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Microstructure and preparation of nano S-W-S new solid lubrication system①

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[Abstract] The method for preparing a new solid lubrication system of nano S-W-S was presented. The microstructure of the S-W-S nano cluster was investigated using TEM and XRD. The system is a mixture clusters of both monocrystal and polycrystal of layered hexagonal structure with one tungsten atom linking with two sulphur atoms, and the week Van der Waals' force bonding together the different layers. The changes of electronic structure were studied with XPS. The hybridization of different electronic shell orbitals of the sulphur atom in the nano cluster is regarded as the quantum size effect. The clusters are found to be of a closed spherical structure without any dangling bond.

[Key words] solid lubrication system; nanometer cluster; quantum size effect
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1 INTRODUCTION

It is well known that the solid lubrication materials commonly used at high temperatures, low temperatures or(and) in vacuum are graphite, metallic sulphide MX_2(where M stands for W and Mo, X for S, Se and Te), C_{60} and etc. The good lubrication property of these conventional solid lubrication materials is mainly due to the weak linkage between crystal surfaces, which results in a rather large surface friction coefficient, and the new surfaces with unsaturated dangling bonds and void bonds generated during lubrication process. For film workpieces with surface of MX_2 type, cracks will emerge during lubrication, with the breakage of some covalent bonds and the formation of some unsaturated bonds. Chemical reactions are thus expected to occur during the lubrication process, and the advantages of conventional lubricants are greatly reduced or even disappeared. For examples, graphite may lose its lubricant character in vacuum, and in a dry environment the linking bond between crystal surfaces of conventional bulky WS_2 becomes difficult to break up, hence its lubrication effect is greatly reduced. Therefore it is a topic of great practical significance to find a new solid lubricant with excellent lubrication properties in different environments.

In this paper a new S-W-S solid lubrication system was found by investigating the character of conventional solid lubrication systems with the aim to improve their microstructure properties. The TEM, XRD, XPS techniques are employed to study the microstructures of the new lubricant, and its lubrication mechanism will also be discussed.

2 EXPERIMENTAL

2.1 Preparation of S-W-S nano solid

Chemical pure W powders with diameter about 100 μm were further granulated into 30 ~ 50 nm by the mechanical physical solid state reaction methods (MPSSRM)[1~5]. The W nano powders were then put into a quartz tube furnace, which was vacuumed to 5×10^{-3} Pa and filled with H_2S and annealed at a high temperature for about 30 min. After that, the W powders were further granulated with the MPSSRM for about 24 h and 48 h, respectively. Nano solid with diameters 50 nm, 10 nm were finally obtained.

2.2 Experimental devices

The particle diameters of the S-W-S nano cluster were directly observed in an H-800 electron microscopy (75 kV). The electron diffraction experiment was also performed on this apparatus, and the diffraction patterns corresponding to monocrystalline and polycrystalline structure for S-W-S nano clusters were both obtained.

The phase analyses for the S-W-S nano clusters were performed on a D-500 X-ray diffractometer (with Ni filtered, Cu K_α radiation, 40 kV, 35 mA, scanning velocity 1.2 (°)/min), and the diffraction patterns for WS_2 single phase were obtained.

To study the influences of the quantum size effect of nano clusters on the electronic structure, an ESCALAB-MKII electron spectrometer was employed. Four different types of samples, W powder of 100 μm, 50 nm and S-W-S powder of 50 nm and 10 nm, were analyzed. The base pressure is 7×10^{-8} Pa

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in the specimen preparation chamber and 5×10^{-8} Pa in the analysis chamber. The exciting source is Al K_α (1 486.6 eV) radiation, 15 kV, 20 mA. The surface of sample was cleaned with argon ions for 5 min before measurement at a current of 20 μA. The binding energies of W $4f_{7/2}$ and S $2p_{3/2}$ electron were determined, and the peaks at the electron energy spectra were fitted.

3 RESULTS AND DISCUSSION

3.1 Microstructure of S-W-S nano cluster

Fig.1 shows the X-ray diffraction pattern of S-W-S nano powder cluster of 50 nm. It indicates that S-W-S nano powder is hexagonal single phase WS_2. The crystal is similar to that of graphite. The crystal is of a regular hexagonal structure and thus the atoms form net planes. The overlapping of several layers makes up a sandwich type structure. The neighboring layers are linked by Van der Waals' force, which is rather weak and hence the linkages are easy to break up. The layer distance is determined experimentally to be 0.615 nm, which is close to the length of the *c* axis of a graphite cell(0.67 nm).

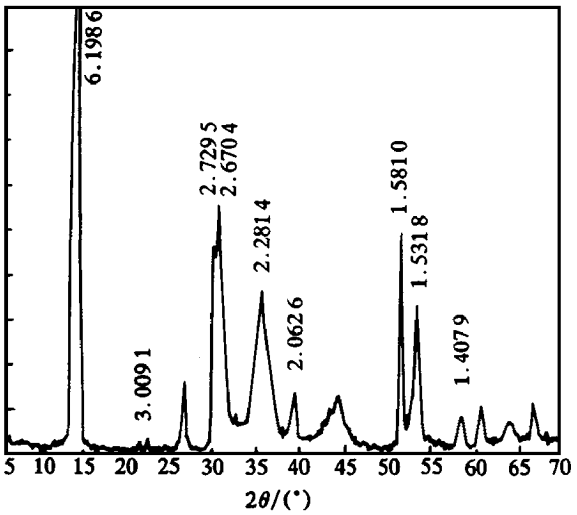

Fig.1 XRD pattern of S-W-S nanometer cluster

Fig.2 is the electron diffraction pattern of S-W-S nano powder clusters, whose majority is monocrystal WS_2 of regular hexagonal shape (Fig.2(a)) and minority is polycrystal WS_2(Fig.2(b)).

Fig.3 shows TEM image of S-W-S nano powder clusters. The grain diameter is about 10 nm and rather homogeneous in size. According to the characteristic of the nanometer cluster structure, the volume for grain boundary is about 50 % of the total volume.

Previous experiments[6] indicated that clusters of 3 ~ 10 nm in diameters usually are of spherical or elliptical shape, and in addition the S-W-S nano clusters here are of closed structure without any dangling bonds microscopically.

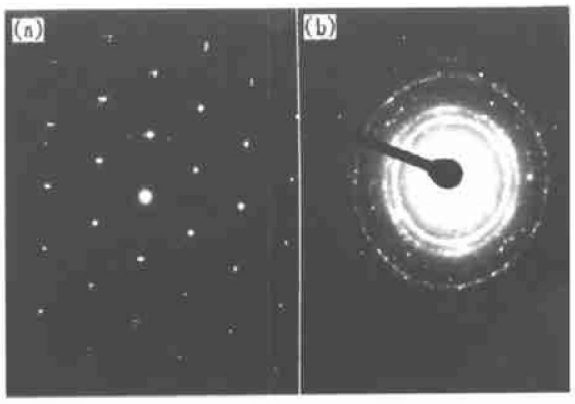

Fig.2 Electron diffraction patterns of S-W-S nanometer clusters
(a) —Monocrystal in S-W-S nanometer cluster;
(b) —Polycrystal in S-W-S nanometer cluster

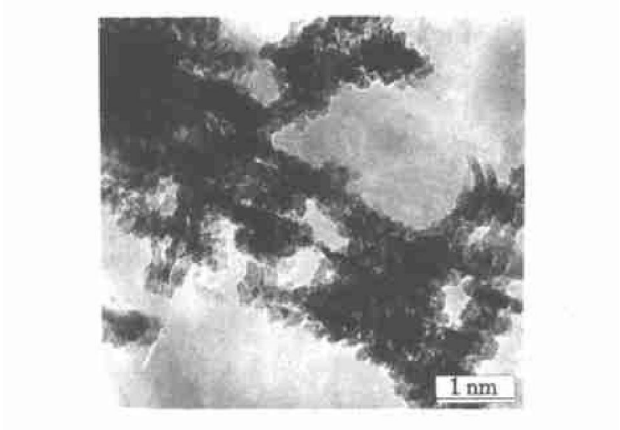

Fig.3 TEM image of S-W-S nano cluster

3.2 Quantum size effect and electronic structure

Many experiments have shown that nanometer clusters have a pronounced quantum size effect[7~9]. Such an effect makes the quasi-continuum energy bands of atom split into separated energy levels. Kubo[9] indicated that the electrons at the boundary of a nanometer cluster do not obey Fermi statistics any more, and the relation between the average energy spacing of electrons δ and the energy change is

$$\delta = \frac{E_F - E_0}{N}$$

where E_F is the Fermi energy, E_0 is the bottom energy of an energy band, and N is the number of valent electrons. As the energy level spacing of nanometer clusters appears, the electrons become more difficult to be excited, which results in the difference in the electronic configuration of nanometer clusters from that of the conventional solid. Thus the corresponding electronic structures are also different.

In S-W-S clusters, the electron configuration of a W atom is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^4 6s^2$ and that of an S atom is $1s^2 2s^2 2p^6 3s^2 3p^4$. In nanometer clusters, the atoms in the crystal are

ordered structure, while the atoms in the boundary between crystals possess disordered characteristic. The volume ratio of disordered atoms is about 50 % of the total volume[10]. At the boundary surface, both the ordered structure and the disordered structure influence the property of the cluster, making the properties different from not only those of the ordered crystal state but also the properties of amorphous state which is ordered at short ranges and disordered at long ranges. It is expected that as the grain diameter of the cluster changes, the corresponding electronic structure and properties will also be modified.

The shifts of binding energies of $W4f_{7/2}$ and $S2p_{3/2}$ electron of cluster specimens of different diameters were investigated with ESCALAB-MKII electron spectrometer. Table 1 shows that the decrement of diameter of clusters makes the binding energy of $W4f_{7/2}$ and $S2p_{3/2}$ electrons shift to a higher energy. For $W4f_{7/2}$ electron, the binding energy is $E = 30.8$ eV when the powder is 100 μm in diameter, and as the diameter decreases to 10 nm, the binding energy is 34.0 eV. The shift is an increment of 3.2 eV. For bulky crystals of WS_2, the binding energy for $S2p_{3/2}$ electron is $E = 162.60$ eV, while the binding energy for clusters of diameter about 10 nm is about 163.50 eV with a shift energy of 0.9 eV to a higher energy level. Experiments have shown that as the grains become nanocrystalline, the quantum size effect results in a shift of the binding energy of electrons and a change in electronic structure.

Table 1 Binding energies of $W4f_{7/2}$ (E_{Bi}) and $S2p_{3/2}$ in different diameters

d	$W4f_{7/2}$		$S4p_{3/2}$	
	E_{Bi}/eV	ΔE_{Bi}/eV	E_{Bi}/eV	ΔE_{Bi}/eV
100 μm W	30.8			
50 nm W	32.0	+1.2		
100 μm WS_2			162.60	
50 nm S-W-S	33.2	+1.2	163.15	+0.55
10 nm S-W-S	34.0	+0.8	163.50	+0.33

In order to well understand for the microscopic physical phenomena resulting from the quantum size effect, the spectra fitting analysis was performed for $S2p_{3/2}$ electron in S-W-S cluster of diameters 50 nm and 10 nm. Fig.4 is the fitting result for $S2p_{3/2}$ electronic spectra corresponding to S-W-S cluster of 50 nm (Fig.4(a)) and 10 nm (Fig.4(b)) in diameter respectively. In Fig.4(a), there is a satellite peak appearing at the higher energy side of the principal peak (163.15 eV) of $S2p_{3/2}$ electron. After a fitting procedure, a fitted peak (s_1 in Fig.4) is obtained at 164.8 eV. In Fig.4(b) a satellite peak is also visible at the higher energy side of the principal peak (163.5 eV) at electronic spectrum of $S2p_{3/2}$. The fitted peak (s_2 in the Fig.4) is at 165.2 eV. s_1 and s_2 are indications of the overlapping between the orbitals of $S2p_{3/2}$ electron and its neighboring electrons. A quantitative analysis for the principal peaks and satellite peaks in Fig.4 indicates that mole fraction of the principal peak of $S2p_{3/2}$ electron in cluster of 50 nm is 76.47 %, that for satellite peak (s_1) is 23.53 %; the results for cluster of 10 nm are 74.29 % for the principal peak and 25.71 % for the satellite peak (s_2), respectively[11]. As can be seen, the electronic number involved in the orbital hybridization process increase from 23.53 % to 25.71 % when the diameter of S-W-S cluster decreases from 50 nm to 10 nm. The quantum size effect results in an increment of 2.18 % in electronic number of orbital hybridization. Smaller diameters in clusters favor the enhancement of orbital hybridization.

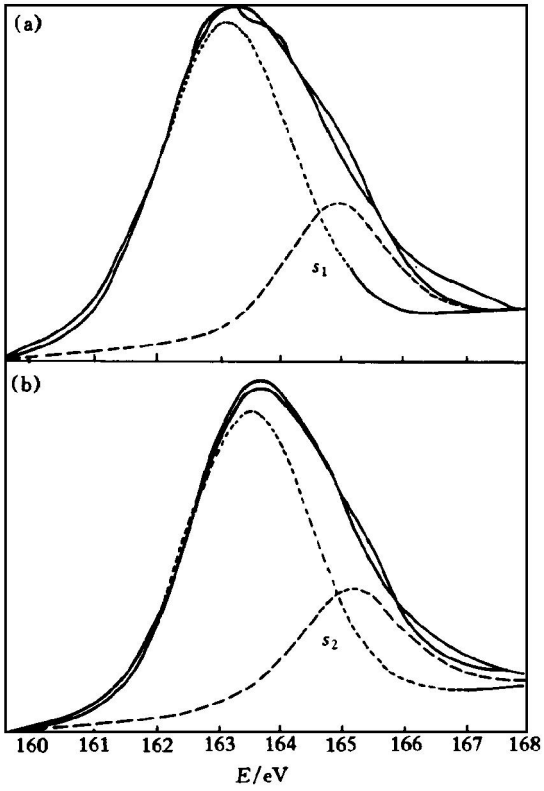

Fig.4 XPS spectra of S-W-S nanometer clusters ("—" marks of fitting line)
(a) —50 nm; (b) —10 nm

4 CHARACTERISTIC OF NANO S-WS LUBRICATION SYSTEM AND ITS LUBRICATION MECHANISM

From the analyses of the microstructure of S-W-S nano solid lubrication system, it can concluded that the structure of the S-W-S nano solid is a hollow-spheroid with a layered structure of regular crystal hexahedrons, whose surfaces are mainly composed of regular hexagon net planes with the layer spacing of

about 0.615 nm. Being self-closed structure without any dangling bonds, the 10 ~ 100 nm S-W-S nanoclusters are very stable in chemical properties, and hardly form any chemical compounds with other atoms during lubrication process[6].

The friction coefficient for conventional bulky WS_2 powder is about 0.03 ~ 0.04 in the environment of dry nitrogen vapor. The coefficient for S-W-S nano solid lubrication system is expected to be better, which makes it a new excellent solid lubrication material and promising for application. It can be used independently as a powder lubrication solid for mini-bearing, and can also be used together with some of lubricating oils to form some new synthesized lubrication products.

As S-W-S nano solid powders are very fine powder clusters, they contact with an uneven lubricating surface with the roughness in the order of μm, which can be regarded as point-touch. At any instant, the relative motion between a nano cluster and any moving object can be treated as a sphere with a rotating axis around the center of the cluster rolling on a plane with a point contact, which can be classified as a rolling lubrication system.

5 CONCLUSIONS

1) By means of mechanical-physical solid state reaction method and chemical treatment with H_2S gas at a high temperature, S-W-S nano clusters are obtained.

2) The microstructure of the S-W-S nano solid lubrication system is a spheroid with layered hexagonal crystals. Its surface is a hexagonal network formed by molecular group S—W—S with different layers linking together by Van der Waals' force. The quantum size effect enhances a tendancy of the orbital hybridization between electron shells. The S-W-S cluster is a closed structure with excellent stability in its chemical properties.

3) During lubrication process, the S-W-S nano solid is not involved in any chemical reaction. The cluster has a point contact with the uneven lubricating surface, and thus can be treated as a rolling lubrication process.

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