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# **A Study of Tribological Properties of Water-Based Ceria Nanofluids**

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## **ABSTRACT**

This paper presents an investigation on the potential tribological properties of the water-based cerium dioxide nanofluids. The nanofluids with different nanoparticle concentrations were prepared in a materials laboratory. A stable dispersion of nanoparticles in the fluids was achieved with an appropriate percentage of surfactant sorbitan monostearate. The stability of particle dispersion was studied using a Zeta-potential measuring device. Additive conglomerate size in the nanofluids was measured using Dynamic Light Scattering (DLS) device. It has been observed that the dispersibility of nanoparticles played an important role in the frictional properties of the nanofluids. The tribological properties of the water-based nanofluids were evaluated using a Pin-on-disc tester under different loading conditions. A significant improvement on tribological properties of the water-based cerium dioxide nanofluids was observed. The worn surfaces of the contact elements were characterised using SEM and a Nano-tester. According to the test results, the significant reductions of the friction coefficient and the anti-wear property of water-based cerium dioxide nanofluids are attributed to the deposition of nanoparticles on worn contact surfaces.

***Keywords: Nanofluids; Rare Earth Nanoparticles, Dispersibility; Water; Friction; Wear***

## **INTRODUCTION**

Nanofluid technology is a relatively new field although nanofluids have become attractive due to their enhanced thermal conductivity over conventional fluids. In particular, little information in tribological properties of nanofluids is available (1-2). The majority of published papers are focused on oil based nanofluids and nano lubricants. Many experiments on numerous inorganic nanoparticles have been done (3-15). Owing to their outstanding tribological properties and good environmental-friendly feature compared with the traditional organic lubricant

additives that contain P, S, Cl, elements, inorganic nanoparticles certainly become more desirable in future lubrication applications. Tribological properties of metal oxide nanoparticles such as  $\text{TiO}_2$  (16-18),  $\text{SiO}_2$  (19),  $\text{Al}_2\text{O}_3$  (20),  $\text{Fe}_2\text{O}_3$  (21),  $\text{ZnO}$  (22),  $\text{CuO}$  (23) and  $\text{ZrO}_2$  (24) used as oil lubricant additives have all been investigated. Considerable improvement in the tribological performance of the base oils have been demonstrated when these nanoparticle additives are used. Furthermore some of the rare earth metal oxides have also been studied. Together with  $\text{CaCO}_3$  nanoparticles,  $\text{CeO}_2$  nanoparticles were tested in 40CD oil (25). It is reported that the additional  $\text{CaCO}_3$  and  $\text{CeO}_2$  nanoparticles in 40CD oil have improved anti wear property of 40CD oil by 33.5% and friction reduction property by 32% respectively (25).

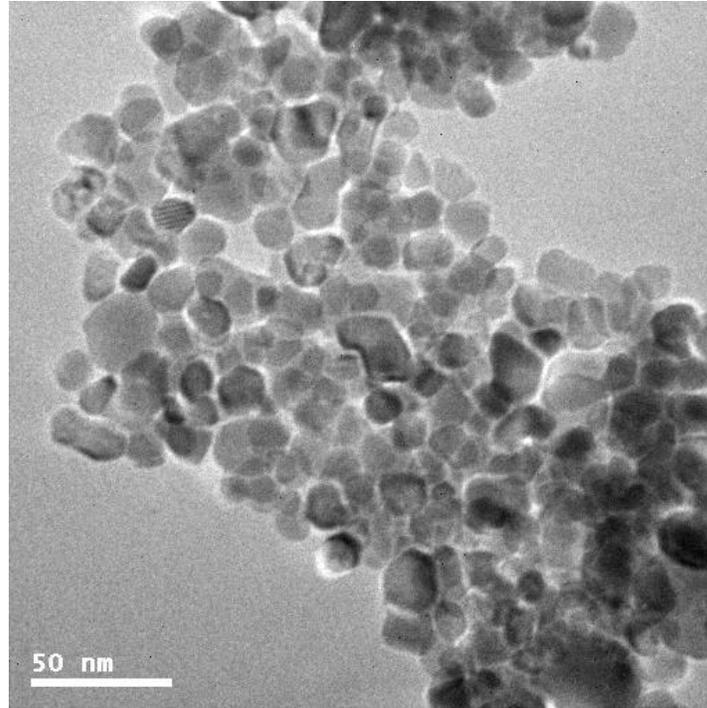
However, very limited research has been done about inorganic nanoparticles employed as additives in water-based nanofluids, despite their great potential in engine cooling/vehicle thermal management, polymer, wood, metal, ceramic, glass machining and similar circumstances where oil contamination must be avoided. A recent investigation in friction and wear characteristics of water-based  $\text{ZnO}$  and  $\text{Al}_2\text{O}_3$  nanofluids has reported that nanoparticles have a great effect on the friction and wear characteristics of the fluids (2). This is echoed in the findings that the tribological properties of oleic acid modified  $\text{TiO}_2$  nanoparticles in water made huge improvements on the maximum non-seizure load and friction and wear reduction were shown in a self-mating steel contact experiment (26). Similar lubricating properties were also found by S. Radice and S. Mischler using  $\text{Al}_2\text{O}_3$  nanoparticles in aqueous suspensions (27). Third body effect of nanoparticles was considered to be the possible mechanism for the tribological improvement (28). Nanoparticles in oil based lubricants tend to form agglomerates due to their high surface energy. Distribution of the nanoparticles in oil based nanofluids and nano lubricants plays a vital role in dictating many important constitutive properties (1-2, 4, 7). However, little information is available for the effects of dispersibility of ceria nanofluids on the tribological properties of the water-based  $\text{CeO}_2$  nanofluids.

In this study, the tribological properties of the water-based cerium dioxide nanofluids were investigated and both the friction coefficient and the wear of the nano fluids were characterised. The effects of both dispersibility of  $\text{CeO}_2$  nanoparticles in the water-based nanofluids and nanoparticle concentrations in the nanofluids were studied together with the mechanisms of friction reduction and anti-wear behaviour.

## EXPERIMENTAL DETAILS

### Nanoparticles and Surfactant

CeO<sub>2</sub> nanoparticles of 10-40nm diameters and 99.9% purity (Shandong Yitong, China) were employed, as shown in Fig.1. Deionised water was used as base media and sorbitan monostearate as one of the widely used surfactants was used to improve the dispersibility of the nanoparticles in water.



**Fig.1 CeO<sub>2</sub> nanoparticles under TEM.**

### Nanofluids Preparation and Characterisation

The tested nanofluids were composed of the rare earth metal nanoparticles (Cerium Oxide) and deionised water with or without surfactant. Both CeO<sub>2</sub> nanoparticles and a suitable amount of surfactant sorbitan monostearate were added into the deionised water. The blend was firstly heated up to 55°C and dispersed with an ultrasonic homogenizer for two minutes. Subsequently, the mixture was heated up to 70°C and maintained at the temperature for one hour while stirring using a rotor–stator homogenizer (Sonics VC 750) with a speed of 10K rpm. Finally, the stable milky colour nanofluids were achieved which were employed for the tests within 10 minutes. The nanofluid sample with low additive concentration: water+0.05wt% CeO<sub>2</sub>+1% surfactant was prepared for particle size and zeta-potential measuring in order to ensure a good accuracy (low

additive concentration is required). For the tribology tests, the water-based nanofluids with different nanoparticle concentrations were prepared in order to investigate the effects of nanoparticle concentration on the tribological properties of the nanofluids. The surfactant concentration was doubled to 2wt% in order to ensure a good stability of the suspensions when various amounts of CeO<sub>2</sub> nanoparticles were applied. All additive concentrations in this study are presented in weight ratio. No sedimentation was observed in the prepared nanofluids for four days.

Particle conglomerate size in the nanofluids with and without surfactant was measured using Dynamic Light Scattering (DLS) (*Malvern Zetasizer-Nano Series*). Also, since Zeta-potential is known as an important parameter that affects the stability of suspension, Zeta-potential of the fluids with and without surfactant was obtained to reflect the magnitude of the repulsion or attraction between particles.

### **Friction and Wear Tests**

The antiwear and friction reduction properties of the water-based CeO<sub>2</sub> nanofluids with and without surfactant sorbitan monostearate were evaluated using a POD-2 Pin-On-Disc Tester. Each test was carried out with the sliding speed of 50mm/s for 30 minutes at room temperature. The bearing balls of 5mm diameter used in the tests were made of AISI52100 chrome steel with HRc of 60 – 67, and have a surface roughness Ra of 20nm. The disc was made of the identical material, with 27mm in diameter and 12mm in thickness. The sample discs were polished using a p1200 abrasive paper to achieve a uniform surface roughness Ra of around 30nm. Before and after each test, both bearing balls and discs were cleaned with acetone in an ultrasonic water bath for five minutes.

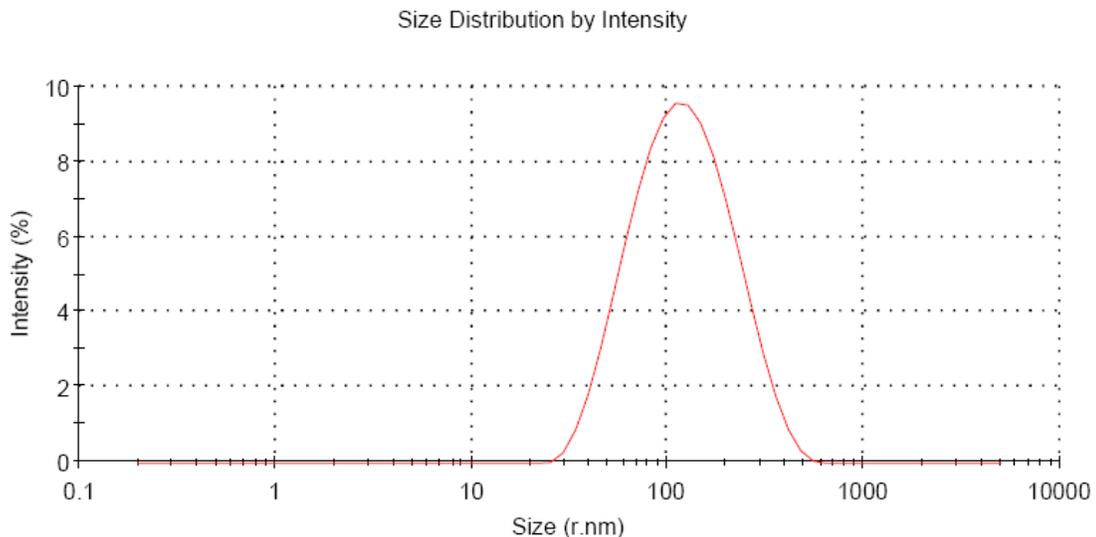
### **Analysis of the Worn Surfaces of the Contact Elements**

The depth of the wear tracks was determined by a Nano-indentation/scratching tester (Micro Material Ltd). The contact load and scanning speed employed in the tests were 0.1mN and 5µm/s respectively. The indenter used for scanning is a conical indenter with 60 degrees head angle and a tip size of 5µm radius. The morphology and the elemental distribution on the worn surface of the tested bearing balls were studied using JEOL-6100 scanning electron microscope (SEM) equipped with energy dispersive spectra (EDS).

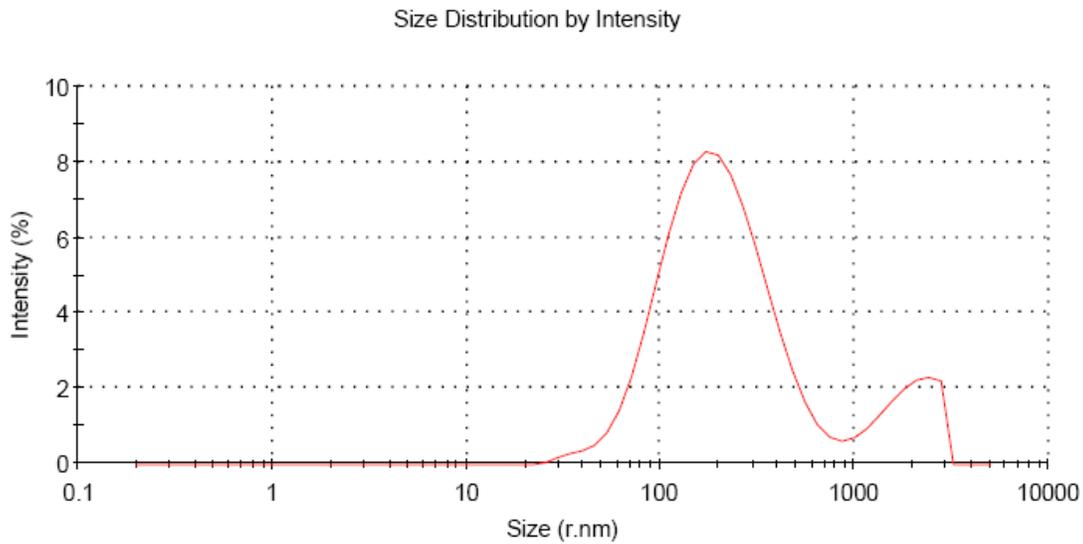
## RESULTS AND DISCUSSION

### Conglomerate Size of Ceria Nanoparticles and Zeta-potential

It is well known that particle size in a lubricant makes a huge difference in most of lubrication applications. The Conglomerate size of CeO<sub>2</sub> nanoparticles in the nanofluids was measured by zeta-potential apparatus. Figs.2-3 illustrate the average conglomerate size of 0.05wt% CeO<sub>2</sub> nanoparticles in the deionised water with and without 1wt% surfactant. Before each measurement, the samples were stirred vigorously using an ultrasonic homogeniser (KINEMATICA PT 10-35 GT). The average conglomerate size of CeO<sub>2</sub> nanoparticles dispersed in the fluids with 1wt% surfactant is around 110nm in radius. By contrast, the average conglomerate size of the CeO<sub>2</sub> nanoparticles in water without surfactant was 193.7nm in radius. CeO<sub>2</sub> nanoparticle clusters formed in the fluids with surfactant have a narrow size span. As shown in Fig.2, with surfactant, there is only one peak appeared in the distribution diagram, which suggests a uniform distribution. However, without surfactant, CeO<sub>2</sub> nanoparticle clusters in the fluids have a much wider size span. As shown in Fig.3, two peaks appear in the distribution diagram and, the second peak indicates a size distribution of nanoparticle cluster with more than 2000nm radius.



**Fig.2 Size distribution of particle conglomerate of water+0.05wt% CeO<sub>2</sub>+1wt% surfactant (Sorbitan monostearate).**



**Fig.3 Size distribution of particle conglomerate of water + 0.05wt% CeO<sub>2</sub> without surfactant.**

PDI (Polydispersity index) and correlation function intercept also confirmed the dispersibility improvement of nanoparticles in fluids using surfactant. PDI readings in Table 1 indicate the regularity of conglomerate size in the fluids. The lower PDI value confers a better consistency of conglomerate size. The PDI value of the fluids, water+0.05wt% +1wt% surfactant, was 0.252 and is much lower than 0.415 of water+0.05wt% CeO<sub>2</sub>. Therefore, it is evident that with surfactant, conglomerate size of CeO<sub>2</sub> in fluids was significantly reduced and also became more uniformly distributed. Correlation function intercept is the signal to noise ratio obtained for the measurement. Correlation function intercept of more 0.8 for both suspensions indicate good data quality.

**Table 1 Dispersibility of nanoparticles in the fluids with and without surfactant**

Water solution	PDI test results	Zeta-potential value	Correlation function intercept	Average conglomerate size (radius)
Water+ 0.05wt% CeO <sub>2</sub>	0.415	+19.7 mV	0.81	193.7nm
Water+0.05wt% CeO <sub>2</sub> +1wt% surfactant	0.252	+44.8 mV	0.88	110nm

Absolute Zeta-potential value of the fluids, water+0.05wt% CeO<sub>2</sub>, was measured to be 19.7mV. Comparatively, the number was increased to 44.8mV for the fluids of water+0.05wt% CeO<sub>2</sub>+1wt% surfactant. Surface charges caused by absorption of ions and molecules generate an electrostatic repulsion force between particles. For small particles, the electrostatic repulsion force can partially counteract gravitation and reduce agglomeration and sedimentation of particles. The similar phenomenon has been observed before (17). Therefore, a higher absolute value of zeta-potential presents a better stability. A greater absolute Zeta-potential value for the fluids, water+0.05wt% CeO<sub>2</sub>+1wt% surfactant, suggests that the stability of CeO<sub>2</sub> nanoparticles in the water-based fluids has been greatly improved by an employment of surfactant. It was also observed that the stabilization of surfactant is reversible. As shown in Table 2, after 24 hours, the absolute Zeta-potential value of the prepared fluids, water+0.05wt% CeO<sub>2</sub>+1wt% surfactant, was reduced to 36.8mV and further reduced to 35.4mV after 96 hours.

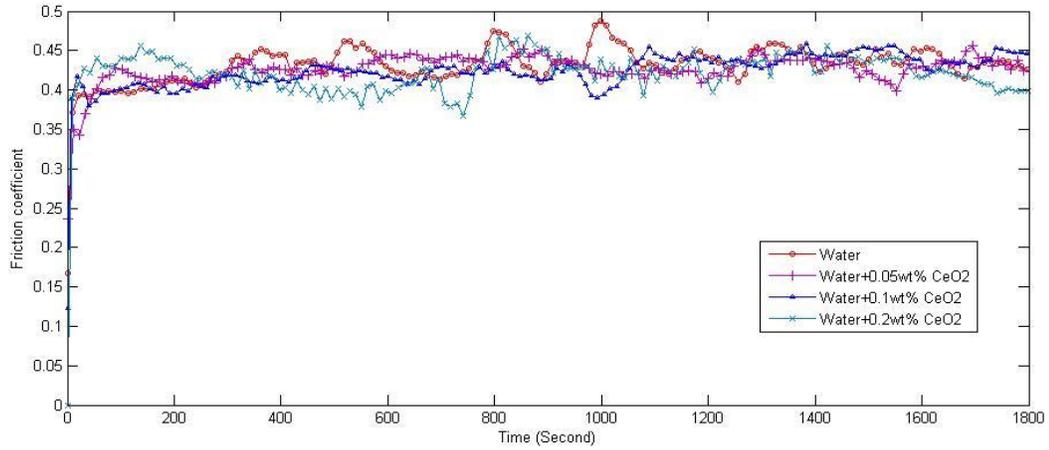
**Table 2 Reduction of Zeta-potential value with time**

Hours after dispersion	0 hour	24 hours	96 hours
Zeta potential reading	+48.8mV	+36.8mV	+35.4mV

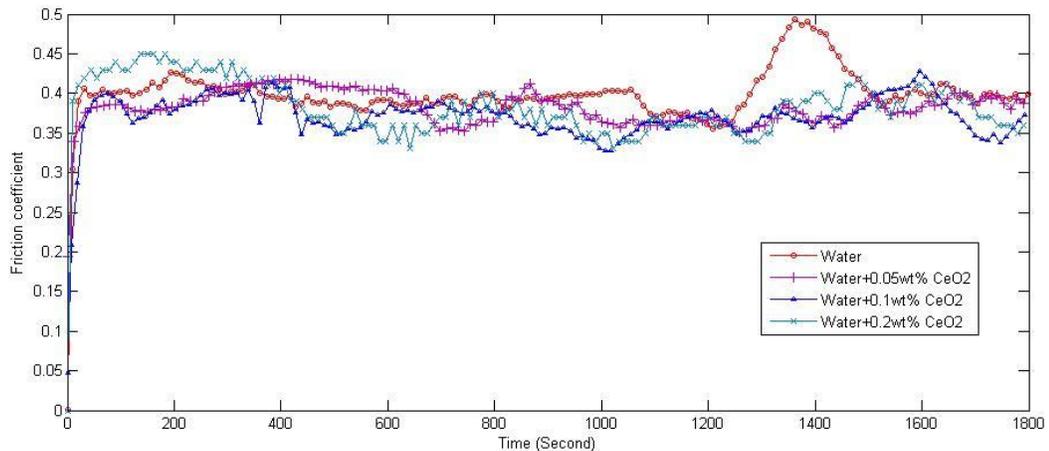
### **Friction Coefficient of the Nanofluids**

Figs.4-5 illustrate how the different nanoparticle concentrations in the fluids affect the friction coefficient at the loads of 10N and 20N without the surfactant. The friction coefficient of the pure deionised water was also obtained as a reference. Evidence collected has shown that at both loading conditions, without the surfactant, the water-based CeO<sub>2</sub> nanofluids did not show any obvious effect on the friction coefficient. A high friction coefficient of more than 0.4 was obtained in all lubricant samples without surfactant. After the tests, the nanoparticle sedimentation was also found in all lubricant samples without the surfactant. It suggests that the agglomeration of nanoparticles accelerates their sedimentation in water, which hugely reduces the concentration of nanoparticles in the fluids. The agglomeration also causes nanoparticles to

form much bigger sized clusters, which can increase the asperity level between the contacting surfaces (29).



**Fig.4 Friction coefficient of the water-based nanofluids with different CeO<sub>2</sub> nanoparticles concentration (without surfactant) under 10N load.**

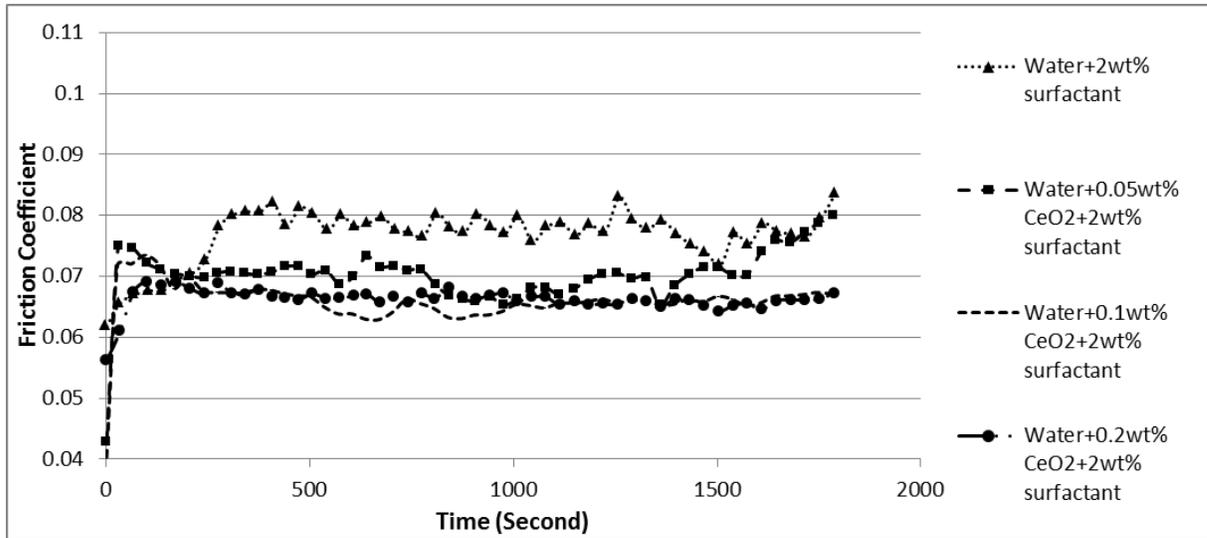


**Fig.5 Friction coefficient of the water-based nanofluids with different CeO<sub>2</sub> nanoparticles concentration (without surfactant) under 20N load.**

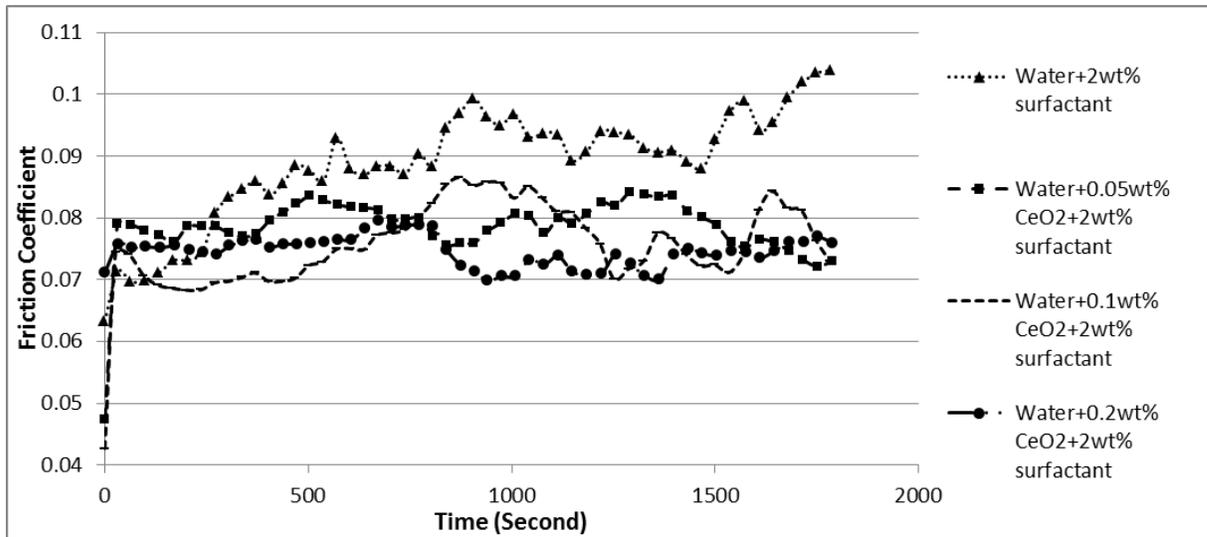
Friction coefficients of the water-based CeO<sub>2</sub> nanofluids with 0.2wt% CeO<sub>2</sub> nanoparticles dispersed with surfactant are shown in Figs.6-7. It is evident that at both loading conditions of 10N and 20N, with 2wt% surfactant, the friction coefficients of the water-based CeO<sub>2</sub> nanofluids

with 0.2wt% CeO<sub>2</sub> were reduced sharply to below 0.1. Compared with the friction coefficient of the same nanofluids without surfactant shown in Figs.4-5, a reduction over 75% was observed.

Because surfactants are used as an additive in the fluids, and very often they can also contribute to the tribological improvement (30). Therefore, it is essential to clarify whether CeO<sub>2</sub> nanoparticles are responsible to the reduction of friction coefficient shown in Figs.6-7. As illustrated in Fig.6, water+2wt% surfactant gives a friction coefficient around 0.079 at a load of 10N. All suspensions containing CeO<sub>2</sub> nanoparticles demonstrate lower friction coefficient at the same condition. The lowest friction coefficient of around 0.067 was observed when water+0.2% CeO<sub>2</sub>+2wt% surfactant was tested, and compared with that of water+2wt% surfactant, a reduction of 15% in friction coefficient was achieved. Water+0.1% CeO<sub>2</sub>+2wt% surfactant delivered the similar friction reduction performance with water+0.2% CeO<sub>2</sub>+2wt% surfactant, however more fluctuations on friction coefficient were found in the experiment of using water+0.1% CeO<sub>2</sub>+2wt% surfactant. Under a load of 20N, as shown in Fig.7, the similar friction reduction phenomenon was also observed. Water with both CeO<sub>2</sub> nanoparticles and 2% surfactant has outperformed water with 2% surfactant alone. Water+0.2wt% CeO<sub>2</sub>+2wt% surfactant demonstrated the best overall friction reduction property and a 10% reduction of friction coefficient was found in the first 900 seconds, compared with water+2wt% surfactant. In the second 900 seconds, the reduction went up to more than 20%. Much stronger fluctuations on friction coefficient were obtained in the experiments under 20N load due to the more intensified stress. It is evident that much less oscillation can be noticed for the lubricants with nanoparticles as shown in Figs.6-7. That is possibly attributed to the third body effect of nanoparticles. Entrapped nanoparticles groups between two surfaces work like a cushion, which may be able to smoothen the rough surfaces, diminish direct contact and reduce adhesion friction.



**Fig.6 Comparison of friction coefficient of water with surfactant and the water-based CeO<sub>2</sub> nanofluids with surfactant under 10N load.**



**Fig.7 Comparison of friction coefficient of water with surfactant and the water-based CeO<sub>2</sub> nanofluids with surfactant under 20N load.**

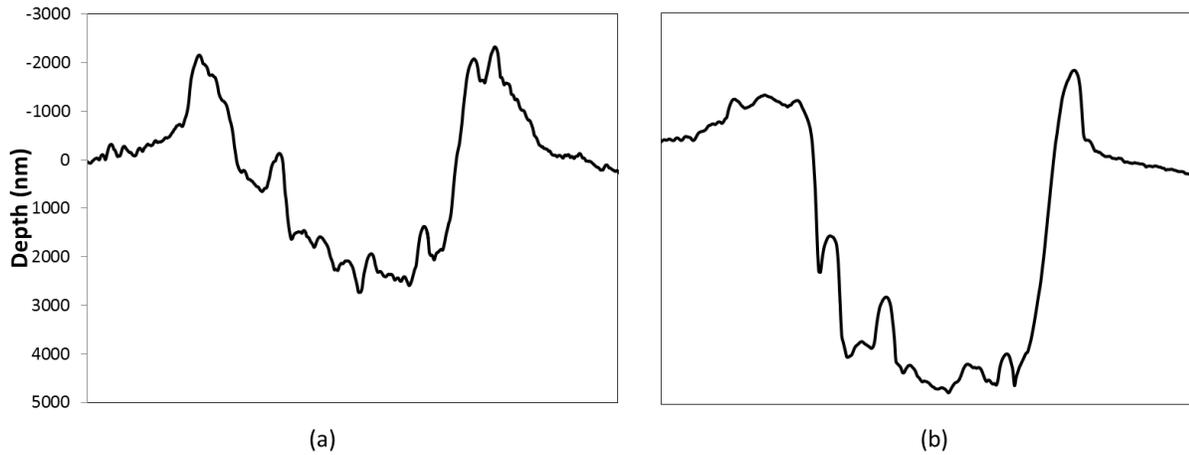
### Anti-wear Property

The worn surface scanning with a nano-indentation tester was performed to measure the topography of the wear tracks of the sample discs in order to reflect the anti-wear ability of the

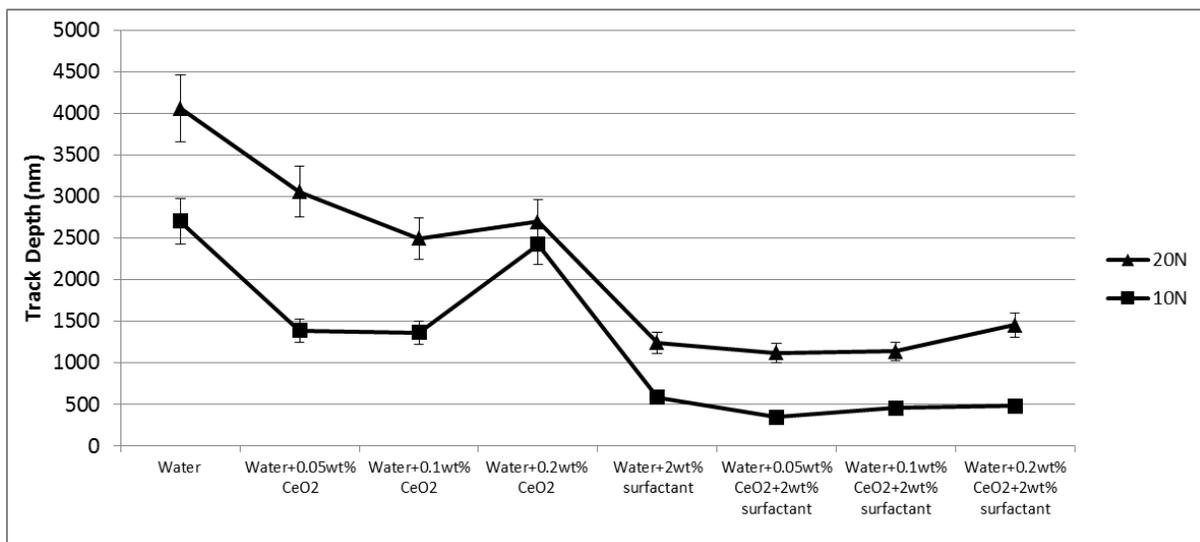
fluids. Fig.8 illustrates the typical depth profiles of the wear tracks generated on the discs during a test. The central positive reading peaks in Fig.8 indicate the depths of two wear tracks on discs.

The influence of CeO<sub>2</sub> nanoparticles and surfactant on the depth of wear tracks is shown in Fig.9. It is evident that the existence of the nanoparticles considerably reduced the depth of the wear tracks. Without surfactant, the smallest track depths of 1365nm at a load of 10N and 2495nm at 20N were found after the water-based CeO<sub>2</sub> nanofluids with 0.1wt% CeO<sub>2</sub> had been tested. Compared with the depth of wear track lubricated with water only, 49% and 38% reductions of the depth from the nanofluids were observed at the loading conditions of 10N and 20N respectively. However, when the particle concentration of the nanofluids was increased further to 0.2wt%, without surfactant, the water-based nanofluids with 0.2wt% CeO<sub>2</sub> caused even higher value of the track depth than that of the water-based nanofluids with 0.1wt% CeO<sub>2</sub> at both loading conditions.

When 2% surfactant was used, only slight reductions were obtained with the employment of CeO<sub>2</sub> nanoparticles. However, the deterioration on the anti-wear performance caused by 0.2wt% CeO<sub>2</sub> was effectively limited with the utilization of surfactant. It is suggested that without surfactant, agglomeration caused by excessive content of nanoparticles is the possible reason for the increase of wear track depth. Agglomeration of particles may form abrasive clusters between sliding pairs, and results in an increase of wear. The improved disparity of the nanoparticles achieved by the application of surfactant reduced the extent of agglomeration, and therefore a better anti-wear performance can be observed. As a popular surfactant, sorbitan monostearate itself has excellent friction and wear reduction ability when it is used as an additive in base lubricants (30-32). This could be the reason for the weakened influence of CeO<sub>2</sub> nanoparticles on the reduction of wear.



**Fig.8** Depth profiles of wear tracks: (a)tested in pure water and (b)tested in water-based nanofluids with 0.1wt% CeO<sub>2</sub>.

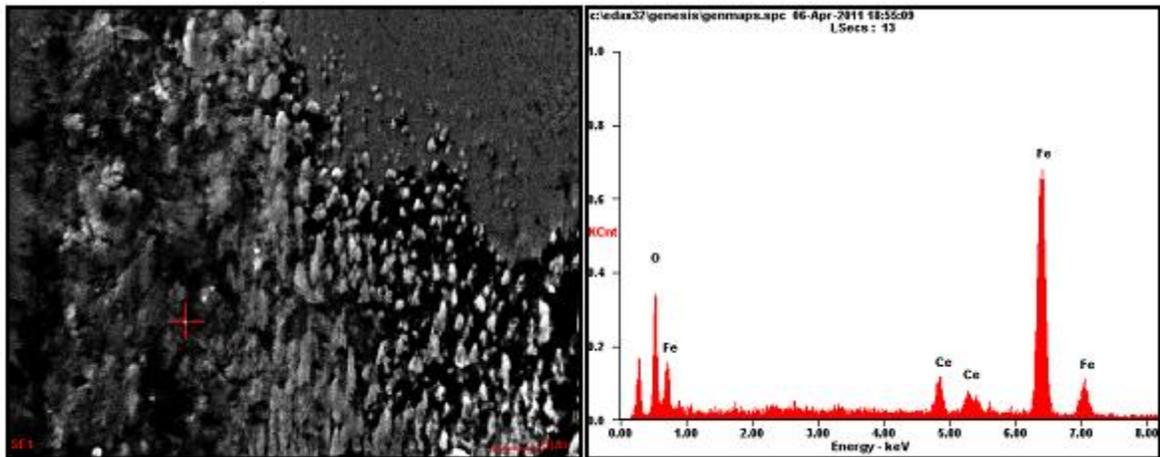


**Fig.9** Depth of wear tracks versus different fluids with different CeO<sub>2</sub> nanoparticles concentration and surfactant.

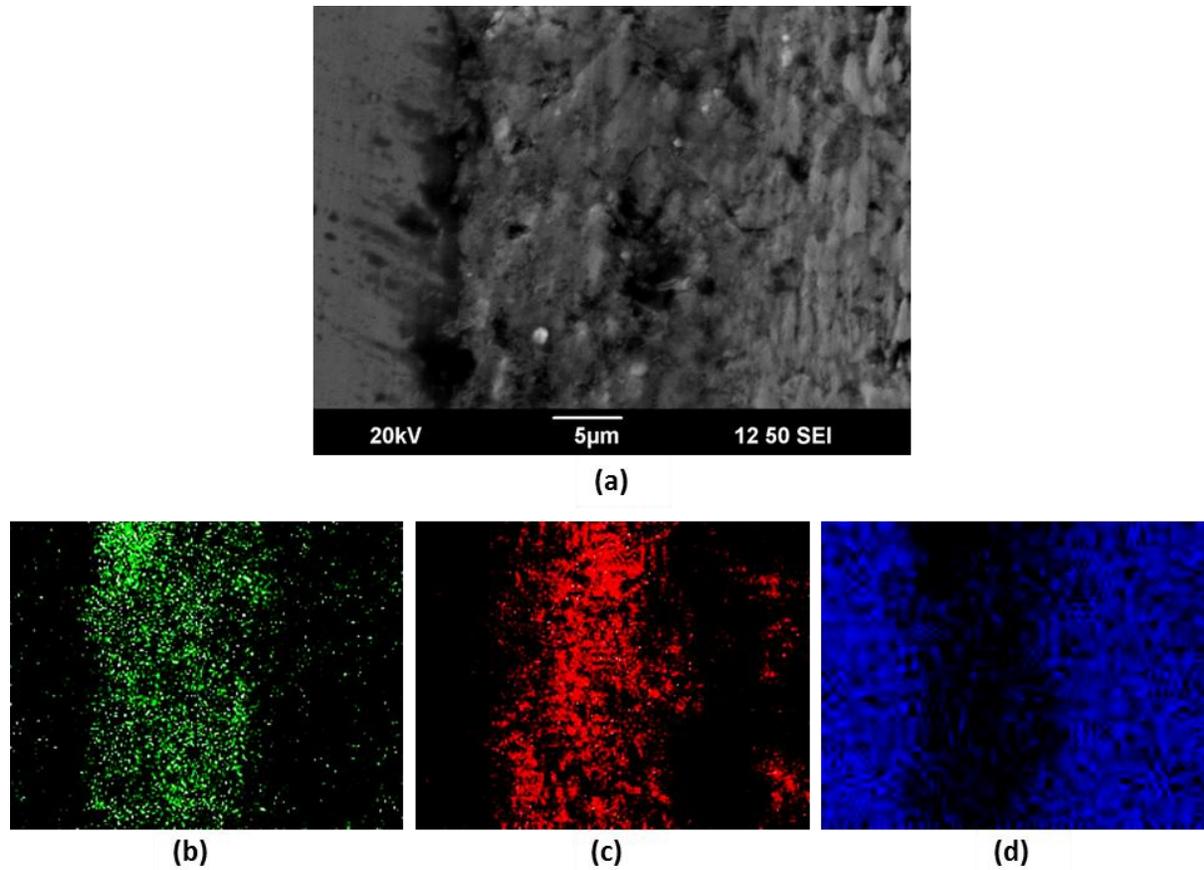
### SEM and EDS Analysis

Fig.10 shows the SEM morphology of the worn surface tested with the water-based CeO<sub>2</sub> nanofluids with 0.2wt% CeO<sub>2</sub>. The elemental distribution analysis was also performed using SEM equipped with EDS. As shown in Fig.10, CeO<sub>2</sub> nanoparticles were found on worn surface

after Pin-on-disc experiment. Element mapping shown in Fig.11 has also confirmed the  $\text{CeO}_2$  nanoparticle distribution on the worn surface. Both Ce and O elements are consistently distributed in the worn area. Fe element indicates a relatively weaker signal in the area where Ce and O elements are densely accumulated. The irregular distribution of the elements is possibly due to the uneven contact stress distribution on worn surface introduced by the geometrical shape of the bearing ball. Fig.10 indicates that  $\text{CeO}_2$  nanoparticles were entrapped and accumulated between contacting surfaces during the tests. As discussed above, it can be suggested that under a friction force,  $\text{CeO}_2$  nanoparticles are firstly entrapped and then deposited on to the contact interfaces due to shear effect. The third body effect of  $\text{CeO}_2$  nanoparticles between the contact surfaces can reduce direct metal contact and consequently adhesion. The possible third body effect resulted from the deposition of  $\text{CeO}_2$  can also fill up valleys on the surfaces, make up material loss and therefore, protect the contacting metal pairs.



**Fig.10 SEM morphology and element analysis of worn surface.**



**Fig.11 Element distribution on worn surface: (a) SEM morphology (b) distribution of Ce element; (c) distribution of O element; (d) distribution of Fe element.**

## CONCLUSIONS

In this work, the tribological properties of the water-based  $\text{CeO}_2$  nanofluids with and without surfactant have been investigated and the following conclusions can be drawn:

In this work, the tribological properties of  $\text{CeO}_2$  nanoparticles suspended in water with and without surfactant have been investigated and the following conclusions can be drawn:

- a. The dispersibility of  $\text{CeO}_2$  nanoparticles in water was improved by the employment of surfactant sorbitan monostearate. With surfactant, the average particle conglomerate size of 0.05wt%  $\text{CeO}_2$  nanoparticles dispersed in water has been reduced from 193.7nm to 110nm. Measurement of the zeta-potential also confirmed the enhancement of the stability of suspension brought by surfactant.

- b. With the employment of surfactant sorbitan monostearate, CeO<sub>2</sub> nanoparticles in the water with improved dispersibility have demonstrated the considerable friction reduction performance. With 2wt% surfactant, the additive of 0.2wt% CeO<sub>2</sub> in water delivered a reduction on friction coefficient of up to 20%.
- c. Without surfactant, CeO<sub>2</sub> nanoparticles did not indicate any ability to reduce friction in the lubrication system. The agglomeration and sedimentation of ceria nanoparticles may be responsible for their poor lubricating property in water. However the anti-wear property of water was improved effectively when 0.05% and 0.1% CeO<sub>2</sub> nanoparticles were applied. A reduction on wear track depth of up to 49% was observed.
- d. Third body effect is the possible explanation for excellent anti-wear performance of the CeO<sub>2</sub> nanoparticles. Even when surfactant is not applied, a substantial anti-wear property was still demonstrated by the reduction of wear track depth of sample discs.

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