Preparation and tribological properties of Bi nanoparticles as a lithium grease additive

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To improve the wear resistance of the machine parts, strengthened brush plating coatings were prepared by deposition of Bi nanoparticles. The excellent Bi nanoparticles self-repairing additives were prepared via the DC arc plasma evaporation method. The tribological properties of lithium lubricating greases containing Bi nanoparticles were investigated with a four-ball machine, and the morphology, self-repairing mechanism and the elemental composition of worn steel surfaces were analyzed by the scanning electron microscope (SEM) and the energy disperse spectroscopy (EDS). Results show that as-prepared Bi nanoparticles as lubricant additives can significantly improve the tribological properties of lithium lubricating greases as well as load-carrying capacity.

1. Introduction

Nanoparticles have been finding new areas of application, since the special properties are different from their bulk, molecular or atomic forms [1-2]. Self-repair layers can be formed by using the grease containing nanoparticles as additives in various vehicles and equipment which reduce the mechanical load and save fuels. There are many studies on lubricating grease containing various additives. Additives such as nano-materials Al, Zn/ZnS, Cu, Ni have good anti-wear and friction reduction properties [3-6]. Martin [7] found that recycled LDPE can be potentially used as an effective rheology modifier of lithium lubricating greases. Du [6] found that fine sand particles improve the wear resistance of the machine lubrication systems. The mechanisms of the anti-wear and friction reducing mechanism of lubricating oil with combined nanoparticles are associated with the different factors. Anoop [8] found that the aqueous trisiloxane surfactant solutions spread on hydrophobic solid surfaces are driven by the surface tension gradient, and the thin colloidal films containing nanoparticles spread on hydrophilic surfaces are driven by the structural disjoining pressure gradient. Xu [9] found that the spherical nanoparticles act as nano-bearings between the worn surfaces, which can improve the reducing-friction and anti-wear properties by surface polishing. Rapoport [10] drew a conclusion that the nanoparticles serve as spacers to eliminate the metal-to-metal contact between the asperities of the two mating surfaces. Some suggested [11-13] that various boundary films with excellent mechanical and lubricating properties are generated on the wear surface. In hydrodynamic lubrication conditions, fluid film can effectively separate the parts when sliding to keep low friction and wear of parts. Sun Lei [14] studied the tribological properties of a surface by using Bi nanoparticles as oil additives in liquid paraffin. The results indicated that Bi nanoparticles prepared by chemical reduction method have good friction reducing and anti-wear properties as oil additives at low-middle loads. However, few people have conducted research on the Bi nanoparticles prepared by DC arc plasma method and used as lubricating grease additives. Moreover, because of the surface tension effect of nanoparticles, the forerunner of nanoparticles prepared by wet process can form aggregation easily. That is, the congregation of nanoparticles is the bottleneck in lubricating grease application. In this paper, spherical Bi nanopowders with high dispersibility were prepared by DC arc plasma evaporation method. The results show that the dispersible stability and friction-reduction and anti-wear properties of the Bi nanoparticles in lithium lubricating greases are excellent. In the article, the tribological properties and self-repairing mechanism of the Bi nanoparticles additive lubricating oil have been investigated in detail.

The surface properties of nanoparticles modified by surfactant have been changed as compared to those of the original nanoparticles. Therefore, it is very important to study the influence of different addition on the lubricating properties of Bi nanoparticles as additive. The effects of the additive concentration of Bi in different surface conditions on the tribological properties of the grease were studied. The effects of load and testing time on the friction and wear performance are investigated in the paper.

2. Experimental

2.1 Material processing and sample preparation

Bi nanoparticles were prepared by DC arc plasma device as shown in the Fig. 1. The Bi nanoparticles were obtained from the device with appropriate process parameters. First, the Cu block was placed in the water-cooling crucible. The preparation chamber was evacuated to 6×10^{-3} Pa by an external pumping system. Then the preparation chamber was filled with hydrogen and argon (the P_{H2}/P_{Ar} ratio is 1/6, the filling pressure is 0.05 MPa, the current is 250 A). The influence of work pressure on the average diameters of Bi nanoparticles has been intensively investigated in the literature [15].
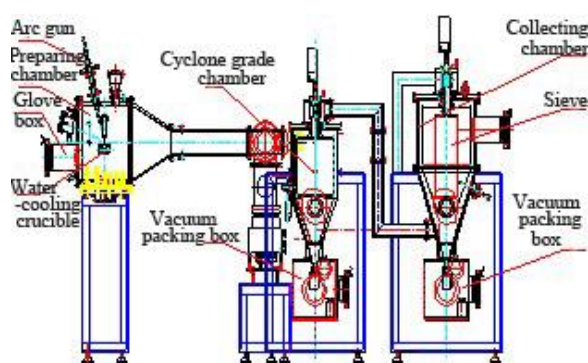

Fig. 1. Schematic diagram of high-vacuum direct current arc plasma evaporation device for preparing metal nanopowder.

Analytically pure lithium hydroxide (LiOH), chemically pure 12-hydroxy stearic acid (HSA) and base oil 500SN were used as raw material to prepare the lithium grease. The details about the preparation of lithium grease were described as follows. First, HSA, LiOH aqueous and 1/3 base oil 500SN were added to a refining container and mixed by vigorous stirring and heating. Second, saponification was conducted at 105~110℃ for 2 h. Then the mixed solution was heated and the water was evaporated by a vacuum pump at the end of the saponification, followed by the addition of another 1/3 base oil 500SN at 170~180°C. Finally, the rest of the base oil 500SN was dropped into the mixture at 195~200℃ and the mixture was immediately cooled to 120~130℃ and further cooled to room temperature in 15 min. The mixture obtained by a three-roller mill for 30 min was used to prepare the target grease samples. Table 1 shows the properties of the prepared base grease.

Table 1. Properties of prepared base grease.

Performance	Standard value
Worked penetration (10^{-1}mm)	220~250
Dropping point (℃)	180
Corrosion(T3,100℃,24h)	Qualitied
Evaporation loss (99℃). % .⊆	2.0

2.2 Apparatus and experimental method

The JEOLJEM-200CX Transmission Electron Microscope (TEM) was applied to obtain the morphology and size of the Bi nanoparticles. The prepared Bi nanoparticles and the grease were mixed by mechanical stirring and ground for 30 min in three-roller mill. The lithium grease with different concentrations of Bi nanoparticles was studied after it was dispersed in octane solvent with surfactant 12-hydroxystearic acid (HSA). The anti-wear and friction reduction properties of Bi nanoparticles as additives in lithium grease were evaluated on a four-ball apparatus made in Jinan Testing Machine Factory (Jinan, China). The wear scar diameters of the three lower balls were measured by using a Sony-W5 optical microscope at an accuracy of ±0.01 mm, and the friction coefficients were automatically investigated by using a strain gauge equipped with the four-ball tester. The balls with a diameter of 12.7 mm, hardness of HRc 61-64 were made of GCr15 bearing steel (AISI-52100). The tests were evaluated by using a MMW-1 four-ball machine at a rotary speed of 1200±60 rpm at room temperature for 30 min. According to the experiment data, we can get the function curve of friction coefficient and load, together with the function curve of wear scar diameters and load at different loads (196, 294, 392 and 490N). The morphology and the elemental distribution of the wear scar surface and the elemental composition of the surface film were analyzed by SEM of JEM-6360L model equipped with EDS.

3. Results and discussion

3.1 Analyses of as-prepared Bi nanoparticles by TEM

TEM was used to visualize the size and shape of the prepared nanoparticles [16-17]. Fig. 2 shows the TEM image of the prepared nanoparticles. The prepared particles are randomly distributed with spherical shape and smooth surface. Fig. 3 shows the size distribution of as-prepared Bi nanoparticles. The result shows that Bi nanoparticles have an average size of 27 nm, most of which range from 10 to 30 nm.
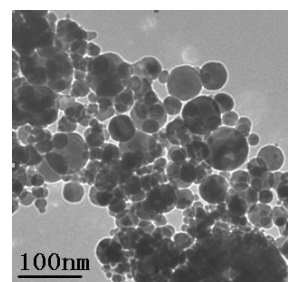

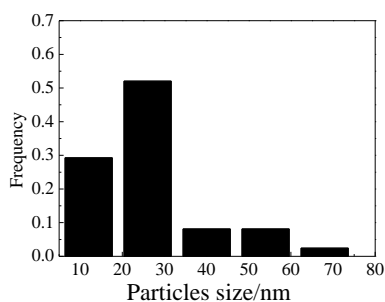*Fig. 2. TEM image of as-prepared Bi nanoparticles.*

Fig. 3. Size distribution of Bi nanoparticles.

3.2 Effects of different Bi content and surface conditions on the tribological properties

In experiment, the original Bi nanoparticles and those with modified surface were added to the base grease. Fig. 3 shows the WSD (Fig. 4.a) and friction coefficient (Fig. 4.b) as functions of the concentration of Bi nanoparticles (load: 392N, speed: 1200 rpm, time: 30 min, room temperature). It is seen that the original nanoparticles as additives in the base grease have better performance than those with modified surface. Fig. 4 (a) shows that the WSD decreases with the increase of original Bi concentration as the additive concentration is below 2wt.% . But the WSD tends to slightly rise with the further increase of additive concentration above 2wt.%. And when the additive concentration reaches 2wt.%, the WSD is 0.58 mm and is reduced by 13.4wt.% as compared with the base grease. The results indicate that Bi nanoparticles have an excellent anti-wear, especially when the additive concentration is 2wt.%. Fig. 4(b) shows that the friction coefficient declines markedly with higher additive concentration of Bi nanoparticles in the base grease. But the friction coefficient tends to slightly rise when the additive concentration is over 3wt.%.
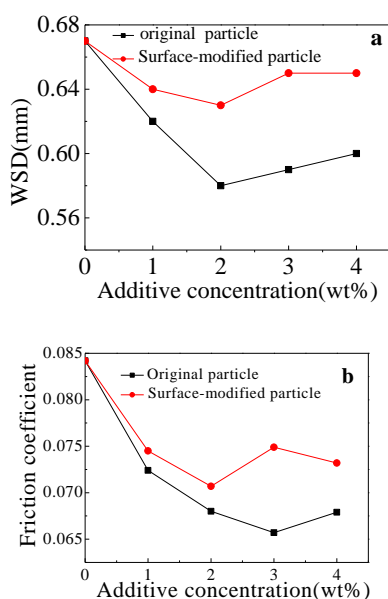
The tribological properties of surface-modified Bi nanoparticles would get worse, which can be attributed to the following reasons. It is easier for the original Bi nanoparticles to form a liquid metal film on the wear surface because of the high frictional mechanical energy for their high surface activity. In other words, Bi nanoparticles prepared by the DC arc plasma evaporation method have higher surface activity than the surface-modified nanoparticles. The results show that Bi nanoparticles are effective in the improvement of the friction-reducing and anti-wear abilities of the lithium grease, which is attributed to the formation of the boundary lubricating and protective layers on the worn steel surfaces. The protective film prevents the direct contact of wear surface and leads to better tribological properties.

3.3 Effects of the loads on the tribological properties

Fig. 5 shows the variations of WSD (Fig. 5 a) and friction coefficients (Fig. 5 b) with load under the lithium grease (speed: 1200 rpm, time: 30 min, room temperature). In general, the WSD and the friction coefficient values of balls modified by greases with 2wt.% unmodified Bi nanoparticles are relatively less than those of the base greases without nanoparticles.
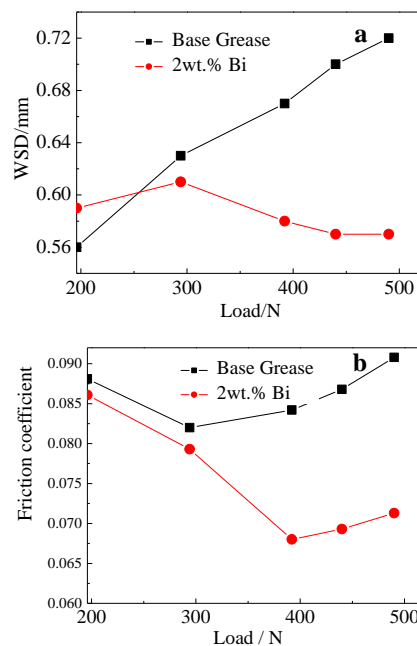

Fig. 4. WSD and friction coefficient as a function of additive concentration (load: 392N, speed: 1200 rpm, time: 30 min, room temperature).

Fig. 5. Variation of WSD and friction coefficient of steel/steel contact with load.

Fig. 5 shows the variations of WSD and friction coefficients with load under the lubrication of base greases containing 2wt.% unmodified Bi nanoparticles (speed: 1200 rpm, time: 30 min, room temperature). It is seen that the base grease containing 2wt.% Bi nanoparticles as additives can effectively improve the load-carrying capacity.

The WSD of grease containing Bi nanoparticles is larger under 196 N. A possible explanation is that the energy generated by friction is not high enough to melt the nanoparticles under 196 N. So Bi nanoparticles serve as wear particles and increase the WSD. However, as we improved applied load, we increased the load-carrying capacity of base greases containing 2wt.% Bi nanoparticles. It can be clearly seen that the greases containing 2wt.% Bi nanoparticles have a lower friction coefficient. The reason may lie in that the stable suspension of Bi nanoparticles in base greases can be readily transferred onto the contact zone of rubbing steel surfaces and deposited thereon to form a surface with a protective and lubricious layer, resulting in reduced friction coefficients and wear scar diameters [18].

In conclusion, under a lower load, a majority of Bi nanoparticles do not melt due to low frictional mechanical energy. There is no striking difference in the friction coefficients and WSD between the grease containing Bi nanoparticles and the base grease. However, under a higher load, the energy produced by friction is high enough to melt the majority of Bi nanoparticles. The embossed high-energy areas are preferred to be welded on. And boundary lubrication films of Bi are formed. The films prevent the metal-to-metal contact between wear surfaces and consequently result in the reduction of the friction coefficient and WSD.

3.4 Effects of the testing time on the tribological properties

Fig. 6 shows the variations of friction coefficient with testing time under the lubrication of four samples (base greases, base greases +1wt.% Bi nanoparticles, base greases + 2wt.% Bi nanoparticles, and base grease +3wt.% Bi nanoparticles). The friction coefficient of the base grease at the beginning of the test is the lowest among the four samples. It increases from 0.069 to 0.092 after three minutes and then decreases gradually to 0.078 and remains stable after 21 minutes. The friction coefficients of the base grease containing 1wt.%, 2wt.% and 3wt.% Bi nanoparticles at the beginning are all higher than those of the other base greases, but they decrease monotonously as the testing time elapses. At the end of the test, the friction coefficient of the base grease containing 2wt.% Bi nanoparticles is just 0.062 while it is 0.082 of the base grease. At the beginning of the friction test the friction energy is not high enough to melt most of the Bi nanoparticles and they serve as wear particles. As the testing time goes on, the cumulated friction energy is high enough to melt them and the melted nanoparticles are deposited on the wear surface.
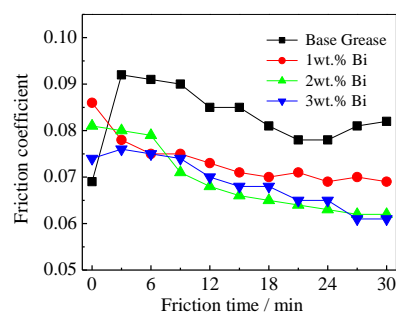

Fig. 6. Friction coefficient as a function of testing time under the same conditions (load: 392N, speed: 1200 rpm, room temperature).

3.5 SEM analysis of the worn surfaces

Fig. 7 shows the SEM morphologies of the worn steel surfaces and the distribution of elements on the worn surface (load: 490N, speed: 1200 rpm, time: 30min, room temperature). The SEM micrographs of the worn surfaces lubricated with base grease and base grease containing Bi nanoparticles are shown in Fig. 7 (a) and (b), respectively. Fig. 7 (c) shows the SEM micrographs of the steel surfaces lubricated with base greases containing 2wt.% Bi nanoparticles with a higher resolution. Surface elemental distribution of Bi of the worn steel surfaces (Fig. 7 (c)) is shown in Fig. 7 (d). It can be seen that the distribution of Bi on the wear scar is nearly homogeneous. It is also clear that the worn surfaces of the steel balls in base greases (Fig. 7 (a)) show signs of severe scuffing, deep grooves and rough wear scar, possibly due to friction among balls during sliding process. In contrast, the worn steel surface lubricated by the base greases containing 2wt.% Bi nanoparticles shows few signs of mild scuffing and almost no signs of deep grooves (Fig. 7 (b)), which can be attributed to the energy produced by friction which is high enough to melt the Bi nanoparticles in the grease with the increase of load. The melting nanoparticles deposit and weld on wear surface to form a protective and lubricious layer. The liquid films serve as supporters on the worn surface and flow like rolled particles. However, the abrasion caused in the presence of liquid films is much less than that in the presence of particles because of the great elasticity of the films and low internal friction of liquid metal. In addition, as a result of high energy in prominent area, it was noticed that the film mainly existed on raised parts. However, sheet, granular and irregular holes, which are displaced mainly on the bottom of the groove, are shown in Fig. 7 (c). The friction energy is relatively low in these areas during the rubbing, so the Bi nanoparticles are deposited on these areas to make the friction surface flat.

Fig. 8 and Table 2 show the EDS spectra and element contents of the two places marked (A and B) in Fig. 7 (c). The results indicate that the content of Bi is high apart from the elements Fe, Cr, Si, which are contained in steel balls and lithium greases. Besides, the content of Bi in sheet area is much higher than that existing in holes. A conclusion can be drawn from the above results that films of boundary lubrication exist exactly on the surface of

wear scar and the deposition of Bi nanoparticles plays a more important role than that filling into the pit.
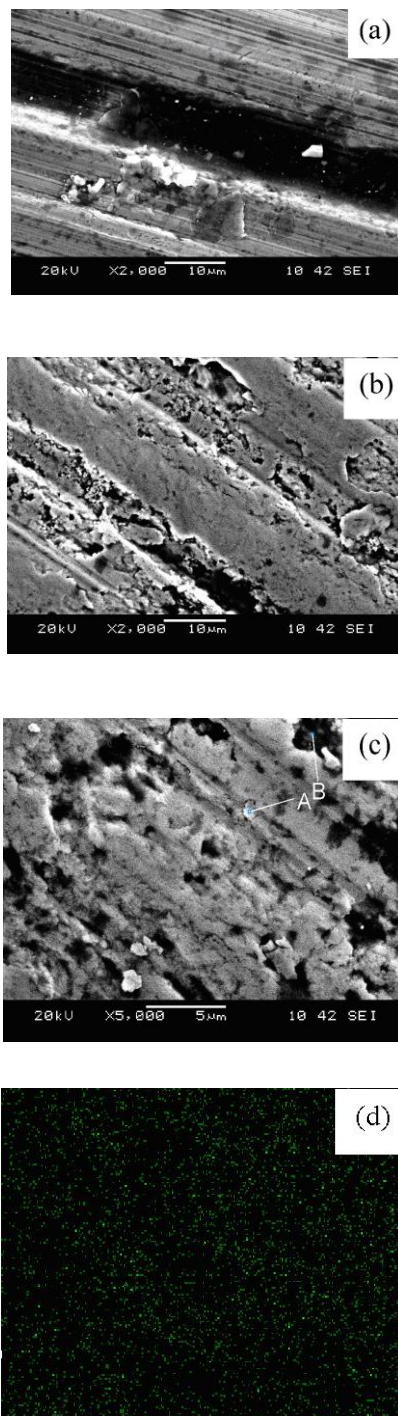

Fig. 7. SEM morphologies of the worn steel surfaces and surface distribution of elements (load: 490N, speed: 1200 rpm, time: 30 min, room temperature). (a) morphology of wear surface modified by lithium grease (×2000); (b) morphology of wear surface modified by 2wt.% Bi/lithium grease (×2000); (c) amplified image of the marked areas in (b) (×5000); (d) surface distribution of Bi.
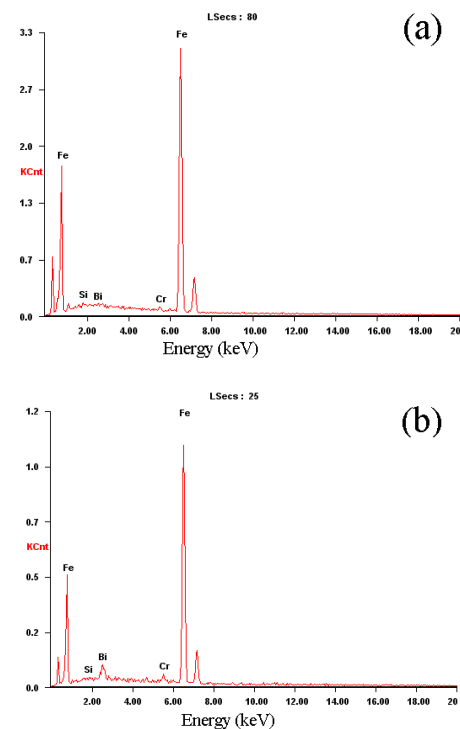

Fig. 8. EDS spectra of worn surfaces: (a) and (b) are EDS spectra of A sheet and B groove area in Fig. 7 (c), respectively.

Table 2. Elements content of steel ball worn surfaces of A and B in Fig. 6 (c).

Element	Content of element in A /wt.%	Content of element in B /wt.%
Fe	91.85	97.39
Cr	1.63	1.03
Si	0.46	0.63
Bi	6.06	0.95

3.6 Friction mechanism and relevant model analysis of the lubrication

The microstructure characters of friction surface under different friction additive concentration, load, testing time are analysed and the mechanism of friction is confirmed. When the load and the testing time increase, the smooth self-repair coatings are formed on the surfaces of the metals, which avoid direct contact of metals. This friction mechanism is illustrated in Fig. 9. Under certain conditions, Bi nanoparticles exist in base greases among the friction surfaces (Fig. 9 (a)). During the process of friction and shear, the molecules of Bi nanoparticles are rebuilt due to the effect of load and surface energy. Bi nanoparticles have an affinity interaction with the metal surface, which shows polarity under the friction conditions. At this time, they spread to the micro-friction surface, forming an anti-wear layer. Meanwhile, under boundary lubrication conditions, the friction at the high temperature

makes Bi nanoparticles form a protective anti-wear film with a rolling lubrication function, filling the micro ravines on the friction surface. From Fig. 7, the wear can be found in both A and B, with a large number of Bi elements which could prove that the Bi nanoparticles melt and rearrange themselves regularly around the steel balls to form the absorption film (Fig. 9 (b)). It is easier for smaller molecules to rearrange themselves, and it takes them less time for phase transformation in response to the shear and load action. Then, under the action of induction force and absorption potential energy from the absorption film, the Bi nanoparticles next to the absorption film also gradually rearrange themselves in order. As time passes, there are more and more rearranged and ordered molecules, and the degree of the order of the surface molecular layer increases. Meanwhile, the depth of the ordered film also increases continuously before it stays stable when it reaches the limit of the effective action of the surface force (Fig. 9 (c)). The presence of such a film can significantly reduce the surface abrasion induced by the mechanical movement.
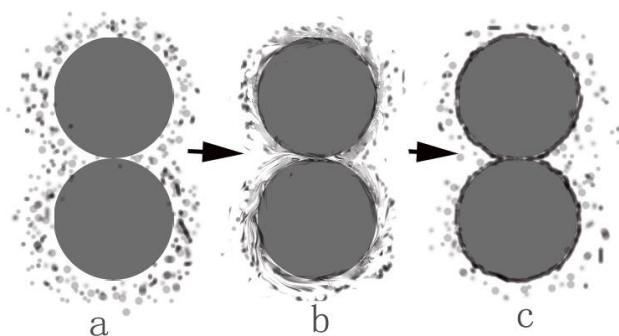

Fig. 9. The process of the friction mechanism.

4. Conclusion

The following conclusions are drawn based on the experiments and analyses performed:

(1) Spherical Bi nanoparticles have been prepared by DC arc plasma method with high purity and mean particle size of 27 nm. The base grease containing original Bi nanoparticles has better tribological properties than that containing surface-modified Bi nanoparticles. The best additive concentration of original Bi nanoparticles is 2wt.%. Compared to the grease without nanoparticles, the WSD and the friction coefficient could be reduced by 13.4wt.% and 19.2wt.% respectively.

(2) As-prepared original Bi nanoparticles as lubricant additives in lithium grease can effectively improve tribological properties in terms of anti-wear and friction-reducing ability as well as load-carrying capacity. The state and thickness of the film on the worn surface is closely related to different applied loads and Bi nanoparticles might be a promising lithium grease lubricant additive for steel-steel contact under moderate load.

(3) During the friction process, a protective and lubricious film composed of Bi is formed on the rubbed steel surface lubricated by lithium grease containing Bi nanoparticles. The main mechanisms of the self-repair under rolling friction are the melting and welding of the Bi nanoparticles on the shearing surface. The low internal friction of liquid metal also contributes to improving the tribological properties.

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