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Dispersion effect and auto-reconditioning performance of nanometer WS_2 particles in green lubricant

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Abstract. **This paper reported on dispersion effect and dispersing techniques of nanometer WS_2 particles in the green lubricant concocted by us. And it also researched on auto-reconditioning performance of nanometer WS_2 particles to the abrasive surfaces of steel ball from four-ball tribology test and piston ring from engine lubrication test. The treated and untreated nanometer WS_2 particles were analysed by infrared spectrum. And the elementary component and interior elementary distribution of abrasive surface repaired by nanometer WS_2 particles were analysed by multifunction electron spectrometer. The results showed that the combinative method of ultrasonic dispersion, mechanical agitation and surface modification could improve the dispersion uniformity and stability of nanometer WS_2 particles in the green lubricant effectively. And the optimal ratio of the mass between surface modifier and nanometer WS_2 particles was 1 : 2·5, the optimal treating time was 5 h. And IR analysis indicated that surface modifier could react with hydroxide radicals on surfaces of WS_2 particles and modify the surfaces, and the long lipophilic groups on surfaces of nanometer WS_2 particles could stretch in oil adequately and form steric hindrance layers between particles which prevented particles from conglomerating and depositing. In addition, tribological tests and surface analysis indicated that there were WS_2 adsorption film and reaction film on abrasive surfaces during the tribological tests, which could fill and level up the furrows on abrasive surfaces. As a result, the abrasive surfaces were repaired effectively by nanometer WS_2 particles.**

Keywords. **Nanometer WS_2 particles; dispersion effect; auto-reconditioning performance.**

1. Introduction

Along with the increasing update of automobiles, the compact design and high efficient development of engine bring forward higher requirements to the performance of lubricating oil. Nanometer solid lubricating materials with excellent extreme pressure and antiwear performance can improve the performances of traditional lubricating oils observably and prolong engine's service life ulteriorly. For example, an American company prepared a new type of engine lubricating oil viz. PetrolMoly, in which nanometer MoS_2 particles were added, the traffic test results showed that, compared to traditional engine oil, PetrolMoly could decrease the emission of NO_X by 73% and fuel consumption by 37%, and increase the fuel economy by about 10% (Cornitius 1998; Gaskell 1998).

WS_2 is one of the most lubricous materials known to people. Its microstructure and characteristic are similar to that of MoS_2. A lot of references of literature show that WS_2 can offer a low friction coefficient of 0·03 that the other solid lubricating materials cannot realize. Therefore, WS_2 has a better lubrication performance than that of others. Moreover, WS_2 can be applied in a wide temperature range from –270–650°C under normal atmosphere or from –188–1316°C in vacuum, and it also has an excellent load-carrying property under a high load of 21 MPa. So WS_2 is used in a wide field of spaceflight, aviation and war industry abroad (Prasad and Zabinski 1993; Prasad *et al* 2000; Miyake *et al* 2004). And our past researches have shown that the lubricating performance of WS_2 in oil is good and WS_2 can prolong the service life of green lubricant in a wide range of temperatures (Shi *et al* 2006, 2007). However, nanometer WS_2 particles have very small grain size, large surface area and high surface energy and that it is very easy for them to agglomerate spontaneously and deposit in oil, which seriously restricts the application of nanometer WS_2 particles in engine lubricating oil (Rapoport 2003; Wang *et al* 2005).

Auto-reconditioning technology of worn metal surfaces is a new technique in the field of surface engineering, and during friction, the fricative actions of mechanical friction and tribochemistry lead to the energy exchange and mass exchange between friction pair and lubricating material and thus the formation of physisorption film and chemiadsorption film that compensate the friction loss of friction pair (Xu *et al* 2004). The development and appli-

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cation of nanometer lubricating materials provide a new way for the *in situ* auto-reconditioning of worn metal surfaces. Liu *et al* (2005) and Yu *et al* (2005) conducted studies on the tribological performance and mechanism of nanocopper as additive, and the results indicated that the modified nanocopper additive could significantly improve the wear resistance and reduce friction coefficient of base oil, and that a copper protective film was formed which contributed to the excellent tribological properties of nanocopper additive. Wang *et al* (2001) added CuS nanoparticles into lubricating oil and investigated its auto-reconditioning performances, whose results showed that the CuS deposited film could be formed on surfaces of friction pairs which made the surfaces keep comparatively smooth all along. However, there are rare reports about auto-reconditioning performance of nanometer WS_2 particles by now.

In this paper, a combinative method of ultrasonic dispersion, mechanical agitation and surface modification which can enhance the dispersion effect of nanometer WS_2 particles in green lubricant was studied. And moreover, it covered the auto-reconditioning performance of nanometer WS_2 particles to the abrasive surfaces of steel ball from four-ball tribology test and piston ring from engine lubrication test.

2. Experimental

2.1 *Materials*

- Nanometer WS_2 particles: The nanometer WS_2 particles used here were prepared by the method of wet smash in multi-energy field, its mean diameter being 100 nm and the microcosmic appearance is shown in figure 1.
- Base oil: The green base oil was concocted with several kinds of biodegradable lubricants and its kinematic viscosity was 85·25 $mm^2 \cdot s^{-1}$ at a temperature of 40°C.
- Surface modifier: A kind of high temperature-resistant surface modifier with long lipophilic groups and high molecular weight was used in this work.
- Function additives: Considering the requirements of environment protection and energy saving, the function additives with low phosphorus, low sulphur and low ash were used in this work.

2.2 *Dispersion experiment*

A combinative method of ultrasonic dispersion, mechanical agitation and surface modification was adopted to disperse nanometer WS_2 particles in green lubricant in this study. And to realize this method, we designed a dispersing equipment and figure 2 gives the schematic diagram of this equipment. In the dispersing equipment, stirring rod driven by a rotating speed regulating electromotor drove the grinding media and sequentially agitated and dispersed the materials, and at the same time, an ultrasonic generator whose frequency was 20 kHz and power, 200 W sent forth with high power ultrasonic, which dispersed the circular materials synchronously.

Detailed dispersing steps are given here: First, surface modifier was mixed in proportion with nanometer WS_2 particles. Then dispersing equipment was run for some time to treat the mixture. Finally, the mixture was taken out and added into the green base oil (mass ratio, 1 : 99), and dispersing equipment was started again to treat the oil that included WS_2 for 10 min. In this way, nanometer WS_2 particles could be dispersed equably in green lubricant.

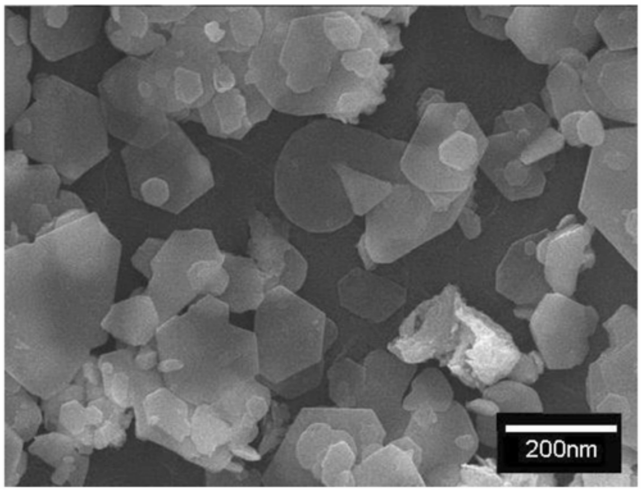

Figure 1. Microcosmic appearance of nanometer WS2 particles.

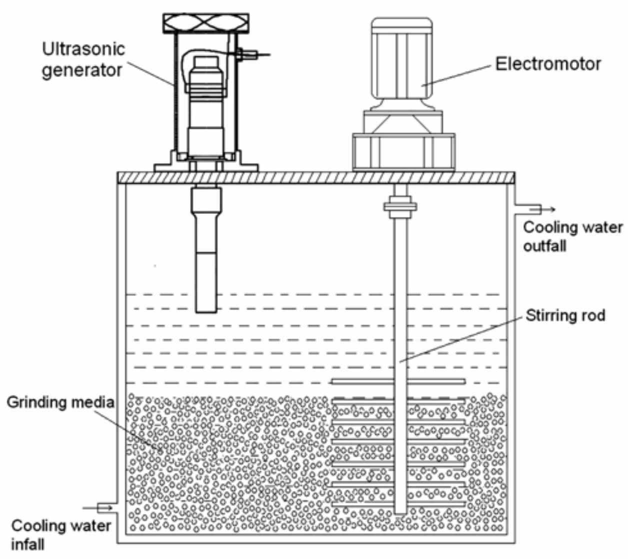

Figure 2. Schematic diagram of dispersing equipment.

In the experiment, the dispersion effect was evaluated on CILAS1064 laser diffraction particle size analyzer and centrifuge (rotating speed: 4000 r/min). Thereinto, mean diameter of particles in green base oil evaluated the dispersion uniformity and sedimentation time on centrifuge evaluated the dispersion stability. And in addition the stable dispersion principle of nanometer WS_2 particles in green lubricant was investigated through infrared spectrogram analysis.

2.3 *Auto-reconditioning experiment*

Auto-reconditioning performance of nanometer WS_2 particles to abrasive surface of steel ball in green base oil was studied on four-ball tribology machine (material of steel ball: GCr15 bearing steel, HRC hardness: 59), and thereinto, the original abrasive surfaces were obtained after the steel-on-steel tribology test of 30 min (load: 392N, rotating speed: 1450 r/min, lubricant: green base oil), and the abrasive surfaces repaired by base oil or nanometer WS_2 were obtained after the steel-on-steel tribology test of 10 min on the basis of original abrasive surface (load: 392N, rotating speed: 1450 r/min, lubricant: green base oil or the oil including nanometer WS_2).

With a view to demonstrate the auto-reconditioning performance of nanometer WS_2 particles to the abrasive surfaces of piston ring in engine, we designed an engine lubrication test-bed as shown in figure 3. On this engine lubrication test-bed, the power machine was refitted from a motorcycle, and the load machine adopted hydraulic system. And in experiment, each test time was 100 h, load, 32 Nm, engine speed, idle speed (1400 r/min). Firstly ordinary engine lubricating oil which was concocted with green base oil and function additives were used to lubricate the engine, and the original abrasive surface of piston ring was obtained 100 h later, then nanometer WS_2 particles were dispersed into the used engine lubricating oil and the mixed oil was used to lubricate the used engine, and the abrasive surface of piston ring repaired by nanometer WS_2 particles was obtained after 100 h.

DMI 5000M metallographic microscope was used to record the abrasive surfaces, PHI550EACA/SAM multifunction electron spectrometer was used to analyse the elementary component and interior elementary distribution of abrasive surface repaired by nanometer WS_2 particles.

3. Results and discussion

3.1 *Influence of surface modifier's content on dispersion effect of nanometer WS_2 particles in green lubricant*

Figure 4 shows the influence of content of surface modifier on the dispersion effect of nanometer WS_2 particles in green lubricant, it can be seen that with the increase of ratio of the mass between surface modifier and nanometer WS_2 particles, the sedimentation time of particles in base oil increased first and then decreased, and the longest sedimentation time was obtained when mass ratio was 1 : 2·5. It might be because that surfaces of nanometer WS_2 particles were modified gradually with the increase of content of surface modifier, which prevented the particles from agglomeration and improved the dispersion stability of particles in base oil, but when the content of surface modifier preponderated over certain value, superfluous surface modifier molecules interacted and resulted in flocculation, which reduced the dispersion stability. Therefore, in the surface modifying nanometer WS_2 particles, the optimal mass ratio between surface modifier and nanometer WS_2 particles was 1 : 2·5.

Figure 3. Photograph of engine lubrication test-bed.

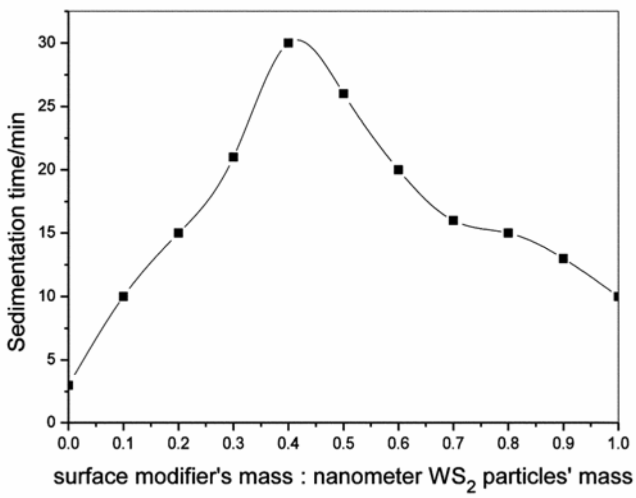

Figure 4. Variation of sedimentation time of particles in base oil with content of surface modifier.

3.2 *Influence of ultrasonic and mechanical agitation treating time on dispersion effect of nanometer WS_2 particles in green lubricant*

Figure 5 shows the effect of ultrasonic and mechanical agitation treating time on the dispersion performance of particles in green lubricant, in which the mass ratio between surface modifier and nanometer WS_2 particles was 1 : 2·5. It could be seen that, when untreated, the mean diameter of suspending particles was almost 10 μm, which indicated that nanometer WS_2 particles agglomerated remarkably, but after the treatment time of 5 h, the mean diameter decreased to 0·8 μm that was close to the mean diameter of the particles before adding, which indicated that high power ultrasonic and mechanical agitation could break the big agglomerations obviously and improve the dispersion uniformity of nanometer WS_2 particles. In addition, the increase of sedimentation time of suspending particles with treating time indicates the enhancement of dispersion stability of nanometer WS_2 particles by ultrasonic and mechanical agitation treatments. Consequently, the optimal treating time was 5 h.

3.3 *Dispersion principle of nanometer WS_2 particles in green lubricant*

Figure 6 shows the IR analysis of nanometer WS_2 particles and surface modifier. It could be seen that there were characteristic adsorption peaks of hydroxide radicals in infrared spectrogram of nanometer WS_2 particles untreated at the wavenumbers of 3500 cm^{-1} and 1600 cm^{-1}, which might be from the preparation process of nanometer particles, but in the infrared spectrogram of nanometer WS_2 particles treated, the characteristic adsorption peaks of hydroxide radicals disappeared, whereas many characteristic adsorption peaks that were similar to that of surface modifier appeared, which means that when treated by high power ultrasonic and mechanical agitation, the agglomerations of nanometer WS_2 particles were smashed and surfaces of nanometer WS_2 particles were activated, then surface modifier reacted with the hydroxide radicals on surfaces of particles and modified the surfaces. When we added the nanometer WS_2 particles modified into oil, the long lipophilic groups on surfaces of nanometer WS_2 particles could stretch in oil adequately and form steric hindrance layers between particles that prevented particles from conglomerating and depositing and led to the stable dispersion of nanometer WS_2 particles in green lubricant.

3.4 *Auto-reconditioning performance of nanometer WS_2 particles in green lubricant*

Table 1 shows the tribological performances contrast of base oil and the oil including nanometer WS_2. It could be seen that nanometer WS_2 particles increased P_B and P_D values of base oil by 16·4% and 66·7%, respectively and decreased worn scar diameter of base oil by 10·3%, which indicated that nanometer WS_2 particles could improve the tribological performances of green lubricant observably.

Figure 7 shows the auto-reconditioning performance of nanometer WS_2 particles to abrasive surface of steel ball in green lubricant on four-ball tribology machine. It could be seen that there were many tiny protruding bodies and furrows on the original abrasive surface, and after auto-reconditioning experiments, we found that the base oil did not repair the abrasive surface but aggravated the abrasion on original abrasive surface, because there were more deep furrows and metal surface peeling off phenomenon on the abrasive surface, as illustrated in figure 7(b), however, in figure 7(c) the abrasive surface became

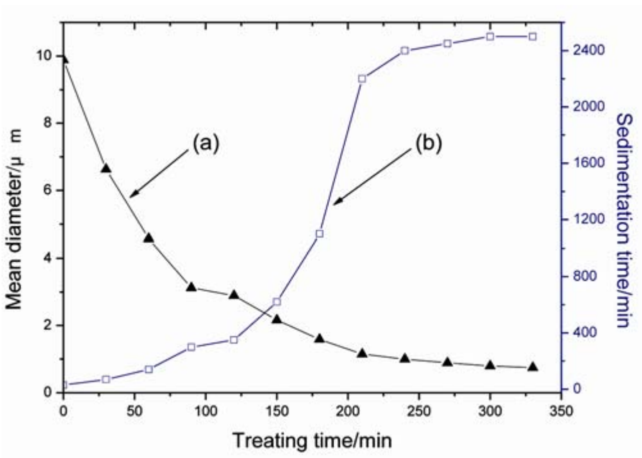

Figure 5. Variation of (a) mean diameter and (b) sedimentation time of particles in base oil with treating time.

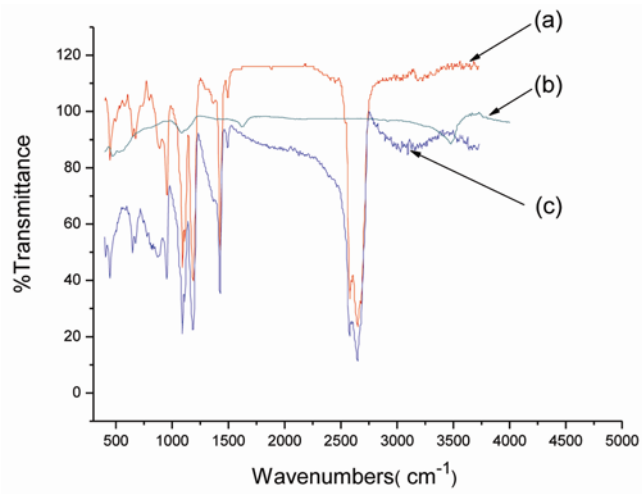

Figure 6. Infrared spectrogram of (a) surface modifier and nanometer WS_2 particles and (b) untreated or (c) treated.

Figure 7. Micrographs of steel balls for (**a**) original abrasive surface and abrasive surface repaired by (**b**) base oil or (**c**) nanometer WS_2.

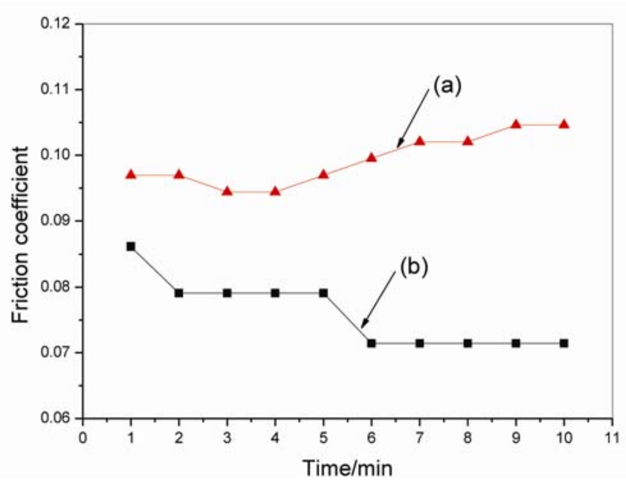

Figure 8. Variation of friction coefficients of (a) base oil and (b) the oil including nanometer WS_2 with time (load: 392N).

Table 1. Tribological performances contrast of two kinds of oil.

Lubricant	P_B value (N)	P_D value (N)	Worn scar diameter (mm)
Base oil	598	1470	0·602
Base oil +1% nanometer WS_2	696	2450	0·540

flat and there were not visible furrows on it, which meant that nanometer WS_2 particles had repaired the original abrasive surface well. And moreover, in figure 8 the variation contrast of friction coefficients of two kinds of oil with time proved that nanometer WS_2 particles could lessen the friction between abrasive surfaces and prevent the aggravation of abrasion effectively.

Figure 9 shows the auto-reconditioning performance of nanometer WS_2 particles to abrasive surface of piston ring in green lubricant on engine lubrication test-bed, and it indicated that during the actual application in engine, nanometer WS_2 particles still could repair the abrasive surface well.

3.5 *Auto-reconditioning principle of nanometer WS_2 particles in green lubricant*

The microcosmic appearance of nanometer WS_2 particles (figure 1) showed that WS_2 particulate has lamellar structure and its bedding surface is so smooth that slippage occurs easily between layers, which indicates that during the lubricating process between friction pair, WS_2 can offer a low friction coefficient.

Analyses of elementary component and the interior elementary distribution of abrasive surface repaired by nanometer WS_2 particles are shown in figures 10 and 11. Figure 10 indicated that there were W and S elements on the abrasive surface which were from WS_2. Figure 11 showed the depth distribution of elements on abrasive surface, according to the molar rate of elements, it could be guessed that there was WS_2 adsorption film on the outer skin of abrasive surface, and inside the abrasive surface, FeS film had been formed.

Consequently, the process that nanometer WS_2 particles auto-reconditioned abrasive surfaces in green lubricant could be considered as a multiple process of mechanical action and chemical action: when the abrasive surfaces contacted each other, nanometer WS_2 particles deposited in the low valleys of abrasive surfaces, and formed an adsorption film which could fill and level up the furrows and reduce the sliding friction. And with increase of tribology test time, the chemical action between WS_2 and the base material of friction pairs happened and the FeS film that has excellent antiwear performance was formed. Both WS_2 adsorption film and FeS film could prevent the abrasive surfaces of friction pairs from direct contact effectively and prevent abrasive surfaces from further abrasion.

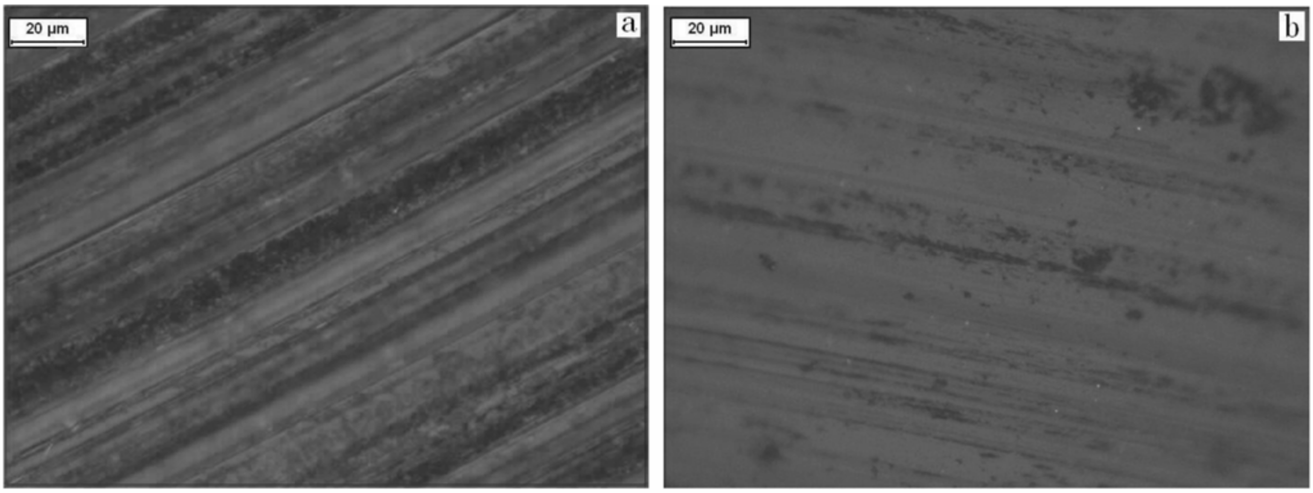

Figure 9. Micrographs of piston ring for (**a**) original abrasive surface and (**b**) abrasive surface repaired by nanometer WS_2.

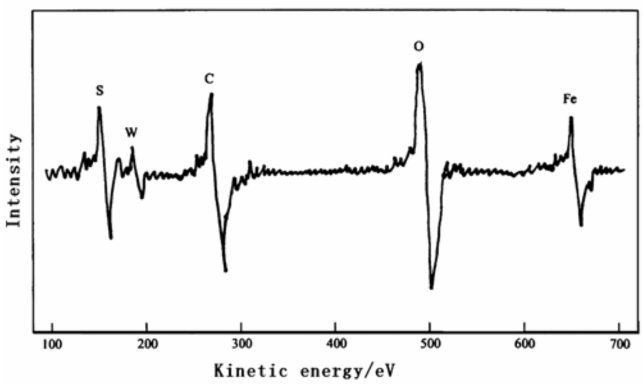

Figure 10. Auger electron energy spectrum of abrasive surface repaired by nanometer WS_2.

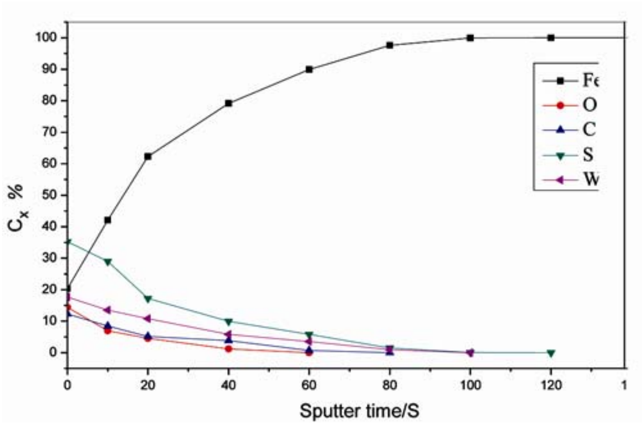

Figure 11. Depth distributing curves of elements on abrasive surface repaired by nanometer WS_2.

4. Conclusions

To sum up, the present study leads to the following conclusions:

(I) The combinative method of ultrasonic dispersion, mechanical agitation and surface modification can improve the dispersion uniformity and dispersion stability of nanometer WS_2 particles in green lubricant effectively.

(II) Tribological tests on four-ball tribology machine and engine lubrication test-bed indicate that nanometer WS_2 particles can auto-recondition abrasive surfaces well.

Acknowledgements

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