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纳米级固体润滑剂的研制和摩擦学性能研究

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The Preparation of Nanonmeter Solid Lubricants and the Study of Their Tribological Properties

Candidate: Wang Heshou
Major: Mechanic Design and Theory
Supervisor: Prof. Zhang Zhiming

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本论文经答辩委员会全体委员审查，确认符合上海大学博士学位论文质量要求.

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答辩委员会对论文的评语

纳米材料因具有特殊的物理、化学性质及应用性能而成为近年来国内外研究的前沿课题之一. 王鹤寿同学的博士学位论文"纳米级固体润滑剂的研制和摩擦学性能研究"选题正确.

论文设计和研制出了纳米球磨机,系统深入地研究了其制备工艺和粉碎模型，成功地研制出具有"核壳"结构的纳米级MoS_2、PTFE和滑石粉，并以钢一钢摩擦副和铜一钢摩擦副为应用对象对其摩擦学特性进行了大量系统深入的研究，采用现代分析仪器初步探讨了作用机理，同时还以蜗轮蜗杆台架进行了考核.

论文的创新点在于：①首次成功地开发了强化粉碎和强化分散一体化制备纳米固体润滑材料新技术，解决了传统机械研磨法只能制备微米级微粒的难题；②对韧性的PTFE材料以γ射线辐照预处理，进行骨架松化，再用本法亦可制备成纳米级微粒；③ 发现了纳米级滑石粉油液对钢一钢摩擦副和铜一钢摩擦副亦具有优良的抗磨减摩节能作用，为开拓廉价的固体润滑剂提供了科学依据.

论文立论正确、自制设备性能优异、实验工作量很大、试验方法合理、分析严密、结论可信、具有创新见地，表明作者具有坚实宽广的理论和系统深入的专业知识，有独立从事科研工作的能力. 论文条理清晰、层次分明、文笔流畅、学风严谨，是一篇很好的博士学位论文，答辩时能正确地回答问题.

答辩委员会表决结果

经答辩委员会委员的投票表决，一致通过王鹤寿同学的博士论文答辩，并建议授予工学博士学位.

答辩委员会主席：**赵　源**

1999年8月8日

摘 要

纳米级固体润滑剂由于其特殊的物理和化学性质而日益受到广泛的重视，并且发展迅速. 目前人们兴趣主要集中在聚集法制备纳米微粒，但因其工艺较复杂、操作精细、成本高而工业化生产较困难. 而工业上广泛应用的机械粉碎法虽具有工艺简单、制备效率高、可大批量生产的优点，但难以达到纳米级，最细也只能达到微米级，目前尚未见有关采用此法制备出纳米级微粒的报道. 在采用机械粉碎法粉碎物料时，可能在物料被粉碎的同时，由于物料表面能的增加，颗粒之间会重新聚集，随着粉碎的进行，颗粒之间的聚集速度增大，当颗粒的被粉碎速度与颗粒之间的聚集速度相等时，粉碎与聚集就达到动态平衡，此时，物料就不能被粉碎得更细，因此本研究认为如果能在加强粉碎以提高物料的被粉碎速度的同时采用“外壳”结构加强颗粒之间的分散以大大降低颗粒之间的聚集速度，物料就可以被粉碎得更细，以致于达到纳米级. 为此，本研究结合粉碎理论和胶体化学理论，在普通机械粉碎法的基础上，设计和制造了强化粉碎以提高粉碎速度和强化分散以降低聚集速度一体化的纳米球磨机，作为生产模拟设备，以此制出三种纳米级固体润滑剂，并对它们和辉煌公司的纳米级氟化石墨进行摩擦学特性的考察及综合对比、分析其摩擦作用机理.

本论文选用工业上常用的固体润滑剂 MoS_2、PTFE 和滑石粉作为主要原料，通过本文所设计和制造的纳米球磨机进行了一系列的制备试验，通过扫描电镜和透射电镜对原料和所制备的样品的形貌和粒径进行分析，研究纳米球磨机的制备工艺参数，得出

较佳工艺参数为：转速为 2 800 r/min、粉磨时间为 12h、钢球直径为 2mm、油体积比为 40 %、钢球填充率为 35 %. 在纳米球磨机较佳工艺的基础上考察了油相粘度、原料添加量和各种表面活性剂对制备纳米级固体润滑剂的影响. 发现较低的油相粘度、较低的原料添加量和对应各种材料而较佳的分散剂相配合可制备出纳米级微粒. 其中分散剂 T154 和石油磺酸钡复配时，可制备出平均粒径为 40nm，最小粒径为 10nm 的纳米级 MoS_2；分散剂 T154 和氯化石蜡复配后，可制备出平均粒径为 20nm，最小粒径为 10nm 的 PTFE；分散剂 T154 和 T306 复配后所制备的纳米级滑石粉的平均粒径约为 120nm，最小粒径为 40nm. 且它们的粒径均匀、分散度好. 此外由于柔韧性的 PTFE 粉碎困难，本研究特别对 PTFE 进行了粉磨前 Co60 辐射的预处理，发现未经辐射或辐射剂量不够的 PTFE 都不能被制备成纳米级微粒，其辐射剂量为 200K 的 PTFE 可被制备成粒径为 20nm 左右的纳米级微粒. 辐射前后其粒径虽无变化，但其分子骨架已被 “松化”. 而 γ 射线与目前较先进的超低温冷冻法相比，具有工艺简单、效率高、成本低的优点，故更适于工业化生产. 采用 IR 验证了所制备的纳米级微粒具有物理吸附了分散剂的 “核壳”结构. 三种纳米级固体润滑剂的结果证实了通过强化粉磨以提高粉碎速度的同时也必须采用分散剂强化分散以大大降低细颗粒聚集速度，这样才可以制备出纳米级微粒. 这可能是机械法制备纳米材料的必要途径.

在四球试验机上对本研究所制备的三种纳米级固体润滑剂及氟化石墨进行了钢-钢点摩擦条件下的减摩抗磨性能、承载能力及采用介入法对铜-钢点摩擦的减摩、抗磨性能和钢-钢、铜-钢面摩擦减摩性能的详细考察并与其他 常用添加剂作了对比和复配试验，结果表明：除在铜-钢摩擦条件下的纳米级 MoS_2 抗磨性反而变差外，四种纳米级固体润滑剂均有优越的减摩性能、

良好的抗磨性能. 纳米级氟化石墨的承载能力较好，其他三种纳米级固体润滑剂的承载能力均较差. 但其他常用的添加剂与纳米级氟化石墨复配后在油相表层产生胶状凝块，影响应用. 而纳米级 PTFE、MoS_2 和滑石粉同上述其他添加剂的配伍性能良好，其中 T301 与它们复配后均有增效性.

本文采用了俄歇电子能谱（AES）等分析仪对摩擦后的表面膜进行了分析，发现纳米级 MoS_2 在摩擦面形成了沉积膜和化学反应膜（FeS 或 Cu_2S 等，其中 FeS 对润滑有利，而 Cu_2S 对润滑不利），而纳米级 PTFE、滑石粉和氟化石墨仅在摩擦表面形成物理沉积膜，主要靠层状结构起减摩抗磨作用.

本文根据上述结果从中优选了最佳配方进行蜗轮蜗杆台架试验，发现纳米级 PTFE 稍优于纳米级滑石粉，传动效率较高、磨损均较小，同时也发现纳米级 MoS_2 有异常磨损，传动效率不高. 通过能谱分析认为 MoS_2 在铜摩擦面上形成的硬脆的 Cu_2S 是造成摩擦磨损增大的原因，因此认为纳米级 MoS_2 不适宜作如蜗轮蜗杆之类的铜-钢摩擦副的润滑添加剂，这与某些报道结论相反. 而滑石粉虽较 PTFE 稍差，但尚是一种价廉的、性能良好的减摩抗磨节能剂，特别适合用于低价的蜗轮蜗杆油脂.

本文所研制的纳米级 PTFE、滑石粉等化学稳定性优良，在目前铜-钢摩擦润滑添加剂品种较少的情况下，为将来进一步研制各种稳定的减摩抗磨节能的润滑油脂产品提供了应用可行性的基础理论数据，同时又为摩擦学中纳米材料的制备和润滑增添了一些新的基础性数据、方法和观点.

关键词 纳米级固体润滑剂，纳米球磨机，摩擦学特性，摩擦表面分析，润滑油，减摩抗磨剂

Abstract

Due to its special physical and chemical characteristics, nanometer-level solid lubricant has received more and more attention and has developed quickly. Currently the main interest of researchers is focused on producing nanon particles by aggregation method, however, these particles are certainly difficult to be produced in an industrial scale because of complicated technology, careful operations and high cost required. Another widely used method in industry, the machine-grinding method has the features of simple technology, high production efficiency and batch production, but the particles from this method are difficult to achieve nanometer level, and the smallest ones can only go to micron level. So far there is no report about nanometer-level particles produced by this method. It is possible that, when being pulverized by machine-grinding method, the particles will reaggregate because of the increase of surface energy. And the aggregation will accelerate during the pulverization. When the aggregation speed equals to the pulverization speed, the particles are in the dynamic balance between aggregation and pulverization, and the size of it will not reduce any more. So by means of combining both enhancing pulverization so as to increasing the pulverization speed and intensifying dispersion by employing "shell" structure to the effect of decreasing the aggregation speed, the particles will be pulverized smaller, even to nanometer level. In this research, combining

pulverization theory and colloidal theory, we designed and manufactured a nanometer ball mill unitizing strengthening pulverization to accelerate the pulverization and strengthening dispersion to decelerate the aggregation. And taking it as a simulation device of production, we prepared three types of nanon solid lubricant. Their friction mechanism was analyzed and they were compared with the commercial nanon-level graphite fluoride on the tribological characteristics.

In this dissertation, three solid lubricants, MoS_2, PTFE and French chalk commonly used in industry, were selected as the main raw materials and samples were prepared through a series of preparation experiments with nanon ball-mill designed and manufactured by the author. By SEM and TEM the shape and particle diameter of raw materials and prepared samples were analyzed and processing technology parameters of nanon ball-mill were studied with the result of the optimal technology parameters as following: rotational speed 2800 r/min; time of grinding 12h; diameter of steel ball 2mm; volume percentage of oil 40%; filling rate of ball 35%.

On the basis of these optimal technology parameters of nanon ball-mill, the effects of viscosity of lubricant oil, quantity of raw material added, and various surfactants used in the preparation of nanon-level solid lubricants were investigated. It is found that low oil viscosity and less quantity of raw material matched with the optimal dispersant to any of the above three solid lubricants are beneficial to preparing nanometer particles. with the help of dispersing agent T154 compounded with oil barium sulfonate,

nanon-level MoS_2 with average diameter of 40nm and minimum one of 10nm can be processed and with the help of dispersing agent T154 compounded with chlorinated paraffin wax, nanon-level PFTE with average diameter of 20nm and minimum one of 10nm can be processed. And when dispersing agent T154 is compounded with dispersing agent T306, nanon-level French chalk with an average diameter of 40nm and a minimum one of 10nm is produced. Moreover all of them have even particle-diameter and good dispersivity. In addition we specially pre-process PTFE by Co60 irradiation before its smashing and grinding because flexible PTFE is difficult to be ground. It was shown that any PTFE non-radiated or inadequately radiated cannot be manufactured into nanon-level particles, and PFTE with radiation of 200K can be made into about 20nm-diameter particles. The reason of this phenomenon is that their molecule skeletons have been unbent although there is no change of diameter of particle after irradiation. Comparing to current considerably advanced cryogenic cooling method, the γ-ray radiation method is simple in technology, high in efficiency and low in cost, so that it is more suitable for industrial production. It is testified that the nanon particles prepared by the author have the core-shell structure physically absorbing dispersing agent. The experimental results of three nanon-level solid lubricants showed that adopted dispersing agent to strengthen dispersion of particle in order to decrease aggregating speed of particles, as well as raising pulverizing speed by means of strengthening grinding, is necessary for preparing nanon-level particles. This may be the requisite path to obtain nanon-materials by mechanical method.

In this research, we experimented in detail on the anti-friction and anti-wear property and loading ability of the three nanon-meter solid lubricants prepared and of graphite fluoride lubricant under the condition of steel-steel point contact rubbing. Also the same experiments were carried under the condition of copper-steel point contact rubbing and on the condition of steel-steel and copper-steel surface contact rubbing. And then comparing and compounding experiments on these lubricants with other common additives were performed. All the above experiments are carried out on a four-ball test machine and the results were shown as following: all four nanon-meter lubricants have the capacity of distinguished anti-friction and good anti-wear properties, except the nanon-meter MoS_2 under the condition of copper-steel friction. The load-carring ability of nanon-meter graphite fluoride lubricant is higher than those of the other three lubricants. However compounding of graphite fluoride with other additive lead to colloid clots on the surface of lubricant oil, which will affect the application of the lubricant, meanwhile nanon-meter PFTE, MoS_2 and French chalk can compound well with the additives above.

In this paper, the surface film after friction was analyzed by mean of Anger Electron Spectroscope (AES) and it was found that nanon-meter MoS_2 formed a deposit film and a chemical reacting film, i.e. FeS or Cu_2S etc., where FeS is beneficial to lubrication and Cu_2S is on the contrary, and that nanon-meter PTFE, French chalk and graphite fluoride, whose anti-friction and anti-wear functions mainly depend on layer structure, only formed physical deposit on rubbing surface.

From the above experimental results above the optimal formula was chosen to make experiment on worm-and-gear frame test. It is shown that nanon-meter PTFE is a little better than nanon-meter French chalk because of its relative higher drive efficiency and lower wearing capacity and that nanon-meter MoS_2 has intensive wear with low drive efficiency. It has proved by AES analysis that the increment of friction-wear is owe to the hard and fragile Cu_2S formed on friction surface of copper from MoS_2. So we do not think nanon-meter MoS_2 is suitable for being used as lubricating additive for copper-steel friction gear such as worm gear. This conclusion is contrary to that of existing reports. And although the property of French chalk is a little inferior to that of PTFE, it is still an economic anti-friction, anti-wear and energy conserving additive with good properties, especially for low-costing worm gear oil and grease.

Currently there are a few types of lubricating additives for copper-steel friction, the research of nanon-meter PTFE and French chalk with good chemical stability in this dissertation is bound to provide some basically theoretical data for studying various stable anti-friction, anti-wear and energy conserving lubricant products in the future. Meanwhile it provides some new methods, concepts and basic data for the manufacture and lubrication of nanon-materials in tribology.

Key words nanon-meter solid lubricant, nanon ball-mill, tribological characteristics, rubbing surface analysis, lubricating oil, anti-friction and anti-wear additive.

目　录