

Solid Lubricant Films Deposited by Burnishing, **Fig. 12** Model of the burnished film of MoS_2 (**a**) on a steel substrate and (**b**) on a CdZnSe sub-layer of nanoparticles. Virgin roughness of steel (Ra = 0.1 μ m)

Cross-References

- Bonded Solid Lubrication Coatings, Process, and Applications
- ► Chameleon or Smart Solid Lubricating Coatings
- Solid Lubricants, Layered-Hexagonal Transition Metal Dichalcogenides

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Solid Lubricant: Soft Metal

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Synonyms

Solid lubricants based on soft metals

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Definition

Soft metals, a special class of material with low hardness, have been investigated as surface engineering materials used as solid lubricants in key sliding and rolling mechanical components for reducing friction and improving anti-wear ability as well as increasing equipment service lifetime. This critical review mainly addresses the tribological performance of some typical soft metals along with the operating conditions based on some highlighted characteristics of these soft metals. Some key industrial applications as well as future prospects are also discussed.

Scientific Fundamentals

Introduction

Soft metals, such as indium, silver, gold, tin, lead, and related alloys, have been extensively investigated as surface engineering materials in the form of films or coatings. These metals can provide effective isolation on the surfaces of materials, thereby reducing friction, providing a lubrication effect, preventing seizure, and creating high wear resistance for materials from room temperature to ~1,100°C as well as in vacuum and air atmospheres (Bowden and Tabor 1950). Thus, soft metals play a significant role in solid lubrication. The exceptional anti-wear and anti-friction properties of soft metals depend on the three characteristics of microstructure and properties of soft metals summarized in Table 1.

• The face-centered cubic (FCC) phase structure of soft metals resulting in the isotropy for the crystalline lattice essentially provides the highly viscous, fluid-like lubricating behavior.

Solid Lubricant: Soft Metal, Table 1 Basic properties of soft metals (Lansdown 2004)

Element	Melting point (°C)	Crystalline form	Hardness (HB)
Au	1,063	FCC	18
Ag	960.8	FCC	25
In	156.6	FCC	3
Pb	327.3	FCC	4
Cd	321	-	20
Sn	231.9	BCC (>16°C); diamond- type (<10°C)	5

FCC represents face-centered cubic, and BCC represents body-centered cubic

- Low shear strength of soft metals makes the interior slip easily, resulting in the interesting self-repairing character.
- Low evaporation rate of soft metals serves in varied temperatures, from room temperature to ∼1,100°C as well as in different ambient atmospheres.

Therefore, such high-performance soft-metal coatings are often fabricated onto sliding and rolling mechanical components usually exposed to friction, wear, and corrosion conditions, which effectively increases the service lifetime of key mechanical components and improves the reliability and longevity of the whole machine operation. This is also important in preventing the economic loss and sometimes catastrophic failure. Therefore, soft metal coatings have been widely applied in mechanical transmissions involving sliding friction and rolling friction, machine systems, and the nuclear and aerospace industries, which involve special service circumstances such as high and/or low temperatures, high speeds, high vacuum, and radioactive atmosphere.

When mechanical transmission devices and machine systems operate in extreme environments, in order to best satisfy the technological requirements in these frictional systems, the selection of the optimum form in soft metal lubricants with high performance is important. Different forms of soft metal lubricants are briefly introduced as follows:

- Coatings on harder substrates created by different processing techniques such as ion plating, magnetron sputtering, and the conventional electroplating processes, etc., improve tribological performance to meet the requirements of high temperature and highly operating pressure, exceeding the load-bearing capacities of conventional oil and grease.
- Additives in the nano-scale dispersed in liquidbased mediums such as oil, grease, and water. A tribo-chemically protective film with excellent self-lubricating performance, such as nano-copper or nano-zinc, improves anti-wear and anti-friction properties.
- Dry powder, a direct and effective application method, can improve the running-in conditions of sliding mechanical components. However, the poor adhesion of particles to the substrates is detrimental to service lifetime, especially in continuous applications.
- The introduction of soft metals into hard ceramic composites such as TiN and CrN may improve tribological performance of ceramic composite matrix by reducing the coefficient of friction and improving

anti-wear action due to their unique self-repairing behavior (Kelly et al. 2010).

Based on the above-mentioned, the poor adhesion of dry powder and the easy volatility of liquid-based lubricants fundamentally restrict their wide-scale application, especially in harsh working conditions. Therefore, soft metal coatings with excellent lubricating performance and good wear resistance are the "ideal" form for a wide range of functional applications. Furthermore, increasing requirements for adaptability of mechanical components to alternating and harsh environments, along with sustainable environmental development and the progress of nanotechnology, have been the driving forces behind development of novel alloy deposits and metal-based composite deposits to satisfy the complex service needs of current and future engineering materials.

Besides the influence of the microstructure and inherent properties of soft metals on their friction and wear properties, the tribological performance of soft metal coatings involves the following important parameters: film thickness, the specific ratio of shear stress of coating to substrate, the roughness of both substrate and the paired counterface, operating conditions (velocity, load, stroke, and ambient atmospheres, etc.), as well as the different depositing techniques (Holmberg and Matthews 2009). For example, the optimum thickness of soft metal film is vital to retard the wear of substrates by preventing plastic deformation and crack nucleation in harder substrates. So, in the following sections, the tribological performance of soft metal coatings and related alloys is reviewed on the basis of their operating parameters; some recent progress of soft metal and related alloys will also be presented in brief.

Indium Coating

Indium coatings have mainly been used in key aircraft parts to prevent them from wearing out or reacting with oxygen in air. Note that good anti-wear and anti-friction performance can be obtained at optimum thickness of indium coating fabricated onto substrates in air and vacuum environments. When indium deposits on a steel disc slide against a steel ball in air atmosphere, an even lower coefficient of friction of 0.05 presents in the initial state; however, the coefficient of friction abruptly increases up to 0.5 after 20 revolutions because of the transition of oxidation typically characterized by a shiny metallic to a grayfish color, and finally the disrupting film takes place. The coefficient of friction decreased with increasing load regardless of the varying velocity within an appropriate range, however, increasing velocities greatly speed up the onset of service failure of indium coating. For indium coating in vacuum environment, increasing sliding speed increases the coefficient of friction and wear rate (Holmberg and Matthews 2009). More recently, a "tribo-coating" of indium coating exhibited the excellent tribological performance of friction coefficient of <0.02 in sliding contacts and 0.002 in ball bearings because of good in-situ self-restoration and on-demand controllable lubrication, which is most important to improve reliability and overcome unexpected tribological troubles for the future space system (Adachi and Kato 2008).

In particular, the increasing technological requirements of high-performance frictional systems have required the development of novel multi-functional alloy coating. For Ag-In and Au-In binary alloy coatings fabricated onto steel substrates, it is interesting to note that the greater the free energy of formation of the binary alloy, the lower the friction and wear for interaction of the alloy with the iron surface, which is dominated by the tribo-chemistry interactions (Buckley 1971). Furthermore, Cu-Ni-In ternary alloy coating has been successfully fabricated in titanium alloys in aircraft turbo-machinery to improve fretting fatigue resistance and oxidation resistance at high temperatures (Chamort et al. 1988). Moreover, the addition of a small amount of indium into nitrides results in an increase in the hardness of the material as well as a decrease in the friction coefficient, along with an increase in the oxidation resistance to improve the forming efficiency.

Cadmium Coating

Cadmium coating demonstrates equal tribological performance to that of indium and silver coatings. It is remarkable that an optimum film thickness of coating onto harder substrates can effectively slow down wear loss and decrease the coefficient of friction. On the other hand, studies shows that operating circumstances have a great deal of influence on the anti-wear and anti-friction properties of cadmium coating. For cadmium coating serving in argon atmosphere, a minimum coefficient value of friction was achieved when this coating thickness was in the range of 0.1-1 µm. However, in air condition, serious degradation of cadmium coating took place and the wear process was critically dominated by extensive delamination wear caused by oxidation. Furthermore, it is important to point out that surface roughness moderately influences film service lifetime. For instance, polishing may extend the sliding distance, yet polishing also weakens the adhesion strength of deposits to substrate; thus, an optimum roughness on substrates plays an important role in improving wear resistance without sacrificing bonding strength. Recently, stricter environmental and human health regulations have come into effect, and such cadmium coatings are now being used much less often in modern industry applications because of pollution. Other environmentally friendly metals or alloy coatings may be capable of replacing cadmium coating for wear and corrosion protection (Holmberg and Matthews 2009).

Lead Coating

Lead coatings have been widely investigated as an engineered surface material to improve lapping, decrease friction, and protect machine parts against corrosion. As for its tribological performance, it is typically characterized by a high friction of coefficient of 1-2, normal presence of large-scale seizure, and tearing closely related to its easy plastic deformation. As also true for indium and silver coatings, the tribological performance of lead coating is dependent on the optimum film thickness, the counterpart materials, and metal substrate hardness, as well as surface roughness. When a 30 µm thick lead deposit on a copper substrate was sliding against a steel ball, a decreasing coefficient of less than 0.3 was obtained at elevated temperature of 327°C; however, a thinner or thicker lead coating on steel substrates possessed an increased coefficient value of friction. The different wear mechanisms were dependent on film thickness, e.g., microcutting for the thicker one caused by the mating surface asperities, and fatigue mechanism for the thinner one. Furthermore, if the counterpart is changed to electropolished copper, a 10 µm thick lead coating on copper substrate can provide a minimum value of friction coefficient. As for high surface roughness of the tribo-paired materials, a thinner lead film makes the interaction of substrate to the slider easier. In summary, the inherent factors of lead coating affect its friction and wear properties.

Besides the inherent influence of the tribo-paired material, the anti-wear and anti-friction ability of lead coating, in particular, responds sensitively to normal load and sliding velocity. If the applied load and sliding velocity are in the optimum range, a minimum value of friction coefficient is obtained. Remarkably, a longer wear lifetime of ion-plated lead coating is provided when operating at higher velocity, which was is related with the lubricating effect of lead oxide forming at elevated temperatures.

Especially in space components, lead coating demonstrated interesting anti-wear and anti-friction performance in high vacuum atmosphere. A minimum value of the coefficient of friction was obtained for the film thickness within the range of 0.2-1 µm with surface roughness less than 0.5 μ m (Ra), however, the coefficient of friction increases with increasing film thickness as well as rougher surface. Moreover, there is a controversy that the coefficient of friction increases with increasing speed in vacuum. It should be noted that thicker lead films all showed an increasing coefficient of friction regardless of surface roughness, ranging from 0.05 to 0.46, meanwhile the wear lifetime of lead film was considerably extended (Holmberg and Matthews 2009).

Tribological performance in air is different from that in vacuum, which is believed to be related with the different surface geometry. On the contrary, a minimum coefficient value of friction and a decreasing wear life of this coating at highest load were found in air environment, as well as that in vacuum atmosphere. At elevated temperature, lead film operated in a vacuum showed a very low friction coefficient of 0.06 but very short service lifetime, which is believed to be because increasing load and elevated temperature make lead melting easily, resulting in lower shear strength but increasing wear. If the operation temperature exceeds the melting point of lead, it leads to earlier failure of this coating. However, even at cryogenic temperatures of 20K in vacuum, lead lubricating coating bearings display equal tribological performance as at room temperature because of excellent cold shortness (Holmberg and Matthews 2009).

Lead coating provides desirable lubricating performance within the optimum speed rang in a space environment, especially for ball bearings. However, the generated debris during the operation process seriously limits the service lifetime, and high-precision application of lead film, detrimental ball-speed variations caused by lead film, and ball-to-ball friction cause a high level of torque noise. Lead coating with an optimum thickness can also upgrade the load-capacity of lubricated sliding steel contacts to some degree, typically characterized by the increasing scuffing load as well as low coefficient of friction. Furthermore, it is worth noting that the friction of lead film showed satisfactory adaptability in a wide range of sliding speeds and applied loads.

Conventional single metal coatings do not satisfy the increasing technological demands of high-performance mechanical systems, so it is important to develop multilayered or alloy coatings for enhancing adhesion strength and extending wear life. Using other metals as the interlayer, including Mo, Ta, W, Ag, and Cu, and only a thin copper interlayer at the lead/steel interface can provide adequate improvement. On the other hand, when such metals as Mo, Ag, Au, and Pt were incorporated into lead deposits in small amounts, only copper or platinum added to lead coating effectively extended the wear life – by about fivefold. Stricter environmental and human health regulations have placed some restrictions on a commonly used lead coating; currently, lead as the essential component surface engineering coating has been applied in exploiting other more environmentally friendly alloy coatings to improve key frictional systems in many industrial applications, e.g., binary alloys such as Pb-Ag, Pb-Sn, and Pb-Zn (Hombostel 1991).

Gold Coating

Gold coating typically represents good electrical and thermal conductivities, as well as excellent corrosionand wear-resistance. Therefore, gold coating has been widely applied to electrical connectors and related components in electrical industry. Note that the primary requirements in these applications are electrical conductivity and endurance lifetime rather than tribological performance. However, intensive attention has been paid to gold coating, mainly in the aerospace industry, and this coating possesses excellent anti-wear and anti-friction ability in special working conditions. A thin gold coating fabricated onto steel cylinders at an optimum thickness of 0.1 µm can greatly reduce the wear loss by three orders of magnitude in sliding motion against each other, as compared to uncoated cylinders. It was surprising that gold coating was able to reduce wear loss in air and argon atmosphere, however, the coefficient of friction maintained high at value of about 0.85-0.9.

Moreover, the desired tribological performance of electroplated gold coating on steel substrates can be obtained at the optimum operation conditions, such as appropriate film thickness, optimum velocity, and a suitably applied load. As compared to uncoated steel contacts, a stable service lifetime was remarkably extended by four orders of magnitude for thicker coatings, ranging from 5 to 20 μ m when the testing parameters were controlled at the velocity of 0.0132 m/s and a high applied load of 680 N. Furthermore, when a small amount of nickel is doped into electroplated gold deposits, the wear resistance and hardness of this Au-Ni composite coating can be further improved.

On the other hand, especially in electrical connectors with excellent electrical conductivity, the service stability of this coating is also very important. When gold coating is sliding against itself, the wear process undergoes three states; an initial friction coefficient of 0.3 and then 1.2 dominated by the different wear transition from the initially marginal wear, subsequent cracks at the nickel/ brass interface caused by the large interfacial shear stress, and finally enlarged delamination at the interface. Further, adopting the solid-liquid composite method, the coefficient of friction for gold coating can decrease when using polyphenyl ether as the lubricant. However, the fretting resistant performance of gold coating showed some interesting properties. The coefficient of friction maintained no great change regardless of the changing contact system in dry and lubricating conditions as well as different frequencies and amplitudes (Holmberg and Matthews 2009).

Especially for some key frictional components in extremely harsh working environments, more advanced materials are urgently needed to meet increasing technological demands without sacrificing the inherent properties of gold coating. Therefore, some Au-based or alloy coatings have been developed to improve the longevity and duration stability of high performance machines. The example of Au coating with the incorporation of MoS₂ in different amounts indicates that the anti-friction and endurance life of Au coating has been effectively regulated, and an optimum MoS₂ content in this composite coating would possess a low wear loss event at high contact pressure, which is mainly attributed to the good lubricating effect of MoS₂. For Au-base alloy coating, alloying gold generally increases the strength and hardness but with a slight sacrifice of malleability and ductility as compared to pure gold, such as Au-Ag, Au-Cu, and Au-In, etc. Au-Ag alloy coating sliding steel in argon atmosphere shows a discontinuous increase in friction and wear, accompanied by the onset of metal transfer related with iron solubility in sliding contacts. Such Au-Cu (In) coatings have been applied in bearings, which can provide good operation conditions such as resistance to high pressure, operation at high linear speed, resistance to high temperature, as well as good service lifetime. Furthermore, electroplated Au-Cu-Pd ternary alloy coating has been described as promising in materials for electric/electronic applications for contacts subjected to sliding, fretting, or repeated insertions, so the tribological performance is critical for the functional performance in both kinds of industrial applications. When this coating is sliding against a hard countermaterial, the wear process is dominated by abrasion caused by plastic deformation, namely micro-ploughing. And it worth stressing that the higher ratio of adhesion energy to Young's modulus, the higher the resistance of Au-Cu-Pd ternary alloy coating to adhesive failure (Bozzini et al. 2003).

Silver Coating

Thin silver coating has been widely applied to engineering mechanical components subjected to sliding or rolling operating conditions due to its unique physical properties, such as its chemical inertness, good oxidation resistance, and very high thermal conductivity as well as its easy shear to reduce the friction.

As compared with other single soft metal coatings, including lead and indium, silver coating possesses superior anti-friction capability. It is stressed that the degradation of silver coating is mostly due to abrasive wear, because hard oxide particles are formed by the rising temperature closely related with increasing friction by a typical characteristic of the coefficient of friction from initial 0.15 to 0.5. Moreover, the service life of silver film in air is constant if the velocity is relatively low, otherwise the lifetime is shorter.

Good lubricating ability of silver coating is attributed to the synergy effect of low shear strength in the sliding direction and a material transfer between the tribo-paired interfaces. For silver coating onto a ball, a high wear loss of the coated ball occurs due to micro-cutting caused by surface asperities in the initial stage; subsequently, a continuous removal of silver coating is caused by a non-uniform smearing of sliver flakes around the track, and then a uniform material transfer leads to a steady wear loss, and finally the direct contact of ball to disc takes place when the silver coating completely breaks down. Therefore, during the sliding process a great number of fine abrasive particles like steel and iron oxide are produced, and play an important role in polishing; however, this greatly restricts its further applications, especially for high-precision components. Contact fatigue causes low wear loss between the original film and substrate interface.

On the other hand, the anti-wear ability and failure mechanism of silver coatings are closely dependent on the contact pressure and the sliding speeds, which have been confirmed by two-layer gradient silver coating on steel substrates against a steel ball using a ball-on-disk tester. It was found that there are three different wear regimes: (1) mild wear and elastic-plastic deformation without failure of coating; (2) moderate wear and formation of transfer layer at the contact; and (3) severe wear and no protective transfer layer. It is necessary to point out that this functionally gradient silver film composed of an 8 nm thin IBAD silver bond layer and a 2 µm thick thermally evaporated silver film remarkably extended the service lifetime, which was mainly attributed to better bond strength, as compared with single silver film by thermal evaporation and IBAD. Moreover, the mild wear regime was ascribed to transfer layers of agglomerated wear particles on the contact surfaces, and this transfer layer mainly acted as a protective layer, resulting in low friction after the initial transfer of coating material (Yang et al. 2003).

Silver coatings have been successfully fabricated by different processing techniques, including ion plated, vacuum deposited and gas deposited processes. Among them, ion-plate silver coating was the most suitable applied to certain materials' surfaces for the purpose of anti-wear and anti-friction. Because this coating shows distinct nucleation, small size of nuclei, high density, and can provide larger endurance life and lower coefficient of friction of about 0.15, as compared with other two processing techniques, it results in good adhesive strength of coating to substrates. Moreover, the operating environments considerably influenced the anti-friction and anti-wear properties of silver coating, as well as the deformation. Such hydrophilic and hydrophobic silver coatings fabricated onto the rolling components demonstrated interesting tribological performance compared with unmodified sliver coating when rolling against steel balls in different humid atmospheres. There was no variation in the initial rolling process regardless of different humid atmospheres. However, some discrepancies in the coefficient of friction existed in the steady state among those samples. A feasible explanation is that adsorbed water vapors influence the wear debris agglomeration and the tendency of contacting patch formation, resulting in the discrepancy in the rolling resistance. Furthermore, a thin silver film can greatly reduce the sliding wear loss by three orders of magnitude at the optimum velocity and applied load in argon atmosphere. Surprisingly, an increasing coefficient of friction occurs for both thinner and thicker silver films, which has no great effect on the film service lifetime, while the increasing sliding speeds result in increasing coefficient of friction but decreased wear life (Holmberg and Matthews 2009).

Mechanical components in modern industry face increasing performance requirements, leading to the growing need for advanced Ag-based materials and, thus, for modern friction systems. For example, single Ag coating onto ceramic components including Al₂O₃, Si₃N₄, magnesia-partially stabilized zirconia, and zirconia exhibited good tribological performance in air, i.e., a remarkably lowered coefficient of friction by about 50% and a decreasing wear loss by 1-3 orders of magnitude, especially for zirconia and Al₂O₃. Furthermore, using a thinner titanium interlayer greatly improved the adhesion strength and the effectiveness of silver coating to Al₂O₃ substrates to improve the anti-friction and anti-wear ability in air and in humid atmosphere. The addition of solid lubricants into Ag matrix such as MoS₂ and graphite can provide good anti-friction characteristics of the rubbing surface of sliding pairs, especially for weak-current sliding pairs with high operating life (Braterskaya et al. 1991). Furthermore, silver alloy coatings are generally characterized by high mechanical and multi-functional performance as well as high electrical conductivity in modern industrial applications, especially in key aircraft parts, and are also stable at elevated temperature, such as Ag-Sn and Ag-Pd based alloys (Kwon et al. 2009). Moreover, adding precious Ag metal to hard nitride matrix (e.g., TiN, CrN, and Mo₂N) exhibited outstanding self-lubricating ability even at higher operating temperature, however, this result was also accompanied by a corresponding decrease in hardness (Kelly et al. 2010).

Tin Coating

Legislative pressures and customer demands have been the driving force behind the use of lead-free coatings in the connector industry. More specifically, a tin or tin-alloy coating can effectively reduce the friction force generated within an electrical connector, minimizing insertion and fretting wear. However, it is very susceptible to the fretting conditions, and further severe degradation may occur due to wear resulting from the accumulation of debris within the contact region, reducing the conductive contact area and causing an increasing voltage drop across the electrical connector, further resulting in connector failure. Thus, multilayered coatings and composite coatings have been exploited to increase hardness and wear resistance and to reduce friction without sacrifice of the electrical performance. Typical examples include Cu-Ni-Sn and related Sn-based coatings as well as Sn-PTFE composite. For Cu-Ni-Sn coating, using a nickel layer as the interlayer can greatly improve tribological performance of the non-noble tin-tin electrical contact, which is a favorable effect of nickel interlayer related to its capacity to modify the friction behavior under partial slip in sliding condition regime. However, copper readily oxidizes at elevated temperature, resulting in deterioration of some electrical connectors. If PTFE particles are introduced into ductile tin matrix with an optimum compositional range and within an appropriate particle size range, this composite coating has excellent electrical characteristics and good wear resistant properties (Guenin and Conn 1991; Jedrzejczyk et al. 2009).

Key Applications and Future Prospects

In engineering, soft metal lubricants have been used in almost every type of components using PVD, CVD, and conventional electroplating processes in mass production, evolving in many important industrial fields such as automotive, aircraft and other transportation industries, electronics, consumer goods, and metals manufacturing industries, as well as chemical, food, pharmaceutical, medical, and packing industries for the purpose of reducing the coefficient of friction and extending the wear life as well as the cost and environmental protection. Soft metal coatings play a significant role in many key sliding and rolling frictional components, such as sliding bearings, rolling bearings, gears, seals, cams and tappets, pistons, cylinders, valves, injectors, plungers, rotors, pumps, and transmissions.

With developments in industry and nanotechnology, requirements for the high performance of modern engineering frictional systems become more stringent and complex, which motivates the exploitation of the highly functional performance of advanced soft metal-based coatings. Based on the above-mentioned discussion, attention has been focused on developing high-performance deposits as well as the environmentally friendly processing techniques in the future. In particular, many soft metal lubricants have been exploited by modern emerging nanotechnology, from the original single metal deposits to high-performance advanced coatings, to better satisfy high-performance requirements in modern frictional systems, using the new designing concept including nanocrystalline, functionally graded, and multilayered materials.

Cross-References

- ► Cryogenic Solid Lubrication
- ► Gear Lubricants
- ► Solid Lubricants
- ► Thin Film Lubrication

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