston skirts, shown in Fig. 12, no significant difference can be seen between a piston without surface treatment and a piston that has been shot-treated with molybdenum disulfide. No change in piston diameter was observed after shot treatment. These results suggest there is no need to take factors such as dimension and shape into consideration when conducting molybdenum disulfide shot treatment, therefore manufacturing coated pistons is relatively easy.

13. Conclusions

- Using the WPC treatment process, molybdenum disulfide powder with a purity of at least 98.5% and containing no binder material is adhered to the skirt of an internal combustion engine piston by shooting it at high speed using compressed air, resulting in a 4% reduction in engine friction.
- The treatment causes a sliding resistance reduction effect that manifests immediately and remains sustained over a long period of time.
- The treatment does not cause any changes in the dimensions or shape of the piston.
- The treatment takes only a short time and is suitable for mass production.
- The only waste produced from process is completely recyclable molybdenum disulfide.

14. Afterword

We view this research as contributing to the development of new ways to utilize solid lubricants. In the future we will extend our study to the use of base metals other than aluminum alloy, with a view to finding fast application to various other kinds of sliding parts, contributing thereby to reduced resource usage and environmental preservation.

Pistons treated using the process described in this report are currently used in the 1.3-liter inline-4 two-plug engine newly developed for the Honda Fit car that was released in June 2001, and in the 1.3-liter inline-4 two-plug engine newly developed for the Honda Civic Hybrid car that was released in December 2001.

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