# Preparation and tribological properties of nanoaluminium fluoride as additives to base oil

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Cubical $AlF_3$ nanoparticles have been successfully synthesised by immersing $Ti_3AlC_2$ powders in hydrofluoric acid-assisted solvothermal reaction. The as-prepared products are characterised by an X-ray diffractometer and scanning electron microscopy. The results showed that the $AlF_3$ nanoparticles have a cubical structure and the sizes of nanoparticles are about 100 nm in side length. The tribological properties of cubical $AlF_3$ nanoparticles as a lubrication additive in 100SN base oil were investigated by a UMT-2 ball-on-disc friction and wear tester. The wear scars were measured by a common optical microscope. The results show that under determinate conditions, the friction coefficient of the base oil containing $AlF_3$ nanoparticles is lower than that of pure base oil, and the base oil containing 1 wt% $AlF_3$ samples presented good tribological performance under the load of 15 N. The formation of tribofilm on the rubbing surface could explain the good friction of $AlF_3$ nanoparticles as additives.

**1. Introduction:** In recent years, nanoscale inorganic materials with special sizes and morphologies have attracted much attention in various research fields because of their special physical and chemical properties. In the field of tribology, the application of nanomaterials as lubricating additives has received considerable attention [1]. Numerous nanomaterials have been investigated as additives in lubricating oils to increase the tribological properties, such as metals [2], metal sulphide [3, 4], metal oxides [5–7], metal carbonate [8, 9], rare earth compounds, [10, 11] borates [12, 13] and silicon dioxide [14] etc.

Among the various inorganic nanomaterials, metal fluoride nanomaterials have attracted particular interest as additives in lubricating oils because of their special physical and chemical properties [15, 16]. It is found that the excellent tribological performance can be attributed to the formation of a boundary lubricating film mainly composed of deposited nanoparticles and tribochemical reaction on the contact surfaces [17].

Aluminium fluoride ($AlF_3$) is a high bandgap insulator, and often used as promising coating materials for improving the electrochemical performances and thermal stability of Li-rich layered oxides, such as $Li(Li_{0.2}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$ [18], $Li_{1.1}(Ni_{0.15}Co_{0.1}Mn_{0.55})O_{1.95}$ [19] and $Li(Li_{0.12}Mn_{0.54}Ni_{0.13}Co_{0.13})O_2$, because $AlF_3$ can form a more stable coating layer than oxides and support faster lithium ion extraction and insertion [20]. However, to the best of our knowledge, its application as lubricating additive for base oil has rarely been investigated. Therefore the aim of the work is to explore the tribological properties of $AlF_3$ nanoparticles as base oil additives and investigate the possible lubrication mechanism of the nanoadditive in oil.

## 2. Experimental

2.1. Preparation of $AlF_3$ nanocube: Nanoscale $AlF_3$ was synthesised via immersing $Ti_3AlC_2$ powders in the hydrofluoric acid-assisted solvothermal technique. $Ti_3AlC_2$ powder was prepared by liquid magnetic stirring Ti (99.0% pure, −200 mesh), Al (99.0% pure, −200 mesh) and graphite (99% pure, ∼5 µm) powders (all from the Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) in a 2:1.2:1 molar ratio in absolute alcohol at 70°C. The mixture was heated to 1400°C for 30 min under argon. The resulting loosely held compact was crushed using a mortar and pestle.

Roughly, 3 g of $Ti_3AlC_2$ powders were then immersed in 70 ml of a 40% concentrated HF solution, The mixture was then transferred into a 100 ml Teflon-lined stainless steel autoclave and sealed, then the autoclave was placed in a preheated oven at 200°C for 48 h and naturally cooled down to room temperature. The resulting suspension was then filtered and washed with ethanol several times. Finally, it was dried in vacuum at 70°C for 12 h, and the $AlF_3$ nanocube was obtained.

2.2. Tribological properties of $AlF_3$ nanocubes as a lubrication additive: Different mass fractions of $AlF_3$ nanocubes were dispersed in the 100SN base oil with ultrasonic vibration (1600 W power, 2000 Hz frequency) for 4 h without any active reagent, and then a series of suspended oil samples were obtained. The tribological properties of the base oil containing $AlF_3$ nanocubes and the base oil were investigated using a ball-on-disc mode of a UMT multispecimen tribotester at ambient conditions. The testing of friction reduction and wear resistance was conducted at a rotating speed of 200–300 rpm and a load of 5–80 N for a sliding distance of 200 m. The material of the upper sample is a 440C stainless steel ball with a diameter of 10 mm, hardness of 62 HRC and the counterpart is a 45 steel disc of Φ30 mm × 5 mm in size.

2.3. Characterisation of $AlF_3$ samples: The X-ray diffraction patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu Kα radiation ($\lambda = 0.1546$ nm). The morphologies and structures of the samples were determined using scanning electron microscopy (SEM) (JEOL JXA-840A). The composition was characterised by energy-dispersive spectroscopy (EDS). The wear scars were measured by a common optical microscope.

## 3. Results and discussion

3.1. Characterisation of $AlF_3$ nanocubes: The structure and phase purity of the as-prepared $AlF_3$ were confirmed by XRD, as shown in Fig. 1*a*. All labelled diffraction peaks can be indexed to those of the pure phase of $AlF_3$ with lattice constants $a = 4.928$ Å, $c = 12.445$ Å, which are in good agreement with the values of the

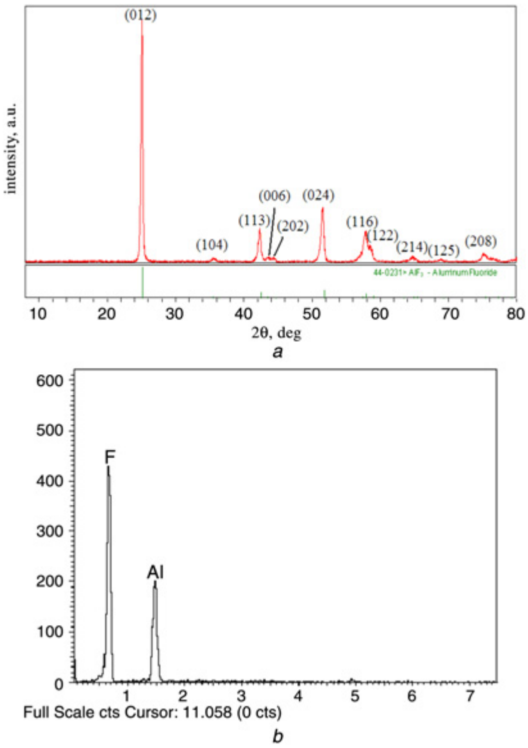


**Figure 1** *XRD pattern and EDS result of the as-prepared $AlF_3$ nanocubes*
*a* XRD pattern
*b* EDS result

standard card (JCPDS No. 44-0231). No characteristic peaks were detected from other impurities, indicating that the sample was of high purity. The EDS result (Fig. 1*b*) demonstrates that the $AlF_3$ nanocubes consist of only elements Al and F, and no other elements were observed. Furthermore, the quantification of the peaks shows that the atom ratio of Al:F is about 1:2.98, which matches well with the stoichiometric $AlF_3$.

The size and morphology of $AlF_3$ samples were identified by SEM. Figs. 2*a* and *b* show typical SEM images of the $AlF_3$ nanocubes. The low-magnification image in Fig. 2*a* shows that the samples consisted of a large number of uniform $AlF_3$ nanocubes, indicating that high-yield and good uniformity of the products could be readily achieved through this approach. From the magnified SEM image (Fig. 2*b*), it is clearly found that the sizes of the $AlF_3$ nanocubes are from 50 to 150 nm in side length.

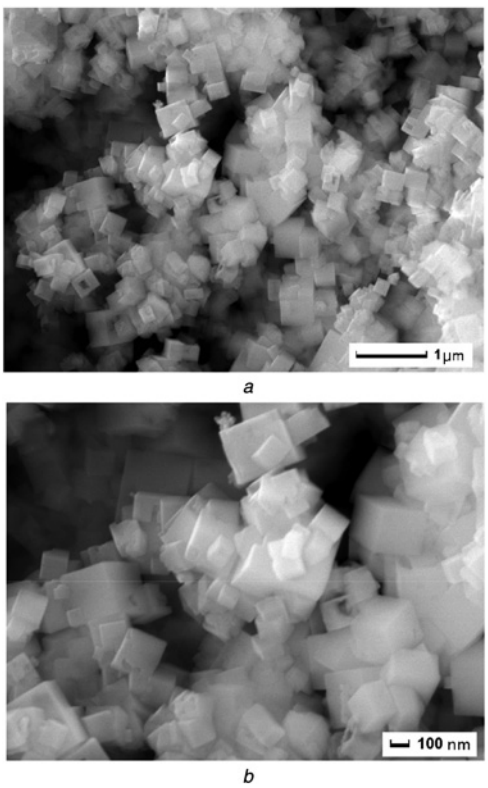


**Figure 2** *SEM images of the as-prepared $AlF_3$ nanocubes*
*a* Low-magnification image
*b* Magnified image

3.2. Effect of $AlF_3$ nanocubes on tribological properties: Fig. 3*a* shows the friction coefficients of the friction pair in 100SN base oil with the $AlF_3$ nanocubes at various concentrations. Clearly, the friction coefficients with the nanocubes were lower than those with only the 100SN base oil. In addition, the friction coefficients decreased when the $AlF_3$ nanocubes concentration increased, and the lowest friction coefficient was obtained at 1 wt%. Compared with the case with pure base oil, the friction coefficient for the oil with 1 wt% $AlF_3$ nanocubes was decreased by 16.27%, which suggests that the prepared nanoparticles could be used as friction-reducing agents for 100SN base oil.

Fig. 3*b* shows the wear scar width (WSW) of the friction pair at various $AlF_3$ nanocubes concentrations. The WSW slightly decreased with the introduction of $AlF_3$ nanocubes (0–1 wt%), then increased with further increase of $AlF_3$ nanocubes ( ≥2 wt %). The lowest WSW was obtained at 1 wt% nanocubes, the WSW in this system decreased by 1.5 wt% compared with the base oil system. It is well known that the perfect cross-linked soap fibre network structure of base oil is conducive to the transmission of lubricant, and is very important for lubrication reliability, also leading to a mixed lubrication and boundary lubrication

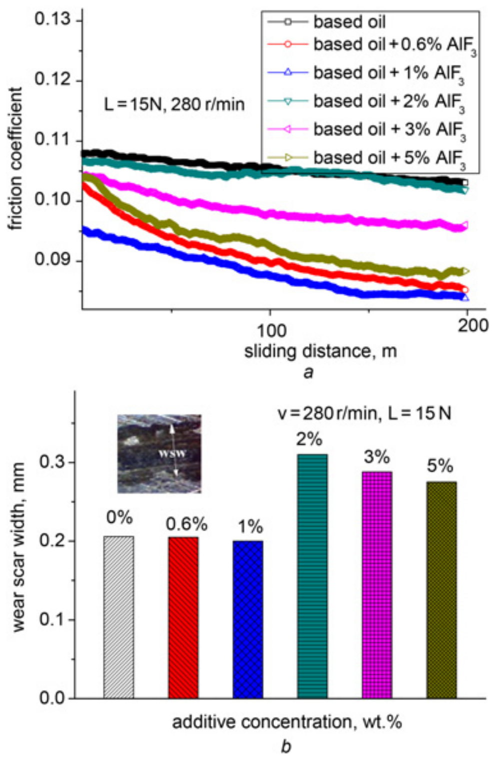


**Figure 3** *Friction coefficient against sliding distance and WSW on disc specimens lubricated with different concentrations $AlF_3$ in 100SN base oil*
*a* Friction coefficient against sliding distance
*b* WSW with different concentrations of $AlF_3$



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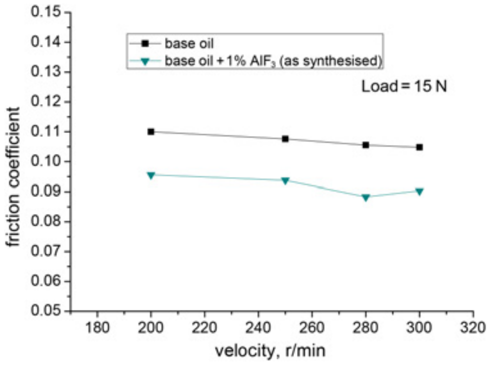


**Figure 4** *Variation of average friction coefficients for the 100SN base oil and the 100SN base oil containing 1 wt% $AlF_3$ nanocubes at different rotating speeds*

state. Therefore, when the amount of the nanoparticles is higher (e.g. ≥2 wt%), nanoparticles in the base oil could destroy the stability of the 100SN base oil colloid system through the interrupted cross-linked soap fibre network structure and block the formation of oil film [1], resulting in a higher friction coefficient. Therefore an appropriate amount of the $AlF_3$ additive is important for the improvement of tribological performance of the base oil.

Fig. 4 shows the average friction coefficient against rotating speed. It can be seen that the addition of $AlF_3$ nanocubes is able to improve the friction reduction ability of the base oil at different rotating speeds; the average friction coefficient of the base oil with 1 wt% $AlF_3$ nanocubes is close to 0.09, whereas it is 0.11 for the 100SN base oil. This meant that the addition of $AlF_3$ nanocubes to the base oil resulted in nearly 17% reduction for the friction coefficient of the base oil. Therefore the base oil containing the $AlF_3$ nanocubes additives has better tribological properties.

The wear scar of a disc after rubbing is shown in Fig. 5*a* (the base oil) and Fig. 5*b* (the base oil containing 1 wt% $AlF_3$ nanocubes). It

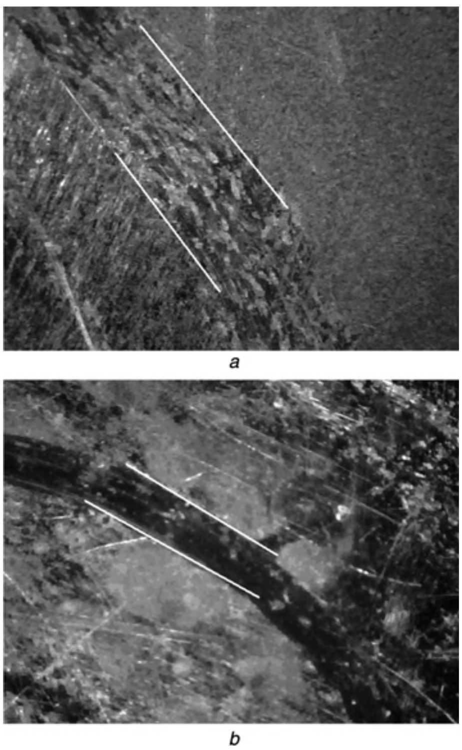

**Figure 5** *Wear scar of disc*
*a* 100SN base oil
*b* 100SN base oil containing $AlF_3$ nanocubes

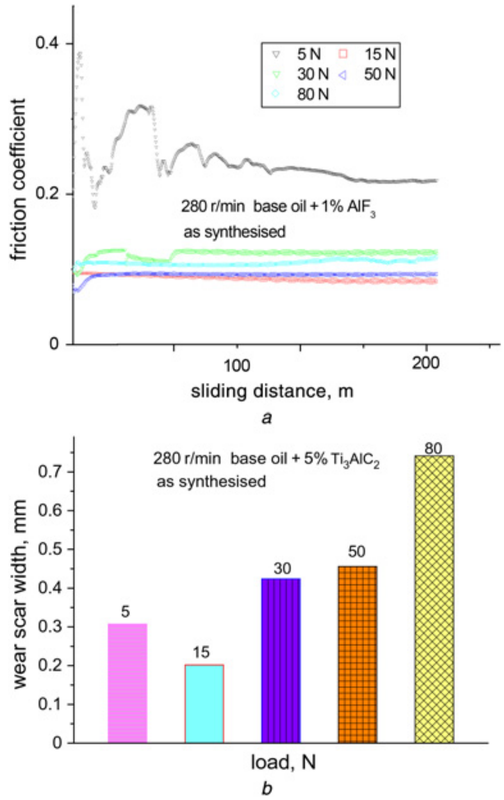


**Figure 6** *Friction coefficient against sliding distance, and WSW of base oil mixed with 1 wt% $AlF_3$ nanocubes additive under different loads at 280 r/min*
*a* Friction coefficient against sliding distance
*b* WSW under different loads

can easily be observed from Fig. 5*a* that the wear scar has evidently rough, thick and deep grooves on the surface lubricated with only 100SN base oil, with almost no signs of the initial surface, that is, the grinding scratches, and the abrasive grooves, clearly indicate much more localised and highly stressed contacts during sliding. Compared with the wear scar of the base oil, the wear scar of the base oil containing 1 wt% $AlF_3$ nanocubes was flat and smooth, as shown in Fig. 5*b* where the mechanical damage is almost negligible.

Fig. 6*a* shows the friction coefficients against sliding distance curves of base oil containing 1 wt% $AlF_3$ nanocubes under different normal loads (5–80 N). Under a lower load (e.g. 5 N), the friction coefficient is unstable and varies in the range of 0.18–0.3. However, under a load in the range of 15–80 N, the friction coefficient of $AlF_3$ nanocubes is stable and about 0.09–0.12. Fig. 6*b* shows the WSW of 100SN base oil containing 1 wt% synthesised $AlF_3$ at different loads. The WSW decreased with the increase of the load in a certain scale, and then increased. The lowest WSW was obtained under 15 N because of the formation of tribofilm in the friction process. However, at the higher load, the formed tribofilm can be easily damaged, resulting in a high WSW [21].

**4. Conclusion:** $AlF_3$ nanocubes with side lengths in the range of 50–150 nm were successfully synthesised via solvothermal reaction by immersing $Ti_3AlC_2$ powders in hydrofluoric acid. The 100SN base oil with the addition of $AlF_3$ nanocubes showed good friction-and-wear properties. The tribological experiments indicated that the lubricating performance was able to be improved by the introduction of $AlF_3$ nanocubes as additives to base oil. The optimal concentration of the nanoparticles is 1 wt%, which exhibits excellent friction-reducing and anti-wear properties. The excellent tribological properties indicate that the as-prepared $AlF_3$ nanocubes will be useful for its further industrial application as a good oil additive in the future.

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