



Optimum hydrophilic modification of lanthanum trifluoride nanoparticles and their application in enhancing tribological properties of eco-friendly water-based bonded solid lubricating coatings

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ABSTRACT

In the article, a novel and facile method for hydrophilic modification of nano-lanthanum trifluoride particles was designed, the experimental results reveal that the surface of the nano-lanthanum trifluoride are absorbed with cross-linked molecules via electrostatic attraction and hydrogen bonds to further improve the water-dispersion capacity of nano-lanthanum trifluoride. In addition, the modified nano-lanthanum trifluorides achieve nano-scale dispersion in water-based bonded solid lubricating coatings, and 5 wt.% of modified lanthanum trifluoride into coatings can greatly enhance the mechanical and tribological properties of water-based coatings, which are superior to that of organic-solvent based coatings. Furthermore, the modified lanthanum trifluoride for promoting the wear resistance of the coatings illustrates more significant compared to unmodified lanthanum trifluoride and lanthanum trifluoride wetted by acrylic surfactant.

1. Introduction

The bonded solid lubricating coatings are typical kinds of solid lubricating material, with a wide variety sources of materials, and the preparation process is simple and economical, which is mainly used to solve the special conditions of lubrication and protection and other issues, which could be illustrate by representative examples as follows: achieving friction-reducing and wear-resistant properties and anti-cold welding performance at extreme low temperatures in space environment; improving the ship corrosion resistance and lubrication protection in marine environment; obtaining anti-wear and friction-reducing performance at automotive transmission of high temperature environment, thereby greatly extending service life of the coated workpieces, which exhibits high scientific research values and economic benefits [1–6]. At present, the common solvent-based bonded solid lubricating coatings, which take various kinds of organic solvents as dispersion medium in the preparation process, which undoubtedly exacerbates the consumption of fossil resources, thus posing a serious threat to the environment and people's health [1,5,7]. Comparatively, the water-based bonded solid lubricating coatings are prepared via taking the water as the dispersion medium, which not only effectively reduces the

utilization of organic solvents, greatly minimizing the depletion of non-renewable resources, but also in line with the concepts of environment-friendly development and sustainable development [6,8,9].

Nanomaterials, as indispensable additives of bonded solid lubricating coatings, possess small size effects, a higher hardness and excellent mechanical strength, which leads to their extensive applications in the field of the lubricating materials to play a vital role in enhancing the mechanical and tribological performances of the bonded solid lubricating coatings [1,6,10–14]. The commonly used nano-fillers, such as cadmium sulfide, antimonous oxides, lead oxides, gold, silver powders and rare earth fluorides, all of which can effectively improve mechanical and tribological properties of the bonded solid lubricating coatings at some degree [15–18], but compared to noxious antimonous oxides and lead oxides, expensive gold and silver powders, the rare earth complexes (lanthanum trifluoride or cerous trifluoride) are kinds of environmental friendly and inexpensive fillers, in detail, lanthanum trifluoride, as nano-reinforcing phase, can significantly strengthen the load-bearing capacity and wear resistance of the lubricating coatings by virtue of the cooperativity of nano-additives and lubricants [6,19–23]. Therefore, it is of great significance to conduct the research of lanthanum trifluoride nanoparticles in application of water-based bonded

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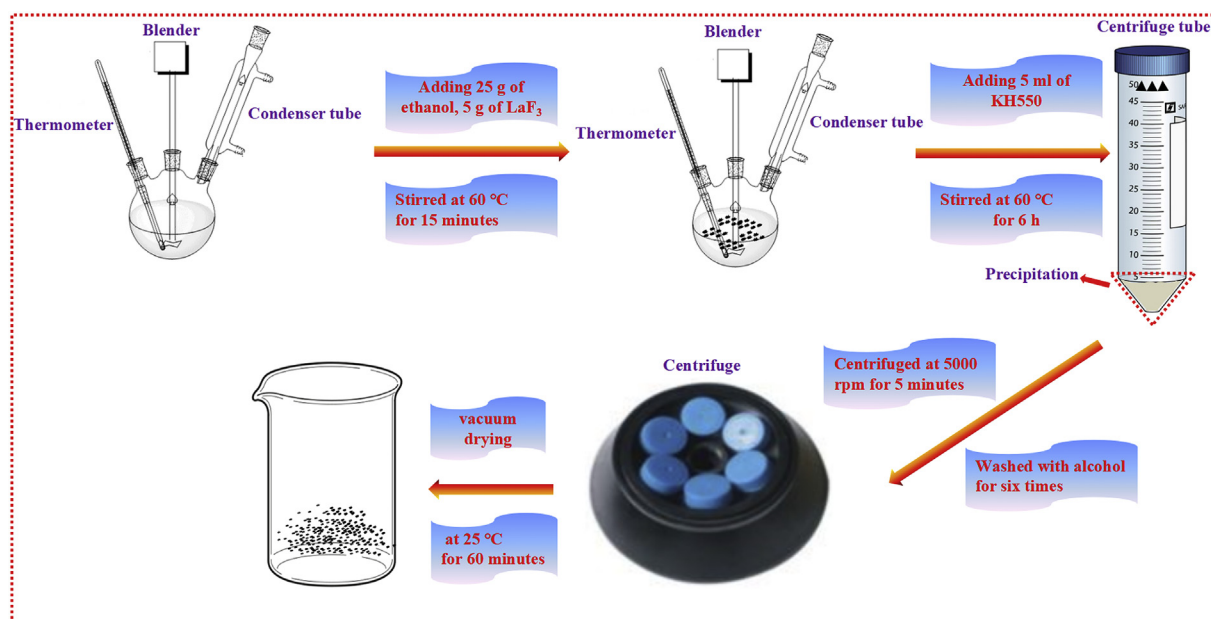


Fig. 1. Entire modification process of lanthanum trifluoride nano-particles.

solid lubricating coatings. Nevertheless, although lanthanum trifluoride nanoparticles possess good application prospects and practical value in the practice of water-based bonded solid lubricating coatings, nanometer lanthanum trifluoride are apt to generate agglomeration in aqueous media even if mixed at higher stirring speed or dispersed with wetting dispersant, which is account of the larger specific surface energy of nanometer particles and the incompatibility between inherent inorganic lanthanum trifluoride nanoparticles and the aqueous medium [24,25]. In consequence, it is essential to take surface modification of lanthanum trifluoride nanoparticles to boost the water dispersion capabilities [26–30].

Up to now, there are some scientific reports about the modification of water-dispersibility of nano-fillers via introduction of amphiphilic acrylic surfactants, to be specific, the hydrophilic molecules were attached to the surface of the nanoparticle so as to increase the aqueous dispersibility of the nanoparticle in the aqueous system [6]; Otherwise, another representative hydrophilic modification of nano-particles, as is shown below, is surface modification via organic silane coupling agent, according to the mechanism of modification, the cross-linking polymer molecules were grafted onto the nanoparticle surface through physical adsorption to enlarge the steric hindrance of the nanoparticle in water medium so as to improve the dispersibility and the stability of the nanoparticle in the aqueous system [31–35]. For instances, silicon carbide and aluminium oxide nano-particles, of which the dispersion capabilities are optimized with modification of nitrogen-containing organic silane coupling agent in waterborne system [31,32]. Summing up, if the surface modifier contains a suitable hydrophobic group, a large number of hydrophilic groups, and one or more active elements, the resulting nano-additives will have good solubility in the water medium [33,34]. It is reassuring that (3-Aminopropyl) triethoxysilane, which is prone to hydrolyze to produce 3-Aminopropylsilanetriol, afterwards, the cross-linking molecules of 3-Aminopropylsilanetriol can form strong physical adsorption with nano-particles [31,35], consequently, there is great potential of taking (3-Aminopropyl) triethoxysilane as a surface modifier applied to the hydrophilicity modification of lanthanum trifluoride nano-powders. However, to the best of our knowledge, there are few systematical works reported on the surface modification of lanthanum trifluoride nanoparticles via (3-Aminopropyl) triethoxysilane to equip them with hydrophilicity, meantime, the investigation of the impacts of hydrophilic lanthanum trifluoride nanoparticles on mechanical and tribological properties of water-based bonded solid lubricating coatings

are particularly scarce, above all, it is interesting and valuable to conduct the corresponding exploration of hydrophilic modification of lanthanum trifluoride nano-particles and further in-depth research of hydrophilic lanthanum trifluoride on the mechanical and tribological performance of water-based bonded solid lubricating coatings.

Herein, the lanthanum trifluoride nano-particles are modified by (3-Aminopropyl) triethoxysilane through surface modification methods, the dispersion of lanthanum trifluoride nano-particles before and after modification in aqueous system was compared and analyzed by means of a large number of characterization methods, and the modification mechanism was deeply investigated simultaneously; In addition, the modified lanthanum trifluoride was introduced to the preparation of the water-based bonded solid lubricant coating, and its mechanical and tribological properties were explored and discussed; Furthermore, lanthanum trifluoride nano-particles was dispersed in deionized water via taking up with three different processing methods, afterwards, by virtue of the method of controlling variables, the three different kinds of modified lanthanum trifluoride were introduced into the preparation of the identical water-based bonded solid lubricating coatings, and make a further inquiry of tribological properties of those three kinds of coatings.

2. Experimental sections

2.1. Modification procedure

The detailed information of materials refers to Supporting Information (section 1.1). As illustrated in Fig. 1, it exhibits the total modification process of lanthanum trifluoride particles, which is described specifically as follows. Firstly, 5 g of lanthanum trifluoride particles and 25 g of ethanol were weighed into a three-necked flask and mechanically stirred at 60 °C for 15 min. Specifically, the three-necked flask was placed in an oil bath apparatus, of which the specific instrument model is DF-101 S Heat collection-Constant temperature type magnetic stirrer which can achieve intelligent temperature control through internal devices such as heating and temperature measurement. Meanwhile, 5 ml of (3-Aminopropyl) triethoxysilane was added into the flask and mechanically stirred at 60 °C for 6 h within the oil bath apparatus. Afterwards, the reaction products was transferred to a centrifuge tube, and centrifuged at 5000 rpm for 5 min, the supernatant was removed to obtain the precipitation at the lower part of the

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