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SYNTHESIS AND TRIBOLOGICAL PROPERTIES OF W-DOPED MoS_2 NANOPLATES

J. XU[a,b], H. TANG[a,b], Q. SHI[c], C. LI[a,b*]
[a]*School of Materials Science and Engineering, Jiangsu University, Zhenjiang,212013, Jiangsu Province, China*
[b]*Key Laboratory of Tribology of Jiangsu Province, Zhenjiang 212013, Jiangsu Province, China*
[c]*School of Mechanical Engineering, Zhenjiang Vocational Technical College, Zhenjiang 212016, Jiangsu Province, China*

The W-doped MoS2 nanoplates have been successfully prepared via solid-state thermal (850°C) reaction between micro-sized MoO3, WO3 and thiocarbamide powders under inert atmosphere in a closed reactor and characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM). It was found that the morphologies of the as-prepared products changed with the doping of WO3 powders. And the sizes of crystallites evidently changed while the contents of dopant increased within a certain limit (3at.%–7at.%). The tribological properties of the as-prepared products as additives in paraffin base oil were investigated by UMT-2 multispecimen tribo-tester. The topography of worn scars was obtained using a common SEM.The friction coefficient of the base oil containing W-doped MoS2 nanoplates was lower and more stable than that of MoS2 nanosheets.

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1. Introduction

MX2 (M = Mo,W;X = S, Se,Te) is a typical example of a layered transition metal dichalcogenide family of materials. Because of their unique physical and electronic structure,the layered dichalcogenides display a variety of interesting properties and phases primarily due to their "two-dimensional"(2D) nature, including highly anisotropic mechanical,optical, and electrical properties[1]. MoS2 and WS2 are the members of this family and have been used for decades in specialised applications as a solid lubricant or an additive for lubricating oils and greases. As a lubricant, MoS2 nanomaterials exhibit low friction coefficients and have a long lifetime in dry air, inert or vacuum environments [2]. To date, MoS2 nanomaterials have attracted considerable attention and have been synthesised by a great diversity of methods, for instance, gas-phase reactions, laser ablation, sonochemical process, hydrothermal synthesis and thermal decomposition [3–6].Therefore, much effort has been devoted to the synthesis of various nanoscale MoS2 with specific morphologies and unique properties.

Doping is one of effective ways to improve material performance in many research fields such as photocatalytic materials, lithium-ion battery materials, information materials, magnetic materials, etc. Doping nanocrystals provides another fundamental approach to modify the properties of nanocrystals by means of tailoring the crystal's compositions [7-10]. It is confirmed that doping can bring about changes in c-axis lattice constant and electronic structure. Recently, some researchers had focused on the tribological properties of the transition-metal diselenide as

*Corresponding author: xjing@ujs.edu.cn

lubrication additive, which had the similar structure to the MoS2 and WS2. Tang et al. [11] investigated the tribological properties of the as-prepared NbSex powders as additives in HVI500 base oil. Recently,we have reported the synthesis of Mo-doped WSe2 nanolamellars [12] and Nb-doped MoSe2 nanoplates [13] and researched their tribological propertied as additive added into the base oil. It was found that the obtained product with the contents of dopant within 3-10 at% showed the best friction performance.

In this study, we reported a facile and efficient solid-state reaction method for the synthesis of Mo1-xWxS2 ($0 \leq x \leq 0.1$)nanoplate using Tungsten Trioxide, molybdenum trioxide and thiocarbamide at 850°C in an argon atmosphere. W-doped MoS2 nanoplates have been successfully synthesized by a facile solid-state reaction and the tribological properties of Mo1-xWxS2 nanosheets as additives in the HVI500 base oil were also investigated and W-doped MoS2 nanoparticles exhibited a better friction and wear property than MoS2 as additives in the HVI500 base oil.

2. Experimental

2.1 Materials

Molybdenum trioxide, tungsten trioxide and thiocarbamide powders were purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China). All chemical reagents were of analytic purity and used directly without further purification.

2.2 Preparation of Mo1-xWxS2 ($0 \leq x \leq 0.1$) nanoplates

For the preparation of W-doped MoS2 nanoplates, the mixed powders (molar ratio: W:Mo:S = 1:99:220, 3:97:220, 5:95:220, 7:93:220,10:90:220, an overdose of 20% S) was energetically ball-milled at 300 rpm (rotation per minute) in the presence of ethanol for 12 h in a planetary ball mill. Then the ball-milled mixture was introduced into 10-ml stainless steel reactor in a nitrogen-filled glove box. The filled reactor was tightly closed with the threaded plug and pushed into the tube furnace. The temperature of the tube furnace was raised to 850°C at a rate of 10°C /min and the heat was maintained at 850°C for 2h. Subsequently the reactor was gradually cooled to room temperature, opened, and the as-prepared powder was obtained. The product was directly characterized without further processing by various analytic techniques.

2.3 Characterization methods

The X-ray diffraction (XRD) patterns were recorded using a D8 advance (Bruker-AXS) diffractometer with Cu *Ka* radiation ($\lambda = 0.1546$ nm). The 2θ range used in the measurement was from 10 to 80° with a velocity of 5°/min. The morphologies and structures of the samples were characterized by scanning electron microscopy (SEM, JEOL JXA-840A).All the measurements were carried out at room temperature.

Friction tests were performed using a UMT-2 ball-on-disc tribometer (CETR, USA)under lubricated conditions. The as-prepared products(Sa1-Sa6) were modified by dispersing agent sorbitol monooleate (Span-80) was distributed into the HVI500 base oil via 60 min ultrasonication, leading to the desired samples with 3 wt.% Mo1-xWxS2 ($0 \leq x \leq 0.1$). The testing of friction reduction and wear resistance was conducted at rotating speed of 400 rpm and load of 5-50 N for 12 min. The material of upper sample is 440C stainless steel ball with a diameter of 10 mm,hardness of 62 HRC, and the counterpart is 45 steel disc of Φ40 mm×3 mm in size. The friction coefficient was automatically recorded during the contact friction.

3. Results and discussion

3.1 XRD analysis

The XRD patterns of MoS2 and W-doped MoS2 in the 2θ range of 10-80° are illustrated in Fig.1. All the reflections have been indexed to the pure hexagonal phase (p63/mmc space group) of MoS2 with lattice constants a = 3.161Å and c = 12.843Å (PDF No. 37-1492). Fig. 1 clearly show that (002) reflection is of the maximum intensity and thereby indicates the presence of a well-stacked layered structure. The diffractogram for Mo1-xWxS2 ($0 \leq x \leq 0.1$) are similar to those of MoS2. The refined lattice parameters are listed in Table 1. The lattice parameter 'a' remains constant for all samples while there is a slight amount of increase in 'c' parameter indicates that tungsten has been intercalating in between the layers thereby expanding the 'c' parameter. This increase is very small because the amount of tungsten incorporated with MoS2 is also lesser in proportion. As proportion of tungsten addition is increased in MoS2, its X-ray intensity also changed which can be seen from Fig.1. When the proportion is increased to 3 at.% - 5 at.%, the intensity is reduced and the widths of the diffraction peaks are broader. The results indicate that the size of particles is decreased. And when the proportion is increased to 10 at.%, the intensity of the diffraction peaks are increased, which means the size of particles is expanded. It is also evident from the diffractogram that the 002 peak is of maximum intensity while the intensities of other peaks such as 103, and 008 reflections are relatively weak, indicating thereby a strong orientation with stacking of the planes along the c axis. It means that even upon tungsten substitution in MoS2, the arrangements of Mo and S atoms remained basically the same as in pure host 2H-MoS2. This is in good agreement with the XRD research of bulk tungsten-substituted molybdenum disulfide reported in the literature[14].

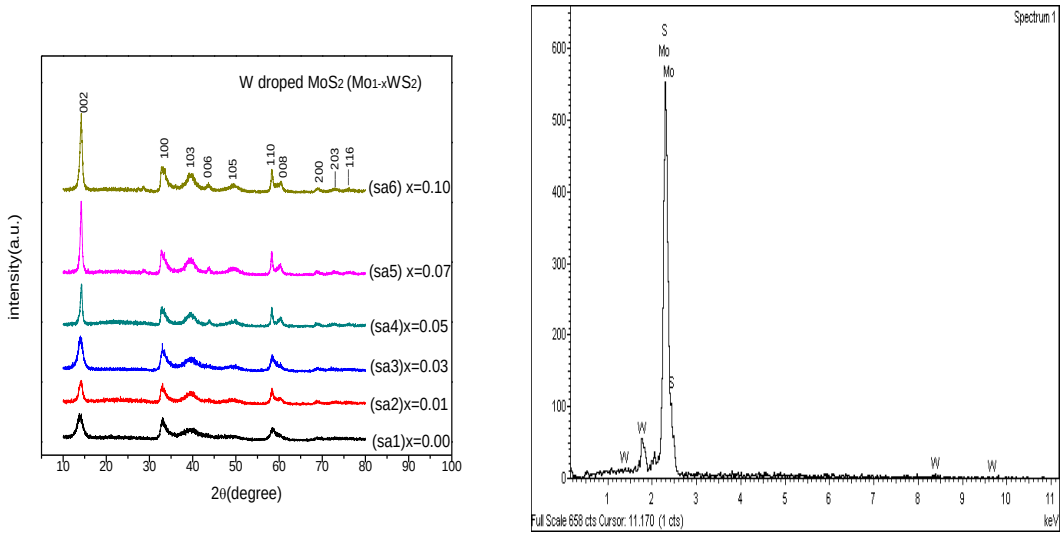


Fig. 1 XRD patterns and EDS result of Undoped and W-doped MoS2 nanoplates calcined at 850°C

Table.1 Lattice parameters for undoped and W-doped MoS2 crystals.

Sample		Parameters		
		a(Å)	c(Å)	c/a
Sa1	MoS2	**3.161(0)**	**12.451(0)**	**3.9389**
Sa2	Mo0.99W0.01S2	**3.161(2)**	**12.453(2)**	**3.9408**
Sa3	Mo0.97W0.03S2	**3.160(2)**	**12.458(7)**	**3.9424**
Sa4	Mo0.95W0.05S2	**3.158(9)**	**12.461(2)**	**3.9458**
Sa5	Mo0.93W0.07S2	**3.161(2)**	**12.465(6)**	**3.9405**
Sa6	Mo0.90W0.10S2	**3.181(0)**	**12.478(0)**	**3.9226**

3.2 SEM observations

The morphology of the Mo1-xWxS2 samples obtained with the reaction temperature of 850°C are presented in figure 2, the SEM images of pure MoS2 and W-doped MoS2 nanoplates are given by contrast. Fig.2a shows that the as-prepared pure MoS2 particles are composed of flakes dominating with diameters of about 1–2 μm and a thickness of about 100 nm. It can be clearly seen that the nanosheets aggregate together. Figure 2b−2f show the SEM images of the W-doped MoS_2 nanosheets at the same reaction temperature. When introduced 3at.% WO3 powder, the size of the nanosheets is decreased and the nanoflakes became scattered. At the same time, part of nanosheets converted to the hexagonal morphology with the diameter of nearly 100 nm and a thickness of about 50 nm (figure 2c). With the introduction of 5 at.% WO3 powder, the size reduction of the nanosheets is very significant and many sheets have coverted to the hexagonal morphology (figure 2d). The size of the nanosheets is decreased with the proportion of Tungsten Trioxide addition increased in a certain limit (1 at.%−5 at.%). And when the tungsten addition is increased to 10 at.% , the as-prepared particles are assemble together and the size is increased (figure 2e,2f).

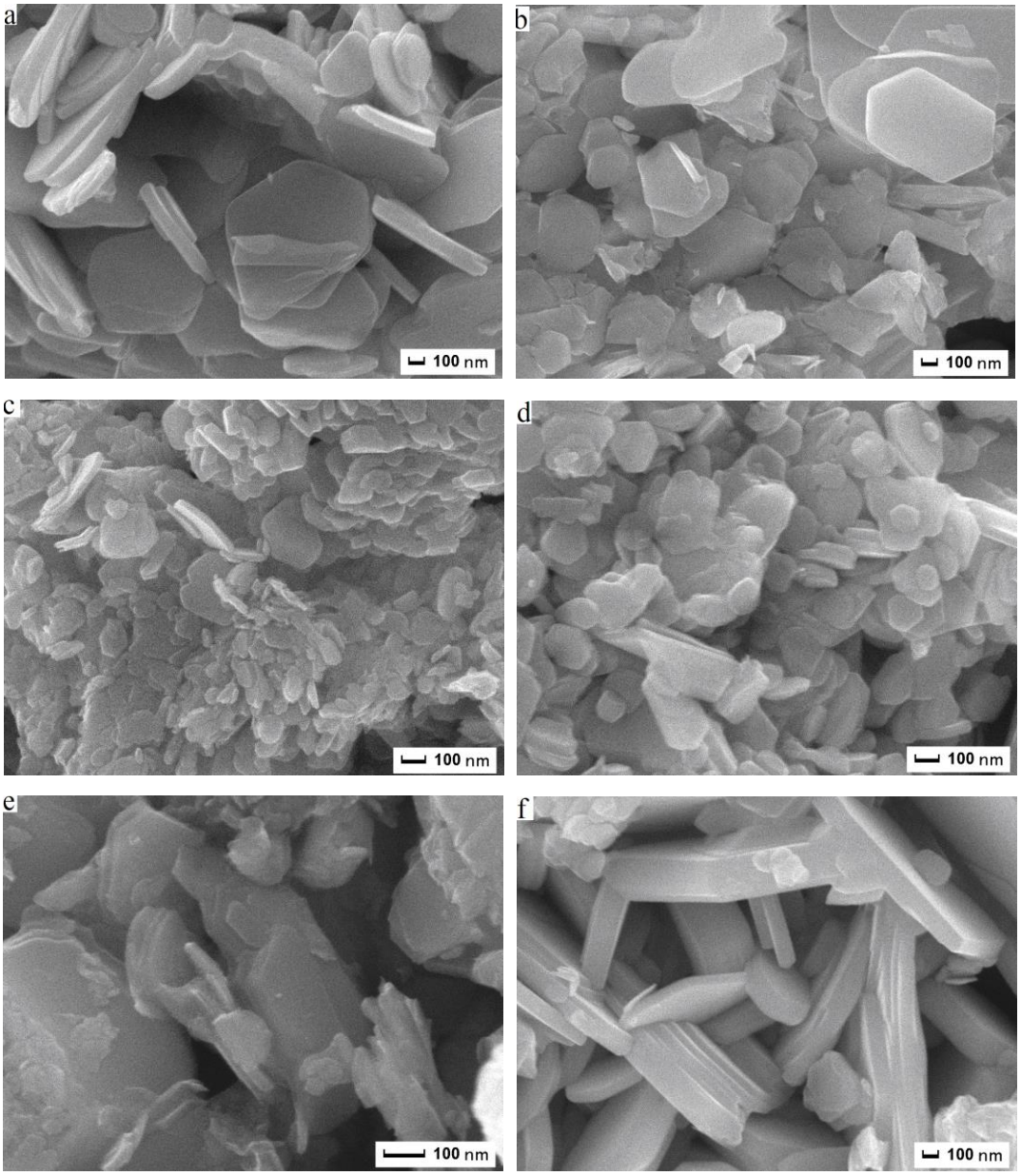


Fig. 2. SEM image of the products obtained at 850°C for a-f (0, 1, 3, 5, 7, 10 at.%)W-doped MoS2,

3.3 Tribological properties analysis

In our previous research [15-18], MoS_2 nanoplates exhibited excellent tribological behavior as a lubricant additive. It was found that basic oil with 3.0 wt.% MoS_2 nanoplates[19] indicates their excellent tribological properties. Accordingly, the tribological properties of basic oil with 3.0 wt.% Mo1-xWxS2 nanoplates were investigated in this paper.

Fig.3 depicts the comparisons of tribological properties among HVI500 basic oil without additives, the base oil containing 3wt.% Sa1−Sa6 at the load of 35 N under the rotating speed of 400 rpm. It could easily be found from Fig. 4 that friction coefficient decreases with the addition of Mo1-xWxS2 nanoplates, as the proportion of W dopant is more than 5at.%, the friction coefficient increases. Therefore, the friction coefficient of the base oil with 3.0 wt.% Mo0.95W0.05S2 nanoplates is lower and more stable than that of the base oil with other tungsten concentration. The average friction coefficient of base oil with 3wt.% Mo0.95W0.05S2 nanoplates was close to 0.075, whereas it was 0.12 for the HVI500 base oil. The lubrication mechanism of layered Mo1-xWxS2 nanoplates is associated with the shearing of the weak van der Waals bonds

between the molecular layers. When Mo1-xWxS2 nanoplates served as an additive in a base-oil, besides molecules of the base oil, nanoplates was also adsorbed on the surface of the steel friction pair to form tribofilm in the friction process. However, Fig.3 shows that a continuous tribofilm may begin to be formed under an optimal W dopant concentration (5at.%). For lower or higher W dopant concentrations, the formed tribofilm is incomplete.

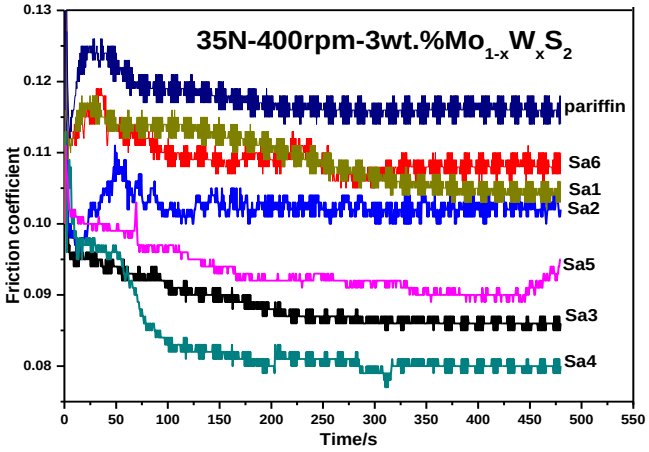
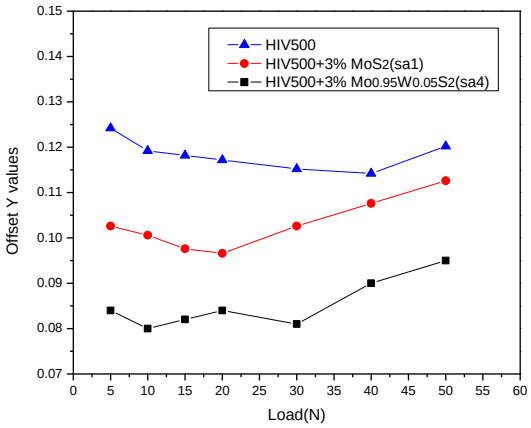
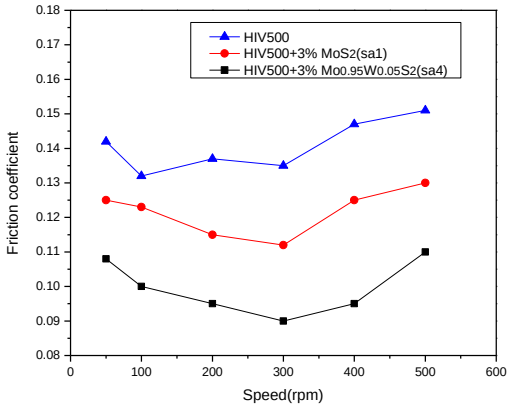


Fig. 3 The HVI500 paraffin base oil and base oil containing 3 wt.% $Mo_{1-x}W_xS_2$ nanoplates at 35N load for 480 second.

Fig.4(a) represents the curve of friction of the base oil without additives, the base oil containing 3wt.% Sa1, Sa4 at the different loads (5 N, 10 N, 15N, 20 N, 30 N, 40 N,50N) under a speed of 500 rpm for 30 min. The friction coefficient of base oil without any additives increases with the load increases. With the addition of 3.0 wt.% Mo1-xWxS2 nnanopaltes in base oil, the friction coefficient reduces remarkably when the load is less than 30 N. The friction coefficient of the base oil with 3.0 wt.% Mo0.95W0.05S2 nanoplates is lower than that of the base oil with 3.0 wt.% Mo1-xWxS2 nanoplates. Fig.4(b) dipects the comparisons of tribological properties among HVI500 basic oil without additives, the base oil containing 3wt.% S1, S4 at the load of 40N under diverse speeds. With the rotating speed of 100~500rpm, the friction coefficient of the base oil containing as-prepared 3wt.% (Sa1 and Sa4) nanobelts/nanoplates is always lower than that of pure base oil, and it decreases with the dopent percent of the additives is 5at.%. The reason of this behavior may be Mo0.95W0.05S2 nanoplates with thinner and smaller size will penetrate more easily into the interface with base oil and form a continuous oil film in the concave of rubbing face, therefore, exhibit a lower friction coefficient and better anti-wear capability.



(a)



(b)

Fig. 4 (a)Variations of friction coefficient of the paraffin base oil and the base oil containing 3wt.% $Mo_{1-x}W_xS2$ (x=0, 0.05) nanoplates with increasing load at 300 rpm for 30 min. (b)Curves of frictional coefficients of HVI500 and the Basic oil with the contents of 3wt.% Sa1 and Sa4 nanoplates at the load of 40N under diverse speeds.

To further study the wear resistance tribological properties of the $Mo_{1-x}W_xS2$ nanoplates, the topography of the worn scar was investigated using Optical microscope and SEM. The wear scar of the steel disc is shown in Fig.5a,c (the HVI500 base oil) and Fig.5b,d (the HVI500 base oil containing Mo0.95W0.05S2 nanoplates) after rubbing with 40N load and 300 rpm rotating speed for 30min. It could easily be found from SEM image that the rubbed surface lubricated by the HVI500 base oil had lots of wide and deep furrows; Compared with the HVI500 base oil, the surface lubricated with Mo0.95W0.05S2 nanospheres only presented slender furrows. From Fig.5d and EDS of Fig.5e, we see that Mo0.95W0.05S2 consist of many irregular nanosheets will penetrate more easily into the interface with the base oil, and these nanosheets could strongly adhere to substrates and form continuous film in concave of rubbing surface, enhancing the tribological properties [20].

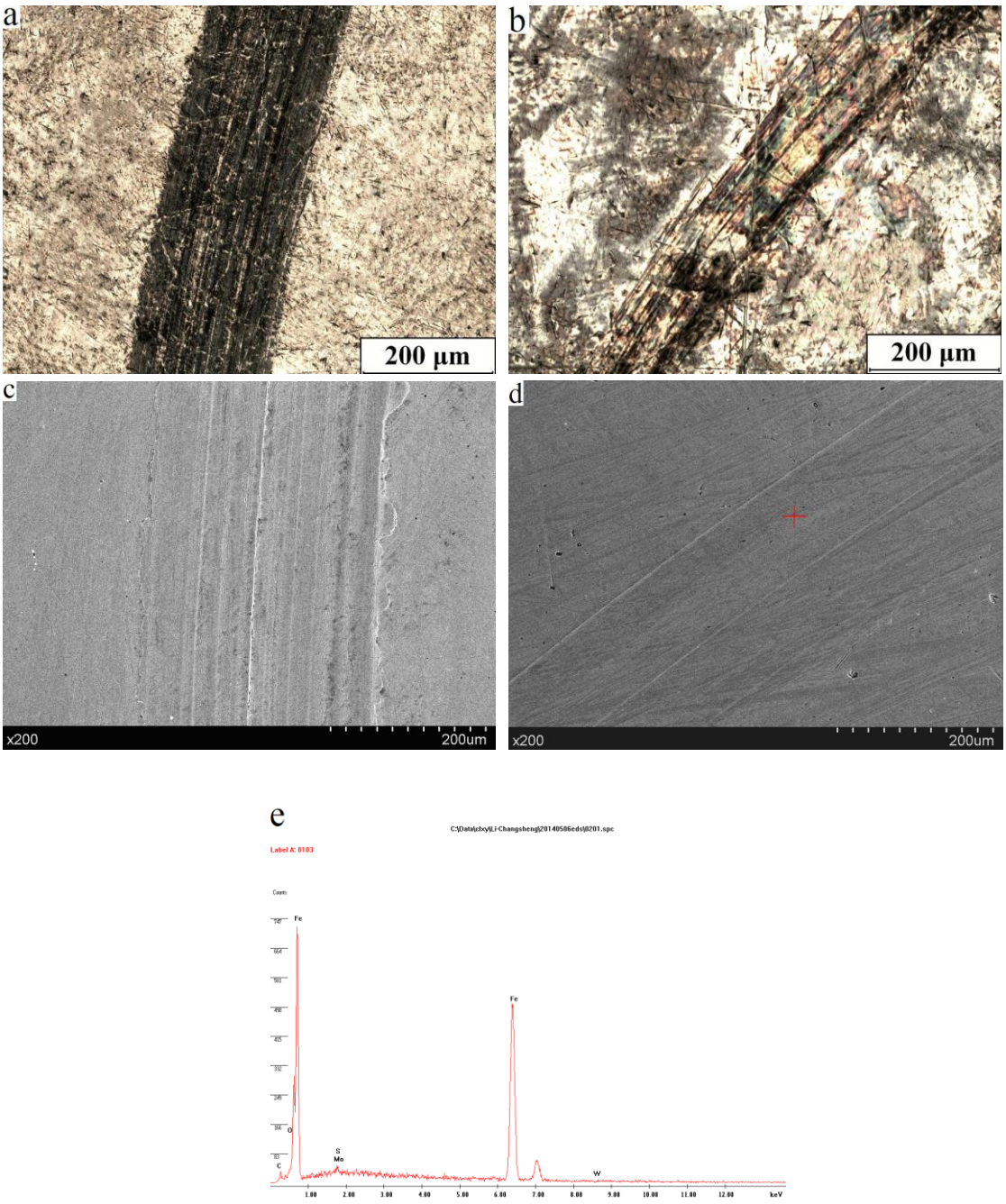


Fig.5 Optical microscope,SEM and EDS image of Wear scar of plate: (a,c)the HVI500 base oil; (b,d) the HVI500 base oil with 3.0 wt% $Mo_{0.95}W_{0.05}S2$ nanospheres using; (e) EDS

4. Conclusions

Considering all the results and discussion above, the following conclusions can be drawn.

1) W-doped MoS2 nanoplates are successfully fabricated by a facile solid-state thermal reaction.From the evaluation of the X-ray powder diffraction patterns, we may conclude that both doped and undoped samples are of 2H-polytype with comparable crystal quality: the (002) basal plane and (100), (110) edge planes reflections are present. In addition, W-doped samples exhibit lattice expansion along the stacking direction. The expansion of interlayer spacing could be

exactly calculated from the XRD patterns of diffraction peaks of (002), (006) and (008), indicating an increase of the d-spacing, most probably due to the influence of W dopant. The resulting morphology, with the exposed prismatic (110) edge planes, makes large edge planes possible. The obtained values are listed in Table 1 together with those of other researchers for comparison. From Table 1, we notice that the a-parameter remains unchanged for the doped samples, while the c-parameter for W-doped MoS2 shows appreciable increase in consistent agreement with the increase in the d-spacing.

2) The addition of W-doped MoS2 nanoplates improved the tribological properties of base oil. The friction coefficient of the base oil with 3.0 wt.% Mo0.95W0.05S2 nanoplates presents better anti-wear capability than others.Because of Mo1-xWxS2 nanoplates with thinner and smaller size will penetrate more easily into the interface with base oil, the base oil with addition of Mo1-xWxS2 nanoplates have lower and more stable friction coefficient under the present experimental conditions. Furthermore, Mo0.95W0.05S2 nanoplates exibit a lower friction coefficient and better anti-wear capability than MoS2 nanoplates.

In a word, Mo1-xWxS2 particles as lubrication additive could improve tribological properties of the paraffin, and obtained the best performance when the content of W dopant is 5 at.%.

Acknowledgements

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