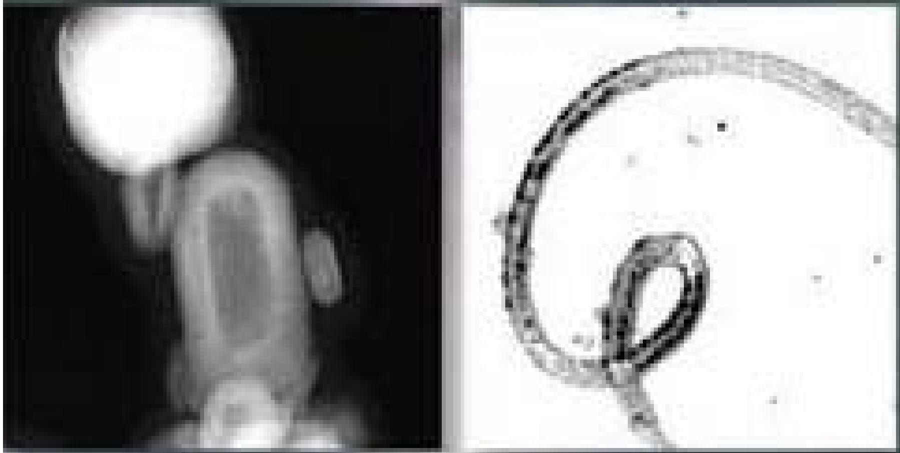
Tribology Series

Nanolubricants



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Nanolubricants Made of Metals

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5.1 Introduction

Metals are the most widely used tribological materials. Rigid metals or alloys such as steel are used to prepare tribo-pairs for rolling or sliding bearings, while soft metals such as Au, Ag, Cu, Zn, Pb, Bi, Sn, In and their alloys are used as solid lubricants in the form of surface films or coatings. The lubricating behaviour of these soft metals arises from the faced cubic crystal structure, which has many more slip-faces and thus exhibits low shear strength along the sliding direction. This lubricating behaviour has a similarity to that of a fluid lubricant with very high viscosity. Lubricating films composed of soft metals may show somewhat self-repairing properties in low friction speed, but for most circumstances they have the following limitations: (a) they have no such behaviour under a higher sliding speed and/or load, (b) they have no capacity to remove friction heat, (c) relubrication is not possible in most instances and (d) application techniques are often complicated. A proposed route to solve these questions is adding these soft metals in the form of powders into a carrier material such as lubricating oils to form a colloidal or partially colloidal dispersion, or into a polymer host to form a self-lubricating material. When the carrier material is oil, the metal powders may be carried to the friction surface by oils to form a metallic thin film under the shearing of the tribo-pairs, and exhibit lubricating behaviour without the above limitations. However, this route also has a technical difficulty since most lubricating oils have the requirement that the solid particles dispersed in them should not be larger than 0.5 μm and not precipitate in the process of usage, which cannot be achieved through traditional preparation technology of a metal powder.

Metal nanoparticles are metal particles in the size range of 1 to 100 nanometres. In the past twenty years, they have attracted extensive research interest, mainly due to the quantum effect, and their properties can be adjusted by the particle size as well as by the surface morphology. The characteristic of these materials that gives special properties, whether in the form of powders or thin films, is their size. When at least one dimension is in the nanometre range, metals will exhibit remarkable and unusual properties that are absent in their bulk phase,

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whether in the form of powders or thin films. A large amount of research concerning the preparation, structure characterization, properties and application of metal nanoparticles has been conducted.

In tribology, it is anticipated that metal nanoparticles are good lubricants when used as additives in lubricating oils for the following reasons [1–4]: (a) metal nanoparticles are so small that a stable colloidal dispersion in oils can be achieved through proper methods, which can avoid the undesired precipitation caused by gravitation, (b) with the formation of a stable well-proportioned dispersion, metal nanoparticles are more liable to be trapped in the rubbing surface and (c) metal nanoparticles are liable to deposit on the rubbing surface. Many studies have been conducted to prove the above conjectures, and some valuable results and conclusions have been achieved. In these works, traditional soft metal lubricants such as Cu, Ag, Pb, Bi, Sn, In and their alloys have been prepared into nanoparticulate materials, the methods to disperse these nanoparticles into lubricating oils to form a stable colloidal dispersion have been developed and the tribological behaviour and mechanism have been studied and discussed. This chapter will give a general summarization of these research works.

5.2 Nanolubricants Made of Coinage Metal Nanoparticles

It is well known that the elements of group 1B consist of gold, silver and copper. They are famous as three inert coinage metals. Copper is the first metal to be harnessed by man, being second only to iron in its usefulness down the ages, and has been called the cornerstone of civilization. Copper is an excellent conductor of heat and electricity. It can be worked into various forms such as pipes, wire, rods, sheets and coins. It can be dissolved in acids, but is resistant to atmospheric corrosion. There are many uses for copper. It is a very versatile metal that has increased in importance to technology and society in the last century. Some major uses are electrical wiring and components, roofing, plumbing, alloys and electroplating. Silver is probably the third metal to be discovered after gold and copper. Chemically, silver is similar to the heavy metals. It is sometimes classed as a noble metal. Silver is somewhat rare and considered a commercially precious metal with many uses. Silver has the highest electrical and thermal conductivity of all metals. It is used for dental fillings, to silver mirrors, as a catalyst for chemical reactions, in water purification, in special batteries and in solar cells. Gold is classed as a heavy, noble metal. It is the most familiar of the precious metals. Gold is considered to be one of the first metals used by humans. The major used of gold is for making jewelry, but it has important applications in electronics, for electrical contacts in making computer transistors and diode wires, and in dentistry. Gold leaf finds many uses in surgery, space vehicles and art works.

The properties and applications of metallic gold, silver and copper have been greatly expanded by decreasing their size in the nanometre range through chemical or physical methods. In the past tens years, gold, silver and copper of different size, shape and surface morphology have been synthesized via different methods. These materials have been found to have remarkable and unusual properties that are absent in the bulk phase, and have important applications in electronics, optics, catalysis, biomaterial and other high-technology fields. Among the three elements, the studies concerning gold nanoparticles were the most abundant, followed by silver and copper. The reason is that for most situations the chemical stability of the particles is crucial to avoid degradation processes such as partial oxidation or undesired sintering of particles, and gold is more stable. In fact, the lack of sufficient stability of many nanoparticle preparations has impeded the development of real-world applications of nanomaterials to some extent. As a result, a number of studies have been conducted concerning the preparation of stable and dispersible metal nanoparticles in the past few years.

Metals of group IB are all 'soft' metals with a faced cubic crystal structure, which are traditional solid lubricants. Generally, they are interposed as a film between sliding and/or rolling surfaces to reduce friction and wear. Their powders (mainly copper or silver for the relative lower costs), in the size range of micrometres, can be used as fillers of polymer materials to enhance the antiwear (AW) and friction-reduction properties, but are not able to be employed in oils because they cannot form a stable dispersion. This problem has been solved to some extent by evolving new methods to prepare stable and dispersible metal nanoparticles along with the advancement of nanotechnology.

5.2.1 Organic Compound Surface-Capped Copper Nanoparticles as Oil Additives

Nanoparticles of group IB metals have been synthesized through various methods. However, most of the resulting nanoparticles (especially naked metal nanoclusters) are inherently unstable and easy to aggregate or erode by circumstances that eventually lead to precipitation when added in oils. The poor stability, solubility and dispersibility of these nanoparticles in lubricating oils have limited their further applications as additives in formulated lubricants to a great extent. An effective solution is to cap these nanoparticles with a layer of judiciously selected organic molecules, which are composed of a polar group and a long alkyl chain. The polar group should have a strong chemosorbing ability in order to cause the surfactant to be chemisorbed on the surface of the inorganic nanocores, while the long alkyl chain should have a suitable length and structure to enable inorganic nanoparticles to be soluble in oils. The capping process could proceed after the noncapping metal nanoparticles have been prepared, but is more effective during the preparation process. The most popular method at present involves the reduction of relevant metal salts or the thermal decomposition of metal organometallic precursors in the presence of a suitable capping agent. The main reported capping agents are long-chain alkyl thiols [5,6], oleic acid [7] and amines [8].

A series of works about the preparation and tribological properties of copper nanoparticles with O, O'-dialkyldithiophosphates (DDP) as the capping agent have been reported. The achieved dialkyldithiophosphate surface-capped copper nanoparticles (DDP-capped Cu nanoparticles), prepared by means of a redox surface modification technique, can readily disperse in common nonpolar solvents and mineral oils to give a transparent solution, and their liquid paraffin (LP) solution remains unchanged for several months in ambient conditions or for 3 days at 140°C. This finding suggests that the organic compound surface-capped metal nanoparticles are capable of being good additives of lubricant oils.

A lot of studies have been conducted to evaluate the tribological properties of surface-capped copper nanoparticles. Zhou *et al*. [5] pointed out that the size and additive concentration of copper nanoparticles have a remarkable effect on their lubricating properties, based on the experimental results shown in Table 5.1. According to the results, DDP-capped Cu nanoparticles with grain sizes of 2 and 5 nm can improve the AW ability of LP effectively. However, DDP-capped Cu nanoparticles 12 nm in size decreased the AW ability of LP to some extent, while nonmodified copper nanoparticles (with a size of 40 nm) as additives in LP caused instant seizure under the same conditions. A rational explanation of the phenomenon

Table 5.1 Antiwear performance[a] of DDP-capped Cu nanoparticles. Reproduced by permission of Elsevier from Zhou *et al*. [5], © (1999) Elsevier

		Grain size of copper nanoparticles (nm)		
Sample	Liquid paraffin	2	5	12
AWS (mm^2)	0.448	0.261	0.393	0.602

[a] Lubricating performance of oils with or without additive is usually evaluated by running tribological tests on a four-ball tester. The tester consists of a steel ball rotating under load on a set of three similar stationary balls. The speed, load and temperature during the test are precisely controlled. After the wear test, round wear scars are formed on the lower three balls and their diameters are measured using a microscope. The diameter of the wear scar (WSD) in millimetres or the area of the wear scar (AWS) is a measure of the AW characteristics of the lubricants. In this case the tests were preformed under conditions of 400 N, 1450 rpm and 30 min.

might be that the smaller the size of copper nanoparticles, the lower is the melting point and the higher the reactivity of the nano-sized copper core. Subsequently, copper nanoparticles of a smaller size are more liable to interact with the surfaces of the friction pairs to form a surface protective film, which contributes primarily to the increased AW ability. In the case of DDP-modified Cu nanoparticles of larger sizes, the reaction activity of the nano-sized copper core decreased, and the interaction between the nano-sized copper core and the rubbing surface became weaker, which was not beneficial to the formation of the surface protective film. Ultimately, nonmodified copper nanoparticles of a very large size act as abrasives during the friction process and cause severe wear.

Li *et al*. [6] have studied the influence of additive concentration of DDP-modified Cu nanoparticles on the tribological properties. Table 5.2 shows the four-ball friction and wear

Table 5.2 Four-ball test results[a] of oil containing DDP-capped Cu nanoparticles at various additive concentrations. With kind permission of Springer Science and Business Media from Li *et al*. [6]

Concentration (wt %)	P_B (N)	P_D (N)	WSD (mm)
0	460.6	1568.0	0.60
0.1	509.6	1568.0	0.35
0.2	588.0	1960.0	0.38
0.3	637.0	1960.0	0.30
0.4	656.6	1960.0	0.30
0.6	686.0	2450.0	0.33
0.8	705.6	2450.0	0.32
1.0	735.0	3087.0	0.31

[a]The WSD value achieved under test conditions of 392 N, 1450 r/min, 75°C and 60 min (referring to ASTM D4172) is a measurement of the AW characteristics, while P_B (last nonseizure load, the last load at which the measured scar diameter is not more than 5 % greater than the compensation value at that load) and P_D (weld point, the lowest applied load at which sliding surfaces seize and then weld), measured according to GB3142-82 (similar to ASTM D2783), are used to evaluate the EP performance of the lubricants.

Table 5.3 Tribological performances of DDP-capped Cu nanoparticles under different loads. Reproduced by permission of Editorial Office of Tribology from Zhou *et al.* [9]

	DDP-capped Cu nanoparticles	
P (N)	WSD (mm)	Friction coefficient
300	0.40	0.93
400	0.45	0.08
500	Seizure	
600	Seizure	
700	Seizure	
1000	0.95	0.08
1200	1.02	0.06
1500	0.94	0.05

Conditions: LP is used as the base oil, at a rotation speed of 1450 r/min, for 30 min.

test results of the commercial base stock (HVI WH150) containing DDP-capped Cu nanoparticles at different concentrations. It can be seen that copper nanoparticles can significantly improve the AW and extreme pressure (EP) properties of the base oil, even at very low additive concentrations. With increasing additive concentrations, the P_B and P_D values increased, indicating that better EP properties can be achieved at a higher additive content. The wear scar diameter (WSD) of the steel ball decreased dramatically at 0.1 wt % of the copper nanoparticle added, and a minimum WSD was achieved at the concentration of 0.5 wt %.

The influence of the applied load and rotating speed on the tribological properties of DDP-capped Cu nanoparticles has been investigated by Zhou *et al.* [9] and Yu *et al.* [10]. The tribological performance of DDP-capped Cu nanoparticles under different loads is shown in Table 5.3. It is observed that DDP-capped Cu nanoparticles exhibit good AW and friction-reduction properties when the applied load is below 400 N or in the range of 1000 to 1500 N. The WSD at higher loads has no obvious change with the lubrication of LP containing DDP-capped Cu nanoparticles. In the tested load range, the friction coefficient reduces as the applied load increases. When the applied load is 1500 N, the corresponding friction coefficient is only 0.05, indicating that copper nanoparticles can perform excellent tribological properties at higher applied loads. It is found that severe abrasion of the test steel balls appears after several minutes of friction in the applied load range of 500 to 900 N, which might be owing to the fact that the copper nanoparticles could not form an adequate lubricating deposited film in this condition.

The study on the influence of rotating speed shows that the friction-reduction properties of Cu nanoparticles increase with decreasing rotating speeds at lower applied loads. At higher applied loads, the rotating speed has little effect on the tribological properties of copper nanoparticles.

The tribological properties of DDP-capped Cu nanoparticles in different base oils were studied by Yang *et al.* [11] and Qiu *et al.* [12]... The research results shown in Table 5.4 indicate that copper nanoparticles exhibit excellent AW and friction-reducing properties in all kinds of oils [11, 12] These apparent performances have some difference due to the intrinsic diversity of oils. The EP properties of the copper nanoparticles are more obvious in

Table 5.4 Wear scar diameters of different base oils with/without 0.7 % DDP-capped copper nanoparticles (abbreviated to NC). Reproduced by permission of Yang X from Yang *et al*. [11]

The category of base oil	WSD (mm)	P_B(N)	P_D(N)
500 SN mineral oil	0.57	431	1568
500 SN mineral oil + NC	0.38	833	1960
Dioctyl sebacate	0.95	431	1568
Dioctyl sebacate + NC	0.41	580	1568
PAO101	0.63	490	1568
PAO101+ NC	0.43	1068	2450
Rap oil	0.58	559	1960
Rap oil + NC	0.46	755	1960

poly-alpha-olefin (PAO) synthetic oil and 500 SN mineral oil, while AW performance is more obvious in dioctyl sebacate.

Improper usage of the lubricating additives would accelerate the invalidation of the nonferruginous accessories relative to ferruginous tribo-pairs. However, as a kind of 'inert' solid lubricant in nature, the function mechanism of copper nanoparticulate additive differs distinctly from the conventional polar or nonpolar organic compound additives, which are based on the chemical reaction of the 'active' elements such as S and P with the rubbing surface to improve the AW or EP properties; i.e. exhibitions of the tribological properties do not rely on the kind of tribo-pair materials. Some research works [13, 14] have revealed that copper nanoparticles have good AW and friction-reduction properties for friction pairs of steel–steel, steel–iron, steel–copper and steel–aluminium to a certain extent.

5.2.2 Copper Nanoparticles Passivated by Carbon Film Used as Oil Additives

Tarasov and his coworkers [13] have developed an energetic method to prepare metal nanoparticles that can be also dispersed in oils. In this method, nano-sized copper powder is produced by the electric explosion of metallic wire (the 'EEW' process) in an inert or active gas. Various copper nanoparticles with different average grain sizes and surface protection films can be used to disperse nano-scale copper powder in oils steadily by varying the gas media, such as argon, carbon dioxide, nitrogen and argon/oxygen mixture. In addition, the surfactant was also used to improve the dispersion stability of these nanoparticles in oils. Figure 5.1 gives an example of TEM images of the as-prepared copper nanoparticles produced in argon via the 'EEW' process.

The researchers have also performed wear and friction tests by using friction specimens made by rubbing medium carbon steel against an as-quenched roller with a hardness of 46 to 48 HRC under the lubrication of a commercial motor oil with/without copper nanoparticles under the following test conditions: normal load 110 and 184 N, sliding speed 1.56 and 2.62 m/s, length of the sliding path 27 km. The average friction coefficient, score limit as well as wear, given with respect to copper nanopowder obtained in different gases at an additive concentration of 0.3 wt %, are presented in Table 5.5. It can be observed that there is a clear tendency to reduce the friction coefficient and decrease the mass loss of wear for all the samples, especially for samples 2, 4 and 5.

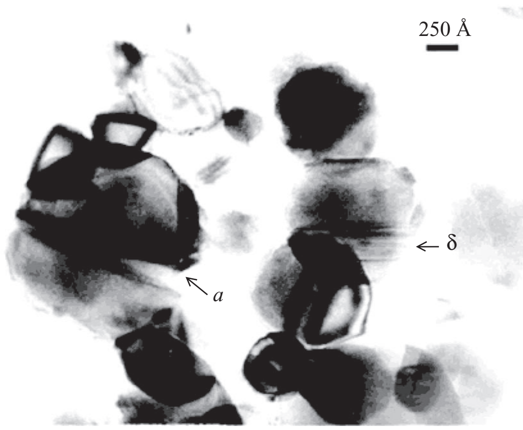


Figure 5.1 TEM image of copper nanoparticles produced in argon via the 'EEW' process. Reproduced by permission of Elsevier from Tarasov *et al*. [13], © (2002) Elsevier

Typical dependencies of the friction coefficient on wear path length (time) by the example of copper nanopowder additive obtained in carbon dioxide are shown in Figure 5.2. The data in Figure 5.2(a) to (c) provide the evidence of improved friction conditions where the nanopowder additive has been used. It can be concluded that copper nanopowder additive to SAE 30 motor oil reduces friction most effectively at higher loads and higher sliding speeds. Based on these results, the researchers demonstrated the feasibility that nanoparticulate copper can adhere preferentially to steel friction pairs and reduce the friction.

The copper nanopowder additive provides changes in worn surface topology and does not impair the lubrication characteristics of the motor oil. Local overheating caused by the direct contact of two surfaces initiates chemical deposition of copper on steel, providing a soft surface limited to the locality of the friction pairs.

5.3 Nanolubricants Made of Low Melting Point Metal Nanoparticles

It is known that many low melting point metal materials, such as indium, tin and bismuth, are good lubricating materials [15]. In particular, bismuth has attracted more interest as a potential thermoelectric and 'green' lubricant material [16]. It has been realized that soft metals

Table 5.5 Results of tribotechnical experiments. Reproduced by permission of Elsevier from Tarasov *et al*. [13], © (2002) Elsevier

Number	Lubricant	Moment of friction (N m)	Mass losses (g)
1	SAE 30	1.308	0.0058
2	SAE 30 + Cu (CO_2)	0.759	0.0028
3	SAE 30 + Cu (Ar)	1.283	0.0079
4	SAE 30 + Cu (Ar + O_2)	0.744	0.0023
5	SAE 30 + Cu (N_2)	0.543	0.0017

(The concentration of copper nanoparticles in oil is 0.3 wt %; rollers are made of steel.)

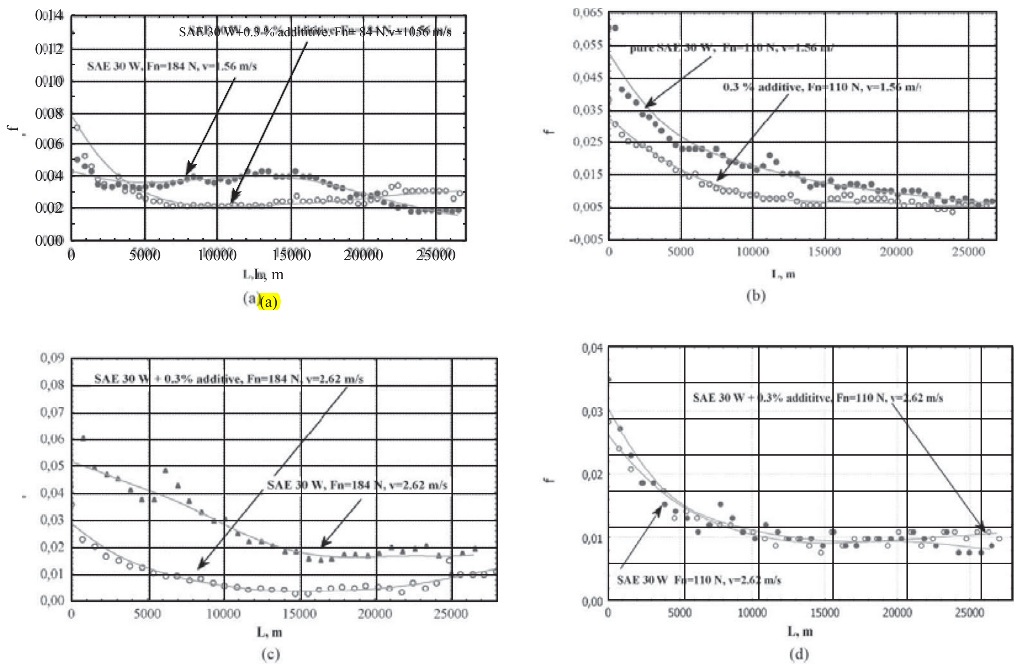


Figure 5.2 Wear path length dependencies of the friction coefficient. Reproduced by permission of Elsevier from Tarasov *et al*. [13], © (2002) Elsevier

with a low melting point on the friction surface can melt into liquid under the flash temperature caused by rubbing, and exhibit a low friction coefficient. Accordingly, it is expected that their corresponding nanoparticles should be excellent lubricants. It is reasonable to expect that the nanoparticles of low melting point metals, particularly in the form of a stable dispersion in oils, are able to move more easily into the rubbing surface and melt on it to form a liquid lubricating film, thus exhibiting a more effective lubricating performance. The problem is how to prepare these nanoparticles with an adequate stability dispersibility in lubricating oils. A simple solution strategy including a 'direct solution-dispersing method' or 'surfactant-assisted solution-dispersing method' has been proposed by Zhao and his coworkers, in which the inherent low melting point characteristic is ingeniously utilized [15, 17, 18]. Through these methods, indium, tin, bismuth and lead nanoparticles have been synthesized successfully. Their tribological behaviours as oil additives have been studied.

5.3.1 Nanolubricants of Indium, Tin and Bismuth via the Direct Solution-Dispersing Method

Zhao and his coworkers [15, 17, 19] present a simple preparation procedure of low melting point metal nanoparticles, which is very different from the conventional solution route. In this method, the bulk metal was melted in a hot organic liquid (which may be oils) and then turned into little liquid drops dispersed in oils by violent mechanical stirring. A dispersion

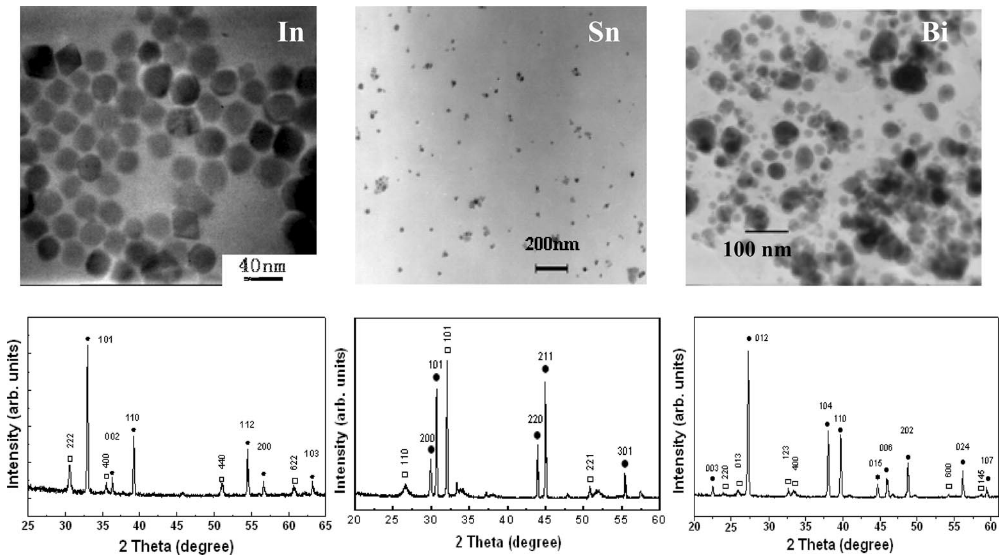


Figure 5.3 TEM images and the corresponding XRD patterns of the as-prepared indium, tin and bismuth nanoparticles. Reproduced by permission of American Chemical Society from Zhao *et al*. [15], © (2003) American Chemical Society, and of Elsevier from Zhao *et al*. [17, 18], © (2003 and 2004) Elsevier

composed of oils and little metal particles could be achieved after the synthetic system was fully stirred and cooled to room temperature. The preparation strategy allows these low melting point metal nanoparticles to be prepared from their bulk materials with ease and without using complicated apparatus and expensive agents, and is really a simple one-step method to prepare metallic nanoparticles.

Figure 5.3 presents TEM images and X-ray diffraction (XRD) patterns of the synthesized indium, tin and bismuth nanoparticles via the direct solution-dispersing method, in which the spherical In, Sn and Bi nanoparticles in the range of 30 to 50 nm can be observed. The size distribution of In nanoparticles is narrower than that of Sn and Bi nanoparticles. The XRD analysis reveals that both the pure metallic state and its corresponding oxide are present in the resulting product, indicating that a portion of metal has been oxidized during the dispersing process.

Based on these results, a possible pathway for the formation of indium, tin and bismuth nanoparticles via the direct solution-dispersing method has been proposed, as shown in Figure 5.4 [19]. At the beginning of the preparation process, large melted metal droplets are broken into small droplets in hot solvent by mechanical stirring, and the fresh surfaces of these metal droplets are oxidized to generate a metal oxide layer. The metal oxide layer can efficiently prevent the coagulation of smaller droplets and further oxidation of inner metal into little droplets. During the dispersion process, the larger droplets bear a shearing force larger than that of the smaller ones. Therefore, the larger droplets reduce faster than the smaller ones and, as a result, the size distribution can be focused down to one that is nearly monodisperse.

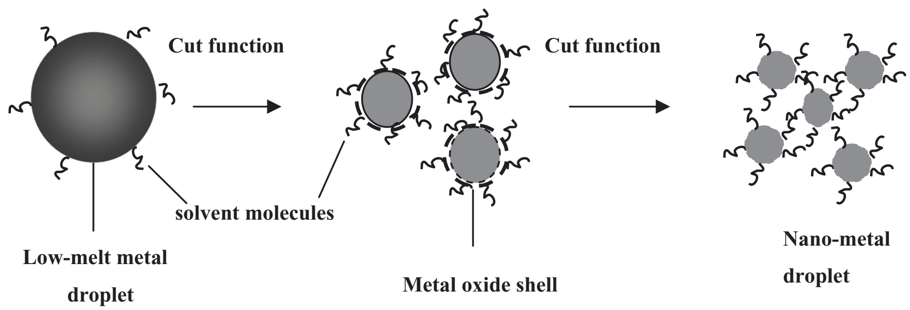


Figure 5.4 Schematic illustration of the formation process of metal nanoparticles by the direct solution-dispersing method

Soft metals such as indium, tin and bismuth are good solid lubricants, but they cannot be used as a lubricating oil additive because of their poor dispersibility in oils. However, their nanoparticles prepared by the direct solution-dispersing method have been found to have better oil solubility and can be directly used as lubricating additives. Their tribological properties have been evaluated on a four-ball tester and the results are presented as follows.

Figure 5.5 shows the variation of WSD with the additive concentration of the In, Sn and Bi nanoparticles in LP, which was used as the base oil [15, 19]. It can be seen that the WSD of pure LP is as high as 0.72 mm. However, the WSD of LP containing Sn nanoparticles are obviously decreased in all the tested additive concentration ranges, indicating that Sn nanoparticles can improve the AW property of the base oil very well. The WSD of LP containing Sn nanoparticles is only 77 % of that of pure LP, even at an additive concentration of 0.12 %, and reaches a minimum value when the additive concentration increases to 1 %. In and Bi nanoparticles also exhibit excellent AW performance in a broad additive concentration range of 0.06 to 1.0 %. They can efficiently improve the AW property of LP at a very low concentration and their AW performance is evidently improved when the additive concentration is increased. These results indicate that the as-prepared Sn, In and Bi nanoparticles have

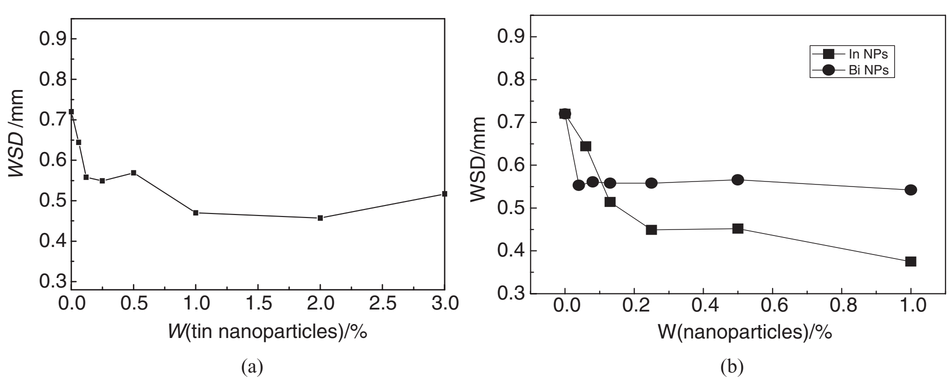


Figure 5.5 WSD as a function of the additive concentration of (a) Sn and (b) In and Bi nanoparticles in LP (under a rotation speed of 1450 rpm and load of 300 N). Reproduced by permission of American Chemical Society from Zhao *et al*. [15], (c) (2003) American Chemical Society

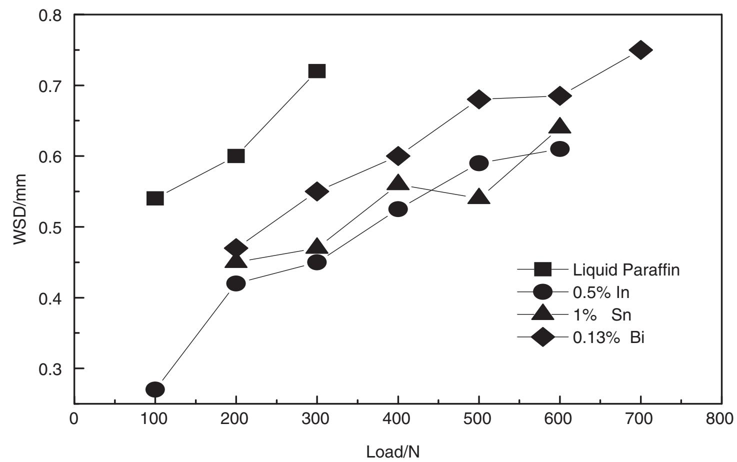
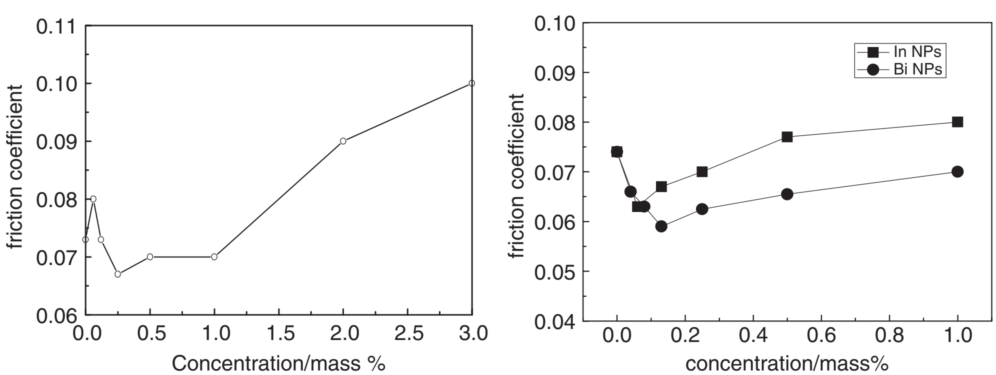


Figure 5.6 Relationship between WSD and the applied load with lubrication of LP and LP containing these different metal nanoparticles

excellent AW properties when used as oil additives. Comparatively, the AW property of indium nanoparticles is better than those of bismuth and tin nanoparticles.

The relationship between WSD and the applied load of LP and LP containing these soft metal nanoparticles is shown in Figure 5.6 [15, 17–19]. It can be seen that the WSD of LP containing different metal nanoparticles are much smaller than that of pure LP, especially for In nanoparticles. During the four-ball friction and wear test, seizure of the tribo-pairs appeared when the applied normal load was above 400 N for LP, but as high as 600 N for LP containing In or Sn nanoparticles and 700 N for Bi nanoparticles. In fact, all of these soft metal nanoparticles have an excellent load-carrying capacity when used as oil additives.

Figure 5.7 shows the variation of the friction coefficient with the additive concentration of the In, Sn and Bi nanoparticles in LP, which was used as the base oil [19]. It can be observed



(a) (b)

Figure 5.7 Friction coefficient as a function of additive concentration of (a) Sn and (b) In and Bi nanoparticles in LP under 300 N

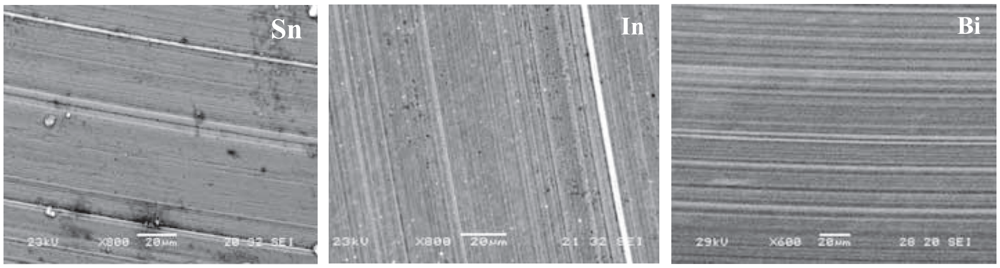


Figure 5.8 Morphologies of the wear surfaces under lubrication of LP containing 1 % Sn, 0.5 % In and 0.13 % Bi nanoparticles at an applied load of 300 N for 30 min. Reproduced by permission of Elsevier from Zhao *et al*. [18], © (2004) Elsevier

that the friction coefficient is sensitive to the addition concentration of these metal nanoparticles. At the concentration range of 0.25 to 1.00 % for the Sn nanoparticle, 0.06 to 0.25 % for the In nanoparticle and 0.04 to 1.00 % for the Bi nanoparticle, respectively, a low friction coefficient can be achieved.

SEM analysis is used to observe the worn surface of the steel ball after the friction test under the lubrication of LP with the as-prepared metal nanoparticles; these results are presented in Figure 5.8 [18, 19]. It can be observed that all wear scar surfaces are relatively smooth and the rubbed traces are shallow. The results imply that these metal nanoparticles can melt and form instantaneous metallic films between rubbing surfaces, which prevents direct contact of the rubbing surfaces, and they exhibit good lubricating properties.

5.3.2 Nanolubricants of Lead and Bismuth via the Surfactant-Assisted Solution-Dispersing Method

The direct solution-dispersing method has been found to be a simple route for the preparation of the low melting point metal nanoparticles such as tin, bismuth and indium, which is based on the low melting point properties to enable the formation and emulsification of liquid metal drops in hot oils and the simultaneous formation of an oxide layer on the outside of the liquid metal drops acting as the stabilizer. However, the spontaneous and simultaneous formation of the oxidation of the metals is somewhat uncontrollable, especially for conditions of longer preparation time or higher synthetic temperature that are required for metals with a relatively high melting point, which will lead to overoxidizing of the products. In order to resolve the problem, an improved method based on the *in situ* formation of a surfactant layer chemisorbed on the surface of metal drops has been proposed by Zhao and coworkers [19, 20]. In this method, larger metal droplets are dispersed to small droplets in solvent containing judiciously selected surfactants such as stearic acid (SA) or polyethylene glycol (PEG) by a stirring force. The fresh surfaces of the generated little metal droplets react with SA or PEG molecules simultaneously to form a closed-packed organic protective layer.

Figure 5.9 shows the TEM images and XRD patterns of Bi nanoparticles stabilized by SA (Bi-SA), Pb nanoparticles stabilized by SA (Pb-SA) and Pb nanoparticles stabilized by PEG (Pb-PEG) prepared by the surfactant-assisted solution-dispersing method [19, 20]. It can be

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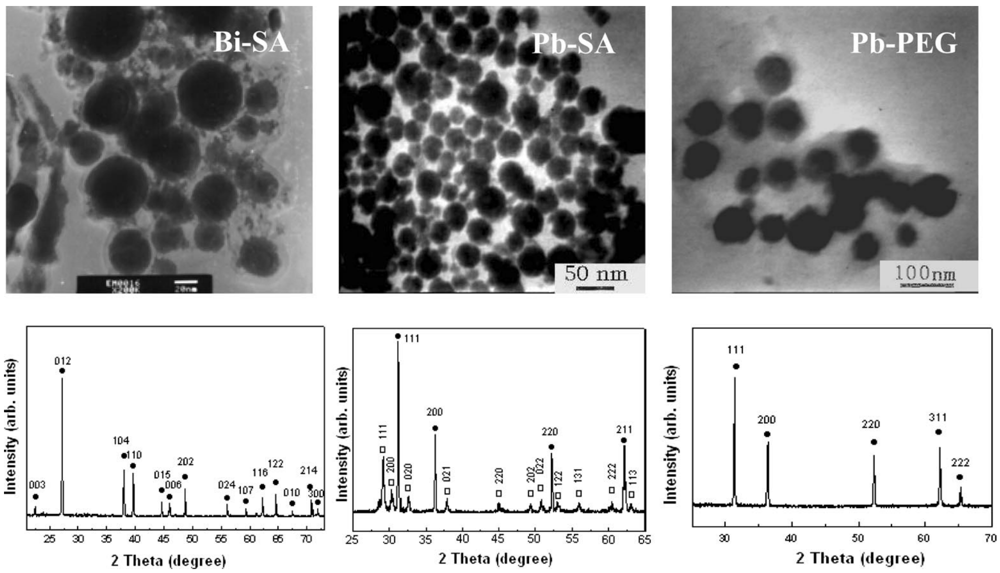


Figure 5.9 TEM images and XRD patterns of Bi nanoparticles stabilized by SA and Pb nanoparticles stabilized by SA and by PEG. With kind permission from Springer Science and Business Media from Zhao *et al*. [20], © (2004) Springer Science and Business Media

observed that the Bi-SA nanoparticles exhibit an irregular shape and a broad size distribution with an average particle diameter of 60 nm. The diffraction peaks in the corresponding XRD pattern can all be assigned to the cubic phase of metal Bi, and no diffraction peaks of the oxide can be found. The result shows that stearic acid can restrain well the bismuth from being oxidized in the formation process of the nanoparticles.

The as-prepared Pb-SA nanoparticles appear to be spherical in shape with an average particle diameter of 70 nm, and have a wide size distribution. In their corresponding XRD pattern, the prominent peaks at scattering angles (2θ) of 31.40, 36.42, 52.45 and 62.42 can be assigned to the scattering from the 111, 200, 220 and 311 crystal planes of cubic phase Pb, but there are some broad and weak peaks that match the crystal planes of PbO well. The Pb-PEG nanoparticles have a spherical shape with an average diameter of 40 nm, and also exhibit a wide size distribution. Their corresponding XRD pattern exhibits five narrow diffraction peaks, which can all be indexed to the cubic phase of metallic Pb, indicating the good crystallinity of lead nanoparticles. The result shows that PEG is better than SA in the prevention of lead oxide formation during the preparation process of lead nanoparticles in the surfactant-assisted solution-dispersing method.

The tribological behaviours of the as-prepared nanoparticles used as oil additives were studied via a series of four-ball friction and wear tests. Figure 5.10 shows the variation of WSD with the additive concentration of Bi-SA, Pb-SA and Pb-PEG nanoparticles in LP. In Figure 5.10(a) [19], it can be observed that the WSD of LP has reduced from 0.72 to 0.53 mm after adding Bi-SA nanoparticles at a very low additive concentration of 0.02 %, which suggests that the addition of Bi-SA nanoparticles can improve the AW properties of base oil. As the additive concentration is increased, the value of the WSD increases very slowly,

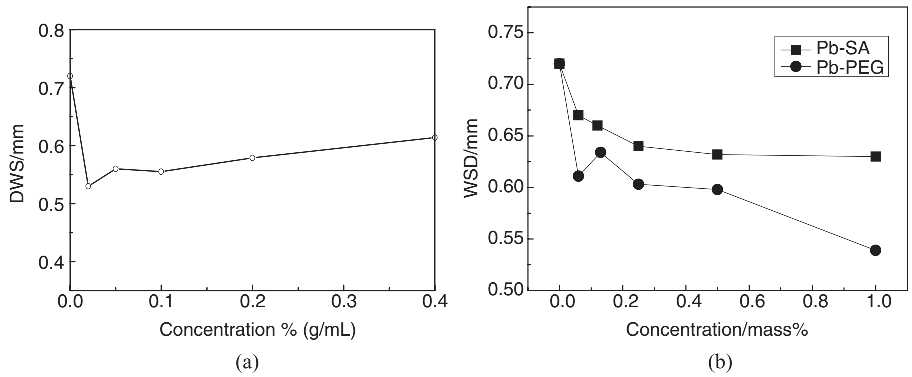


Figure 5.10 WSD as a function of the additive concentration of (a) Bi-SA, (b) Pb-SA and Pb-PEG nanoparticles prepared in LP under 300 N. With kind permission from Springer Science and Business Media from Zhao *et al*. [20], (c) (2004) Springer Science and Business Media

indicating that Bi-SA nanoparticles dispersed in base oils can have AW performance in a relatively broad additive concentration range.

Lead is a kind of conventional lubricant, so the application of Pb nanoparticles as lubricating additives is potentially interesting. It can be seen from Figure 5.10(b) [20] that the WSD values of LP containing Pb-SA and Pb-PEG nanoparticles are much lower than those of base oil in a broad concentration range (0.06 to 1.0 %), especially for Pb-PEG nanoparticles. They can improve the AW property of LP efficiently, even at a very low concentration, and it is evident that their AW performance can be improved by increasing the additive concentration, indicating that lead nanoparticles are good lubricating additives.

The relationship between the WSD of LP and LP plus Bi-SA, Pb-SA and Pb-PEG nanoparticles as a function of the applied load is shown in Figure 5.11 [19]. It can be seen that these

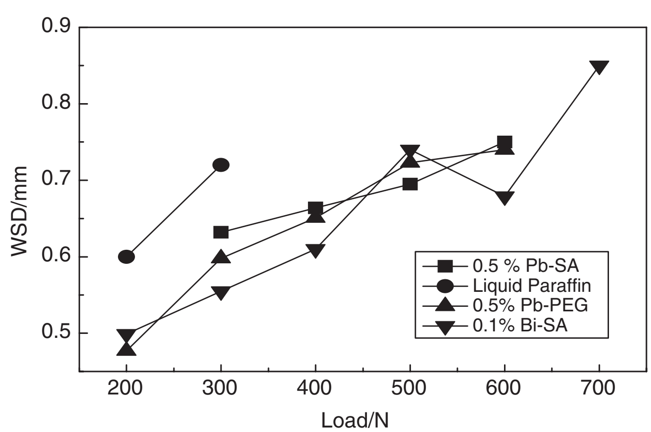
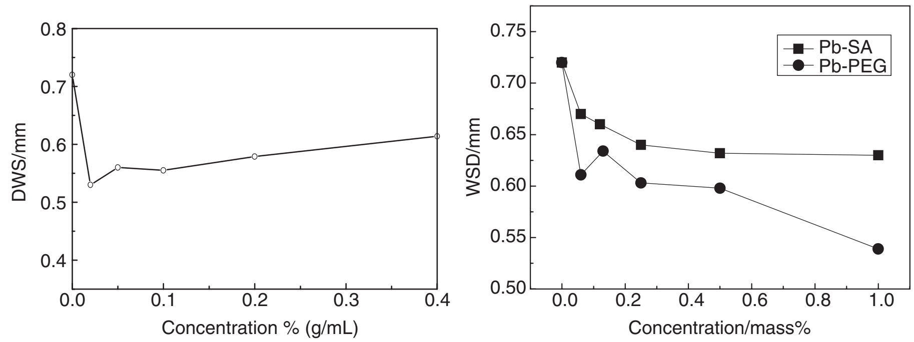


Figure 5.11 Relationship between the WSD and applied load with lubrication of LP and LP containing Bi-SA, Pb-SA and Pb-PEG nanoparticles at certain concentrations



(a) (b)

Figure 5.12 Friction coefficient as a function of the additive concentration of Bi-SA and Pb-PEG nanoparticles in LP under 300 N

metal nanoparticles prepared by the surfactant-assisted solution-dispersing method have excellent antiwear properties under different loads. At the load of 300 N, the WSD values of LP containing 0.1 % Bi-SA, 0.5 % Pb-SA and 0.5 % Pb-PEG nanoparticles are 0.56, 0.63 and 0.60 mm, respectively, which are smaller than those of pure LP. In the friction tests, seizure of the tribo-pairs appeared when the applied normal load is above 400 N for LP, but is as high as 600 N for LP containing Pb-SA and Pb-PEG nanoparticles and 700 N for Bi-SA nanoparticles, indicating that the load-carrying capacity of LP can be greatly improved by the addition of as-prepared metallic nanoparticles. At a load of 600 N, the WSD values of LP containing 0.1 % Bi-SA, 0.5 % Pb-SA and 0.5 % Pb-PEG nanoparticles are only 0.68, 0.75 and 0.74 mm, respectively, illustrating that these metal nanoparticles have excellent antiwear properties at high load.

The variations of the friction coefficient with the additive concentration of Bi-SA and Pb-PEG nanoparticles in LP are given in Figure 5.12 [19]. The friction coefficient is very sensitive to the addition concentration of the Bi-SA nanoparticles. To achieve the best friction-reduction property, a proper additive concentration of the Bi-SA nanoparticles is needed, which is in the range of 0.02 to 1.00 % under selected testing conditions. Comparably, the friction coefficient of LP can obviously be decreased by adding Pb-PEG nanoparticles over a wide concentration range, which suggests that the Pb-PEG nanoparticles could be used as a friction-reducing additive (friction modifier). When the concentration of Pb-PEG nanoparticles is about 0.5 %, the best friction-reducing property is obtained.

SEM analysis is also conducted to observe the worn surface of the steel ball after the friction test under the lubrication of LP with the as-prepared nanoparticles; the results are presented in Figure 5.13 [19, 20]. It can be observed that the wear scar surfaces are all relatively smooth and the rubbing traces are shallow, which is in good accordance with their better AW property.

In conclusion, nanoparticles of low melting point metals, including indium, bismuth, tin and lead, can be easily prepared via the solution-dispersing method. The simultaneously formed oxide layer or the *in situ* generated surfactant layer is retained to prevent the reconjunction of little metal drops during the preparation process and improved the dispersibility of the

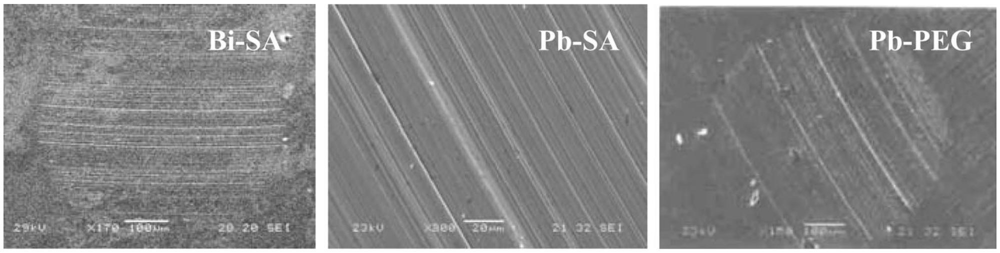


Figure 5.13 The morphologies of the worn surfaces under lubrication of LP containing 0.1 % Bi-SA, 0.5 % Pb-SA and 0.5 % Pb-PEG nanoparticles at an applied load of 300 N and friction duration of 30 min. With kind permission from Springer Science and Business Media from Zhao *et al*. [20], © (2004) Springer Science and Business Media

resulting metal nanoparticles. A series of pilot studies on the tribological properties of these nanoparticles used as oil additives has proved their potential value as novel lubricants.

5.4 Nanolubricants Made of Low Melting Point Metal Alloy Nanoparticles

When two or more kinds of metals are melted together to form a metal alloy, the physical, electronic, mechanical and chemical properties will change considerably. Therefore, nanoparticles of metal alloys are expected to have more fascinating properties in electronics, catalysis and magnetism [21, 22] compared to nanoparticles of single metals. As a result, metal alloy nanoparticles have been the focus of intensive research in recent years [23–25].

In practice, low melting point metals are often used to prepare lubricating coatings in the form of metals alloys to achieve the most optimizing properties, and nanoparticles of alloyed metals are anticipated to have tunable excellent tribological properties as the composition of the alloys is varied. Until today, nanoparticles of In-Sn, Bi-In, Pb-Bi, Sn-Bi and Sn-Cd alloys that can be dispersed in oils have been synthesized and their tribological properties have been studied.

5.4.1 In-Sn, Bi-In and Pb-Bi Nanoparticles Prepared by the Direct Solution-Dispersing Method

Zhao and his coworkers [19, 26–28] have extended the direct solution-dispersing method to the synthesis of low melting point metallic alloy nanoparticles. Figure 5.14 shows the TEM images and their corresponding XRD patterns of the resulting In-Sn, Bi-In and Pb-Bi alloy nanoparticles [26–28]. From TEM images, it can be seen that both In-Sn and Pb-Bi alloy nanoparticles prepared by this method appear to have a spherical shape and have an average particle diameter of 60 and 50 nm, respectively. However, Bi-In alloy nanoparticles prepared by the same method have an evident dendritic morphology, with an average diameter of 5 nm and an elongated shape.

The XRD pattern of bulk In-Sn alloy displays nine strong peaks [27], which are assigned to the reflections for crystalline In_3Sn and $InSn_4$, respectively. Comparably, the XRD pattern of In-Sn alloy nanoparticles contains clearly distinguishable multiple peaks, which can be

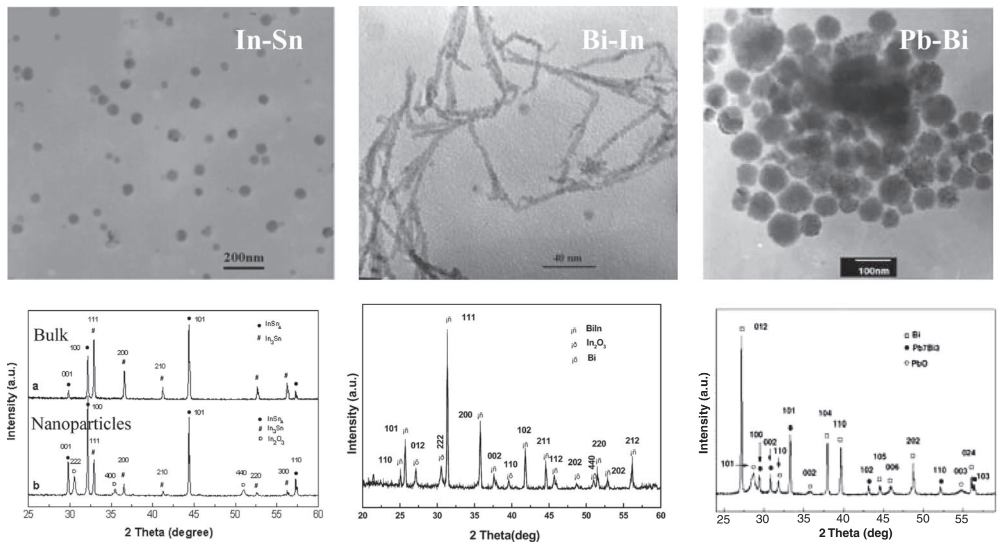


Figure 5.14 TEM images and their corresponding XRD patterns of In-Sn, Bi-In and Pb-Bi alloy nanoparticles. Reproduced by permission of The Royal Society of Chemistry and reprinted with permission from Zhao *et al*. [26], © (2004) American Chemical Society and from Zhao *et al*. [28], © (2006) Elsevier

indexed to crystalline *b*-In_3Sn, $InSn_4$ and In_2O_3. It is clear that In-Sn alloy nanoparticles have the same crystal structure as that of the bulk In-Sn alloy. The XRD pattern of Bi-In dendritic nanocrystals also contains multiple peaks [26], some of which correspond to the tetragonal phase of Bi-In alloy. There also appear weak additional peaks indexed to crystalline Bi and In_2O_3, respectively. The XRD pattern of Pb-Bi alloy nanoparticles displays multiple strong peaks [28] that can be easily assigned to the reflections for crystalline Pb_7Bi_3, Bi and PbO, respectively. This reveals the presence of the equilibrium phase Pb_7Bi_3 and Bi in the nanoparticles. The analysis of these XRD patterns reveals that the resulting products are all mixtures, and one component is one of two corresponding metal oxides; i.e. the oxidization must happen in the preparation process of metal alloy nanoparticles.

Figure 5.15 gives the relationship between the concentration of three kinds of bimetal alloy nanoparticles in base oil and their corresponding WSD values [19, 27]. For comparison, the results of monometallic nanoparticles as additives in oil are also provided. It can be seen that these bimetal alloy nanoparticles are all good lubricating additives, which can improve the AW property of the base oil over a wide concentration range. It is evident that, in the tested concentration range, the AW performance of In-Sn and Bi-In nanoparticles is much better than that of their corresponding monometallic nanoparticles, which might be attributed to their nano-alloy structures. However, this phenomenon is not obvious for Pb-Bi alloy nanoparticles.

Figure 5.16 shows the variations of WSD values with the lubrication of LP containing the as-prepared bimetal alloy nanoparticles under different applied loads [19, 27, 28]. The results of zinc dialkyl dithiophosphate (ZDDP, a commonly used commercial lubricating additive), Sn and In nanoparticles are also presented for comparison in Figure 5.16(a). It is clear that the In-Sn alloy nanoparticles displayed an excellent AW property under the applied load range

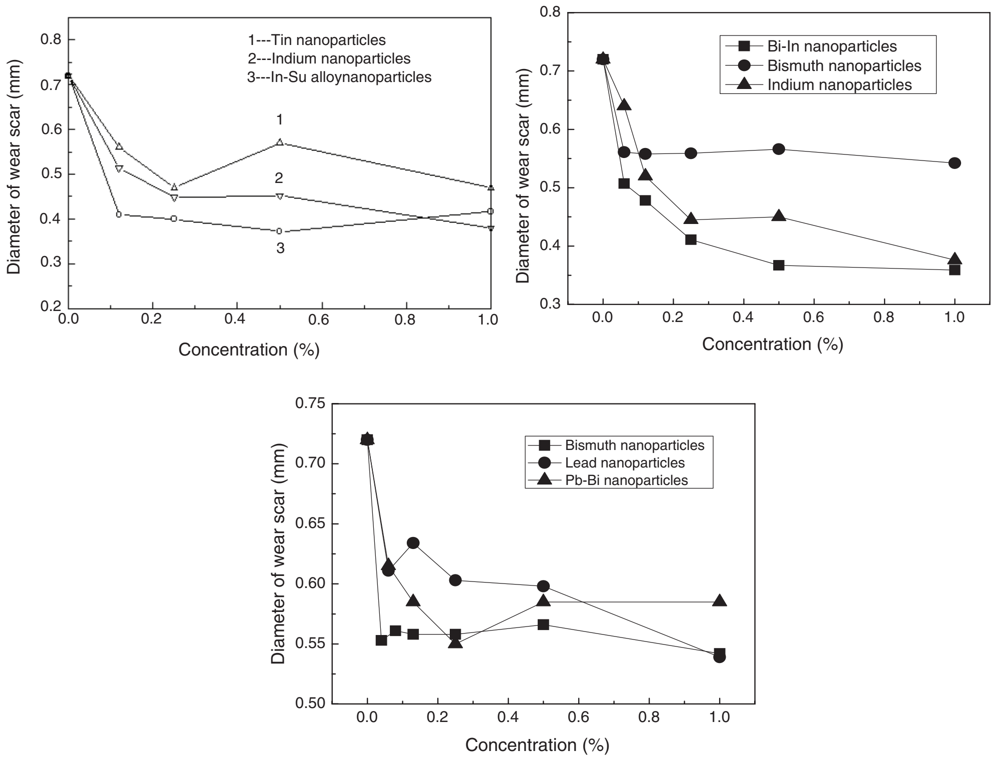


Figure 5.15 WSD as a function of the additive concentration of bimetal alloy nanoparticles and their corresponding monometallic nanoparticles in LP under 300 N. Reproduced by permission of The Royal Society of Chemistry and reprinted with permission from Zhao *et al*. [27] and Zhao [19]

of 300 to 500 N, in which a relatively lower WSD was observed as compared to those of LP containing 4 % ZDDP, 0.5 % indium nanoparticles and 1 % tin nanoparticles. When the applied load was increased to 600 N, the AW ability of In-Sn alloy nanoparticles was adjacent to ZDDP. A similar result can be observed for Bi-In and Pb-Bi alloy nanoparticles.

Figure 5.17 [19, 27, 28] gives the morphologies of the worn surfaces with lubrication of LP containing 0.5 % In-Sn, 0.5 % Bi-In and 0.25 % Pb-Bi alloy nanoparticles, which shows that the worn surfaces are all relatively smooth and the rubbing traces are shallow.

5.4.2 Sn-Bi and Sn-Cd Alloy Nanoparticles Prepared by the Ultrasonic-Assistant Solution-Dispersing Method

When liquids are irradiated with high-intensity ultrasound, the acoustic cavitations can lead to a collapse of bubbles, producing intense local heating (5000°C) and high pressures (1000 atm) in a very short lifetime (heating and cooling rates above 1010 K/s). The transient, localized hot spots can generate high-energy physical or chemical transitions and can be utilized to induce and accelerate reactions [29–33]. A variety of nano-sized metal and alloy particles have been prepared using the sonochemical method in the last few years [34–36].

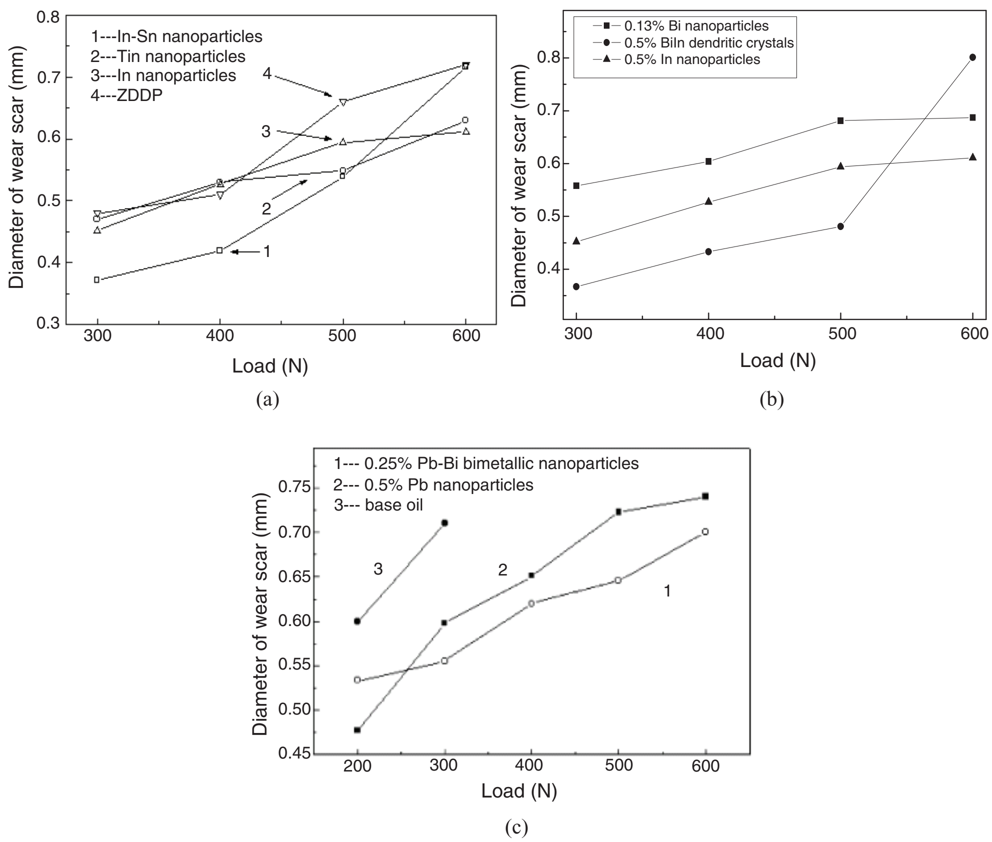


Figure 5.16 Relationships between the WSD value and applied load with lubrication LP containing 0.5 % In-Sn, 0.5 % Bi-In and 0.2 5% Pb-Bi alloy nanoparticles. Reproduced by permission of The Royal Society of Chemistry and reprinted with permission from Zhao *et al*. [28], © (2006) Elsevier

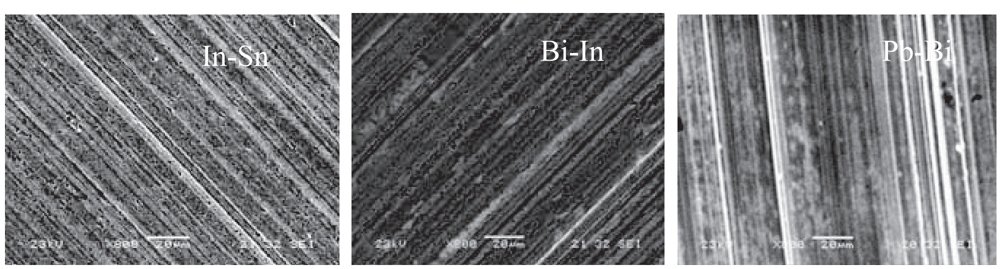


Figure 5.17 The morphologies of the worn surfaces with lubrication of LP containing 0.5 % In-Sn, 0.5 % Bi-In and 0.25 % Pb-Bi alloy nanoparticles with an applied load of 300 N for 30 min. Reproduced by permission of The Royal Society of Chemistry and reprinted with permission from Zhao *et al*. [28], © (2006) Elsevier

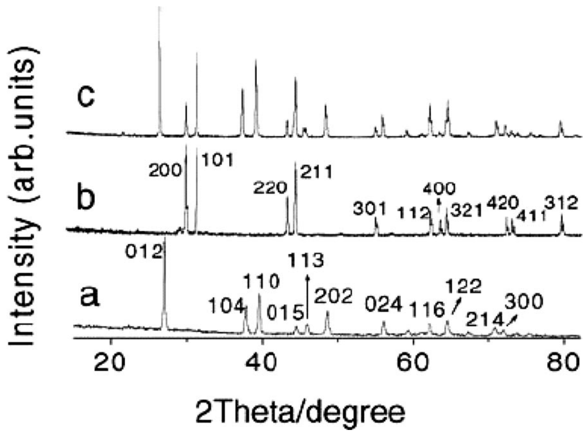


Figure 5.18 XRD pattern of (a) bismuth, (b) tin and (c) the as-produced Sn-Bi nanoparticles. Reproduced by permission of Elsevier from Chen *et al*. [37], © (2005) Elsevier

Chen and his coworkers [37, 38] reported a new sonochemical method used to prepare low melting point metal alloy nanoparticles for use as oil additives. In this method, bulk alloys of low melting point metals were put in oils and then directly dispersed into the oils by ultrasonification at room temperature. The XRD patterns of Sn-Bi and Sn-Cd nano-alloy materials prepared by this method are shown in Figures 5.18 [37] and 5.19 [38]. It can be clearly seen that the all of the prominent peaks of these Sn-Bi alloy nanoparticles in Figure 5.18 could be assigned to those of the metals bismuth or tin. Only one sharp and narrow endothermic peak at 140.8°C was found in its corresponding DTA curve, revealing that the powder consisted of Sn-Bi eutectic alloy nanoparticles and not simply of a mixture of tin and bismuth nanoparticles. Therefore the resulting Sn-Bi nanoparticles were the eutectic alloy consisting of the tetragonal phase of tin and the rhombohedral phase of bismuth. In addition, no other peaks attributed to metal oxides were found in pattern (c) of Figure 5.19, which indicated that no oxidation reactions took place in the process. A similar result was found in the XRD pattern of Sn-Bi nanoparticles.

Figure 5.20 shows the TEM images of as-prepared Sn-Bi and Sn-Cd nanoparticles [37, 38]. It is clear that these nanoparticles are well separated, mostly hexagonal and spherical, and the average particle diameter is in the range of 10 to 25 nm. A proposed growing mechanism of these bimetal alloy nanoparticles includes the following three steps. First, the bulk bimetal alloy melts in LP, which is mainly induced by the energy of collapse of the cavitations of bubbles. Second, the melted bimetal alloy is dispersed into unequal ultrafine liquid particles in the solvent by the results of sonication. Finally, the unequal particles are homogenized to become nano-sized particles by collision and cutting resulting from the process of ultrasonic irradiation. According to this mechanism, it can be assumed that ultrasonic power will have a significant impact on the size distribution of the bimetal alloy nanoparticles and that smaller alloy particles could be generated with increasing ultrasonic power. This has been proved by the experimental results shown in Table 5.6. These researchers also pointed out that the sonication time had little impact on the size of the nanoparticles.

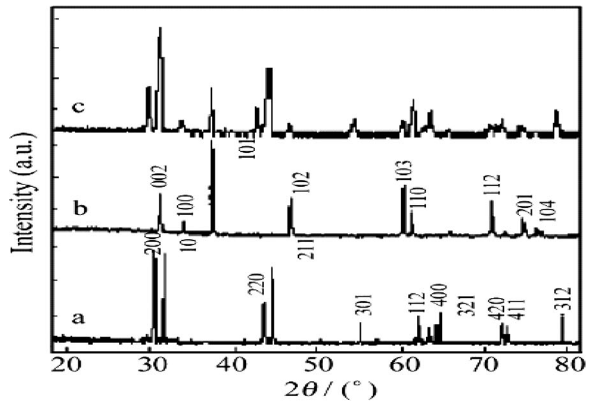


Figure 5.19 XRD pattern of (a) tin, (b) cadmium and (c) the as-produced Sn-Cd nanoparticles. Reproduced by permission of Elsevier and Editorial Office of Chemical Research from Chen *et al*. [38], © (2005) Elsevier and Editorial Office of Chemical Research

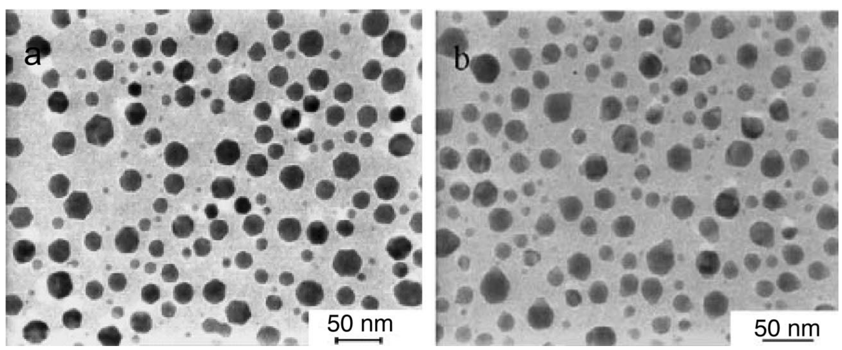


Figure 5.20 TEM images of (a) Sn-Bi and (b) Sn-Cd nanoparticles prepared at 1000 W/cm^2. Reproduced by permission of Elsevier from Chen *et al*. [37[, © (2005) Elsevier and of Elsevier and Editorial Office of Chemical Research from Chen *et al*. [38], © (2005) Elsevier and Editorial Office of Chemical Research

Table 5.6 The size distribution of Sn-Bi nanoparticles obtained at different ultrasonic power. Reproduced by permission of Elsevier from Chen *et al*. [37], © (2005) Elsevier

Ultrasonic power (W/cm^2)	Size range (nm)
700	60–80
800	45–60
900	25–40
1000	10–25

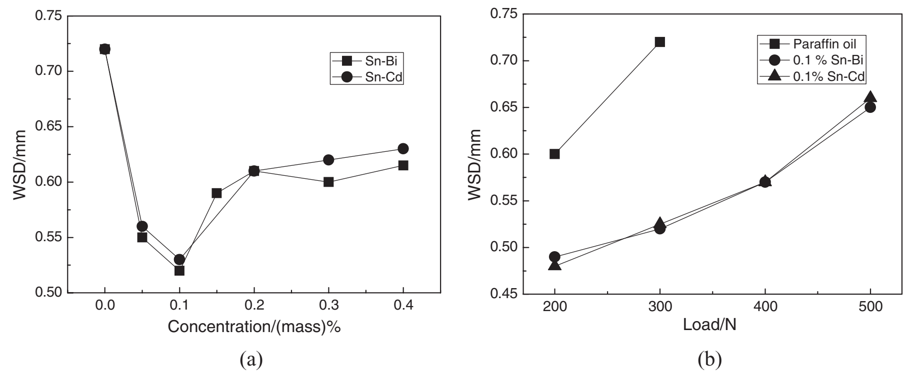


Figure 5.21 (a) Relationship of the WSD with the additive concentration of Sn-Bi and Sn-Cd nanoparticles under 300 N and (b) the WSD as a function of applied load with the lubrication of LP and LP containing 0.1 % Sn-Bi and 0.1% Sn-Cd nanoparticles. Reproduced by permission of Elsevier from Chen *et al* .[37], (c) (2005) Elsevier and of Elsevier and Editorial Office of Chemical Research from Chen *et al*. [38], (c) (2005) Elsevier and Editorial Office of Chemical Research

Nanoparticles of Sn-Bi and Sn-Cd alloys prepared by the ultrasonic-assistant solution-dispersing method are reported to have good oil solubility and can be used directly as lubricating oil additives. The tribological properties of Sn-Bi and Sn-Cd alloy nanoparticles tested in a four-ball tester are shown in Figure 5.21. The variation of WSD with the different concentrations of alloy nanoparticles in LP under 300 N is shown in Figure 5.21(a). Apparently the LP containing alloy nanoparticles gives a smaller WSD in a wide concentration range compared with the base oil, indicating that these bimetal alloy nanoparticles can improve the AW property of LP. At the concentration of 0.1%, both Sn-Bi and Sn-Cd nanolubricants present the best AW property. Figure 5.21(b) shows the variation of the WSD of LP containing 0.1 % alloy nanoparticles at different loads. It can be seen that both kinds of nanolubricants show a better AW property in the load range of 200 to 500 N than pure LP. These tribological data illustrate that these alloy nanoparticles can be used as lubricating oil additives with good tribological properties.

5.5 Mechanism of Metal Nanoparticles Used as Oil Additives

The research and application of nanoparticles as additives in lubricant oils have been ongoing for twenty years. However, the exact or real action mechanism of nanoparticulate oil additives is still unclear. Two hypotheses seem reasonable:

(a) ‘Microrolling bearing’ between tribo-pairs. This hypothesis [39] contends that when nanoparticles are dispersed equably in lubricant oils, each individual particle between the rubbing tribo-pairs can avoid the direct contact of rubbing surfaces and change the sliding friction of tribo-pairs into rolling friction, thus exhibiting excellent AW and EP performance. This process comes into existence when the normal load between the tribo-pairs is very low and the nanoparticles must be dispersed uniformly and keep their rigidity under local high temperature and high pressure in the microcontact zones [42].

(b) Boundary film formation by *in situ* deposition of metal nanoparticles. This hypothesis [13, 41–43] contends that nanoparticles dispersed in lubricant oils can form a layer of depositing film that can decrease the shear strength of tribo-pairs, offset the microdamage and scratch the friction surface. This process can make the surface slick and even, thus favouring stress release, friction reduction, prevention of wear and even the self-repairing of a worn surface. The situation may be more suitable for soft metal nanoparticles such as copper, silver, lead, tin and bismuth.

Li *et al*. [6] have discussed the mechanism of DDP-capped copper and silver nanoparticles as oil additives. In their studies, the traditional electrical contact resistance (ECR) measuring technique, which has been applied to various studies of the contact of tribo-pairs in mixed lubrication or in boundary lubrication, has been used to investigate the *in situ* formation of the boundary film of metal nanoparticles. It is easy to understand that the ECR value between metallic tribo-pairs is very high under hydrodynamic lubrication, but very low (<0.1 ohm) when metallic contact occurs. Of course, the ECR value is larger than several thousands of ohms when a nonmetallic layer exists on top of specimens. For boundary lubrication of a metallic interface with AW/EP additives such as ZDDP blended in lubricating oils, antiwear efficiency relies on the reaction film formation, which acts also as an insulating barrier for electrical current. The ECR can therefore be used to monitor the formation process of the reaction film.

Figure 5.22(a) shows the ECR curve between tribo-pairs lubricated with a drop of pure LP. It is seen that the ECR value fluctuated acutely in the range from several to tens of kilo-ohms. The AW/EP mechanism at this stage may be the 'wearing off the natural oxide layer, reoxidizing the surface, wearing off the oxide layer' process, according to the general cognition of boundary lubrication. If a droplet of LP with ZDDP is added, an obvious increase in the ECR could be observed, indicating the generation of a tribo-film to some extent. A similar phenomenon appears when a droplet of LP containing copper nanoparticles is added. With the addition of ZDDP, the ECR value immediately increased from 20 to 30–50 kilo-ohms and became unstable. With the addition of copper nanoparticles, the ECR value immediately increased from 20 to 50–70 kilo-ohms respectively, and then became steady, indicating a thicker and firmer tribo-film was formed in the process of friction compared to that of ZDDP. This is in accordance with the good AW/EP properties of LP containing copper nanoparticles. In the case of silver nanoparticles, the ECR value tended to decrease at an early stage. The reason might be that silver nanoparticles are more inert than other metal nanoparticles, and can form a metallic silver tribo-film, which has good electrical conductivity.

The formation of tribo-films is further proved by surface analysis on the wear scar by means of SEM, EDS and XPS. It has been shown that the SEM images of the wear scar of steel balls, lubricated by LP with nanoparticulate additives, show a much smoother wear surface. The typical EDS and XPS analysis results usually indicate that the metallic elements in the nanoparticles were deposited and enriched on the worn surface. Figure 5.23 [6] gives the typical element distribution on a worn steel surface lubricated by oils containing copper nanoparticles.

Based on the above results, the researchers deduced that when metal nanoparticles are added into lubricant oils, a homogeneous and stable colloid solution is formed. When the lubricant film between tribo-pairs become thinner, mixed lubrication or boundary lubrication occurs, and the nanoparticles perhaps carry a proportion of the load and separate the two

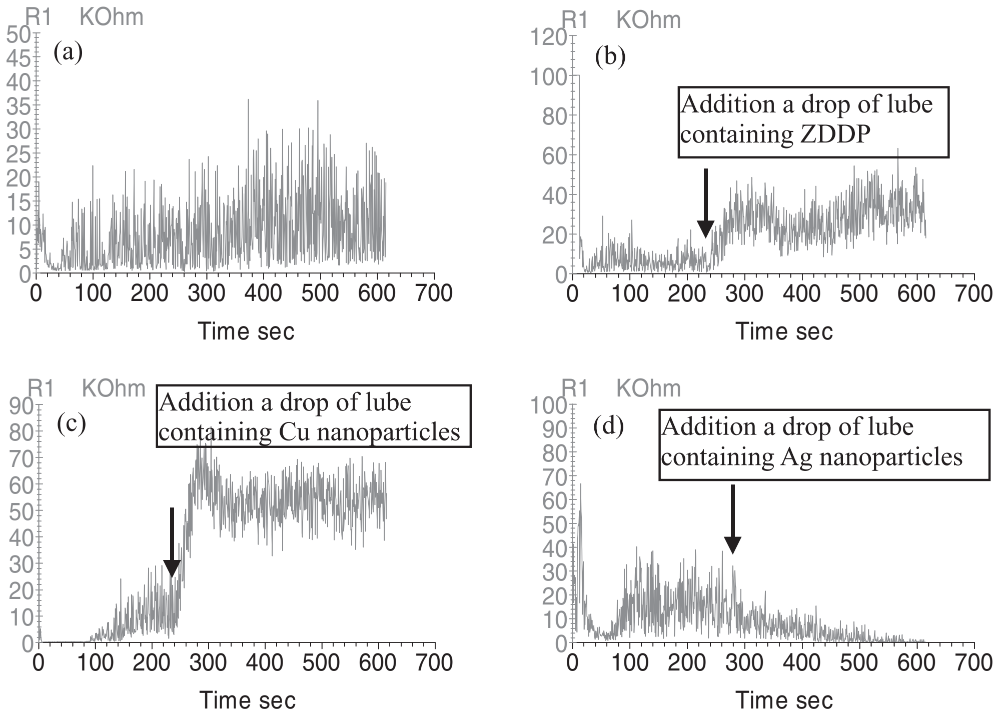


Figure 5.22 Variations of electrical contact resistance between tribo-pairs versus friction time (a) lubricated by pure LP, (b) lubricated by pure LP during the first 250 seconds, then adding a drop of LP containing 5 % zinc dialkyl dithiophosphate (ZDDP), (c) Cu nanoparticles and (d) Ag nanoparticles. Test condition: a steel ball reciprocally rubbing against a steel plate at a frequency of 15 Hz and a normal load of 5 N at 25°C with the lubrication of a drop of oil. With kind permission from Springer Science and Business Media from Li *et al*. [6], (c) (2006) Springer Science and Business Media

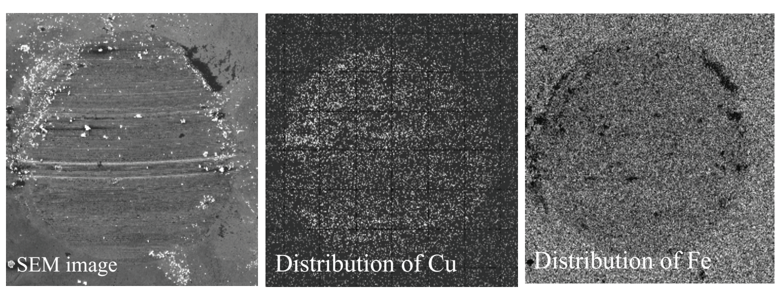


Figure 5.23 SEM micrographs and typical element distributions on a worn steel surface lubricated by 1 % wt Cu nanoparticles in liquid paraffin (four-ball, 1450 r/min, 392 N, 30 min). With kind permission from Springer Science and Business Media from Li *et al*. [6], © (2006) Springer Science and Business Media

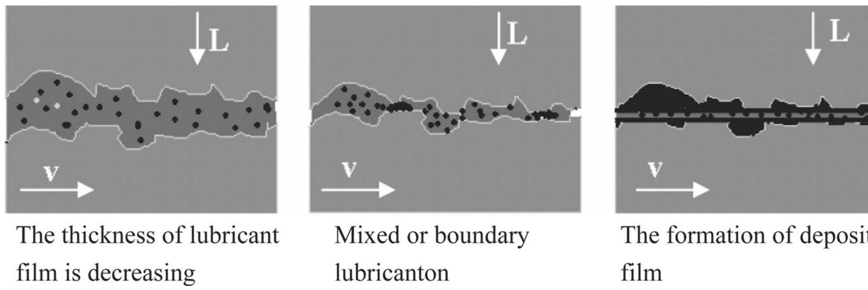
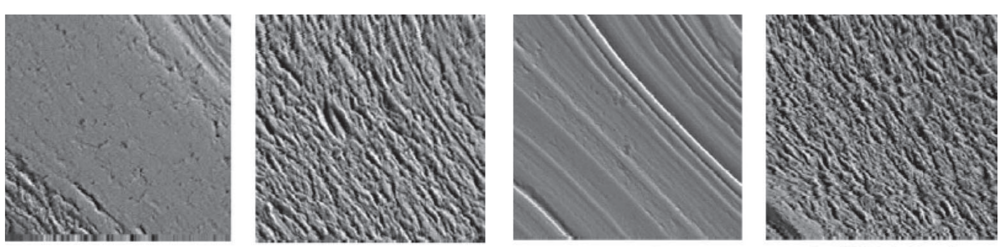


Figure 5.24 Schematic representation of the mechanism of nanoparticles as a lubricant additive. With kind permission from Springer Science and Business Media from Li *et al*. [6], © (2006) Springer Science and Business Media

surfaces to prevent adhesion, benefiting the improvement of the antiwear property. When the shearing is strong, the core/shell structure of nanoparticles may be destroyed, the surface capping layer desorbed and decomposed, the inorganic core melted and welded on to the shearing surface, or the structure may react with the specimen to form a protective layer providing good AW and EP properties. This process is illustrated in Figure 5.24 [6].

Tarasov and his coworkers [13] have also studied and discussed the action mechanism of copper nanoparticles produced by the electric explosion of metallic wire (EEW) process used as an additive in SAE 30 motor oil. In the topology analysis of the corresponding worn surfaces shown in Figure 5.25, it was found that the worn surfaces looked very smooth under high-speed and low-load ($P = 110$ N, $v = 2.62$ m/s) tests conditions, and a rippled pattern was a characteristic of the worn surface obtained at a high load of 184 N irrespective of the sliding speed value. Optical microscopy showed copper agglomerates trapped on the worn surfaces. The microstructure of the copper agglomerates indicated by TEM images shows them to be heavily deformed.

It is pointed out that the addition of copper nanoparticles into lubricating oils can replace or at least cover the real wear particles with those of a more ductile metal, which would provide better lubrication as compared, for example, with steel wear particles. The softer metal would also probably decrease adhesion between the frictional surfaces, which is dependent on the particular metal used as the wear surface. It is also realized that the copper nanoparticles added



(a) 110 N; 1.56 m/s (b) 184 N, 1.56 m/s (c) 110 N, 2.62 m/s (d) 184 N, 2.62 m/s

Figure 5.25 SEM images of worn surfaces after friction tests with copper nanopowder additive (×1500). Reproduced by permission of Elsevier from Tarasov *et al*. [13], © (2004) Elsevier in oils are trapped on the worn surfaces in the form of agglomerates, and have a deformation incompatibility between the nanocrystalline subsurface layer and the underlying base metal during the friction process. The layer behaves like a highly viscous fluid and friction-induced stresses effectively damp inside it. It is reasonable to suppose that the higher the temperature (sliding speed) of the subsurface layer, the more likely it is that such a layer will behave like a fluid and provide lower friction together with a smoother wear surface. This is what might have happened to specimens during a test conducted at a high speed of 2.62 m/s and 110 N, where a smooth wear path was formed. At a higher load of 184 N, plastic deformations were more severe, creating a rippled surface. Based on these discussions, the mechanism of copper nanoparticles from the EEW method can be summarized as: 'local overheating due to direct contact of two surfaces initiates chemical deposition of copper on steel, providing a soft surface limited to the locality of the friction pair to reduce friction and wear'.

It is anticipated that the nanoparticles of low melting point metals and their alloys have a similar mechanism. However, the reported results of EDS analysis on a worn surface reveal that no corresponding metallic elements of nanoparticles were in the rubbing surface [18, 19, 27, 28]. The reason might be that these metallic elements in nanoparticles have less of a tendency to attach on to the friction surface. However, it is reasonable to assume that the low melting point metal and alloy nanolubricants might be melted to form an instantaneous liquid metal film to prevent the direct contact of rubbing surfaces under boundary lubrication conditions, thus generating AW, friction-reducing and EP properties.

For the traditional organic compound AW/EP additives, the tribo-film formation is carried out through the reaction of 'active' elements with the surfaces of the metallic tribo-pair. In other words, the phenomenon of 'corrosive wear' will exist as long as these additives begin to operate on the prevention of severe wear. Thus, under boundary lubrication or mixed lubrication using organic compound additives, the mass loss of trio-pairs owing to 'corrosive wear' will be inevitable. However, the improvement of the friction-reducing and AW properties of the frictional system are mainly induced by the preferential depositing of metal nanoparticles and the *in situ* generation of metallic tribo-film when metal nanoparticles are used as additives. The depositing film is made up of metallic nanoparticles; i.e. the tribo-film formation need not consume the materials of tribo-pairs.

5.6 Perspective

Nowadays, there are much more increasing demands for the development of novel oil additives, mainly due to three factors. The first is the increased complexity, higher speeds and loads, and higher working temperatures that occur in modern machinery. The second is the increasing attention paid to environmental concerns. The third is the increasing use of more highly refined mineral oils and synthetic hydrocarbons for the lubrication of extreme conditions (high/low temperature, erosive circumstance, high vacuum), which usually have very little, or no, inherent antiwear performance.

Traditional organic sulfur and phosphorus compounds, such as zinc dialkyl (or diaryl) dithiophosphate (ZDDP), tricresyl phosphate (TCP) and sulfurised isobutylene (SIB), have been proved to have good AW and EP properties and achieved wide application. However, these AW/EP additives are chemically more or less reactive, and have lower resistance to heat and oxidation than most modern base oils, and cannot be used to formulate oils for high-temperature applications. The more powerful EP additives usually have some corrosive effect in contact with metals and are only used when necessary. In addition, 'active' elements such as sulfur, phosphorus or chlorine in their molecular form are hazardous to human health and plant growth. Large searches for substitutes for these organic compounds as AW/EP additives have been carried out over the past decades, yet no satisfactory results have been achieved until now.

With the rapid development of nanotechnology, nanolubricants made of metals have been proposed and studied. The reported experimental results have proved that metal nanoparticles can improved the friction-reducing, AW and EP properties when added in oils. Compared with traditional organic compound additives, they generate lubricating properties by means of providing *in situ* deposition of a microlubricating film limited to the locality of the friction pair without corrosive effect, and can be used at higher temperatures owing to their inherent character. They have the potential to become the new generation of AW/EP additives.

However, the investigations concerning nanolubricants made of metal have been inadequate until recently. The reported experimental results are very primative to some extent and some technique problems have not been solved: (a) the long-term stability of metal nanoparticles and oils containing metal nanoparticles has not been solved very well; (b) the influence of metal nanoparticles on the base oil has not been revealed; (c) interactions between metal nanoparticles and other additive integrants for formulated oils have not been fully studied. In-depth research of these technical obstacles would stimulate the application of the novel nanolubricants. Additionally, economic pressure is likely to be considered before the best additives available today are replaced by nanomaterials.

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