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Effect of La_2O_3 nanoparticles on properties of molybdenum powder①

WANG Jin-shu(王金淑), ZHOU Mei-ling(周美玲), ZUO Tie-yong(左铁镛),
NIE Zuo-ren(聂祚仁), ZHANG Jiu-xing(张久兴), LIU Juan(刘 娟)
(Key Laboratory of Advanced Functional Materials, Ministry of Education, P. R. China;
School of Materials Science and Engineering, Beijing Polytechnic University,
Beijing 100022, P. R. China)

[Abstract] The properties of La_2O_3-doped molybdenum powder were studied. The La_2O_3 nanoparticles on the surface of molybdenum powder which is produced by the reduction of $La(NO_3)_3$-doped MoO_2 in hydrogen decrease the intensity of feature energy loss peak of molybdenum substrate; but increase that of peak of Mo 3d. The surface of molybdenum powder exposed to the atmosphere can be reduced because the surface is mainly covered with La_2O_3 nanoparticles. As a result, the capability of anti-oxidation of molybdenum is improved.

[Key words] La_2O_3-doped molybdenum powder; XPS; nanoparticle
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1 INTRODUCTION

As one of the alternatives of ThO_2-W cathode, La_2O_3-Mo thermionic cathode (La-Mo) appeared in recent 30 years[1~4]. Although this cathode has good emissivity, it has not been used commercially because of its poor emission stability[5~8]. The microstructure study on this cathode shows that La_2O_3 exists in the form of nanometer and micrometer particles[9]. Large specific surface area of nanoparticles leads to high surface activities. So the chemical reaction of La_2O_3 (nanoparticles) and Mo_2C to produce lanthanum can take place at lower temperature. Then the operation temperature of this material can be lowered. The evaporation rate of active substance lanthanum is very small at lower temperature, so a certain amount of lanthanum at the cathode surface can be kept at operation temperature. Thus the life of La-Mo cathode can be prolonged[10]. Further studies show that there are many La_2O_3 nanoparticles on the surface of molybdenum powder after La_2O_3-doped MoO_2 powder is reduced in hydrogen[11]. The effect of La_2O_3 nanoparticles on the property of molybdenum is discussed in this paper.

2 EXPERIMENTAL

The oxide La_2O_3 (0.2%, 0.53%, 2.0%, 4.0%, mass fraction) in the form of aqueous solution of $La(NO_3)_3$ was added to molybdenum. The doped oxide powders were reduced into metallic molybdenum in dry hydrogen at 1 193 K for 6 h.

X-ray photoelectron spectra (XPS) analysis for the reduced powder was carried out on PHI-5300 spectrometer. Another XPS study was carried out on VGESCALAB MK-II malfunction spectrometer when the powder was exposed in atmosphere for 6 months.

3 RESULTS AND DISCUSSION

XPS analysis result for La_2O_3-doped molybdenum oxide powder reduced at 1 193 K for 6 h is shown in Fig. 1. As shown in Fig. 1, there is an obvious plasma vibrating energy loss peak on the high energy side of Mo 3d of pure molybdenum. As for solid specimen with high density, plasma vibrating energy loss spectrum is an essential part of X-ray photoelectron spectra. The intensity of energy loss peak decreases with increasing the content of La_2O_3. The effect of La_2O_3 concentration on the intensity of plasma vibrating energy loss peak of molybdenum is listed in Table 1. Plasma vibration results from the collective vibrating of electron gas produced in transmitting photoelectron to the surface. The escaping depth for photoelectrons is 0.5~ 2 nm for the metal[12]. Our former studies show that there are some La_2O_3 nanoparticles on the surface of molybdenum particles. The large specific surface area of the La_2O_3 nanoparticles results in unsaturated suspending bonds in the interface of La_2O_3 nanoparticles which is lack of oxygen and with positive electrovalence. The La_2O_3 nanoparticles on the surface attract the electron in molybdenum to prevent it from vibrating during photoelectron transmitting and leaving from the surface. The attraction be-

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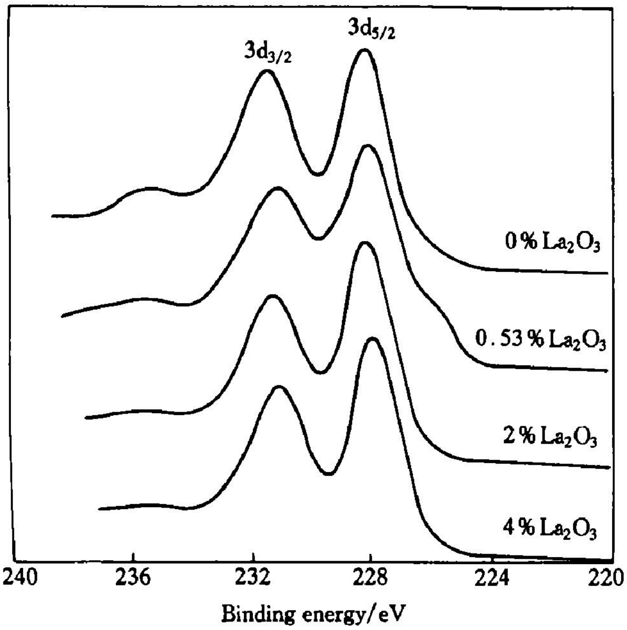

Fig. 1 X-ray photoelectron spectra from doped molybdenum

Table 1 Effect of La_2O_3 concentration on intensity of plasma vibrating energy loss peak of molybdenum

$w(La_2O_3)/\%$	0	0.53	2	4
Peak area/ Counts	942	352	256	150

comes greater with the increase of the content of La_2O_3. When the content of La_2O_3 is up to 4%, the intensive attraction makes the plasma vibrating loss peak disappear.

As for the sample with surface covered unevenly by other substance one part of the surface is exposed to the atmosphere), the intensity of photoelectron peak of the sample is

$$I = I_0 \lambda_1 \{1 - k[1 - \exp(1 - t/\lambda_2 \sin\alpha)]\} \sin\alpha \quad (1)$$

where I_0 is the intensity of photoelectrons escaping in the direction perpendicular to the surface, λ_1 and λ_2 are the average lengthes of inelastic dispersion of free electron in substrate and film, respectively, t is the depth of the film, and α is the scanning angle.

The Eqn. (1) shows that when t, λ and α are constants, the more the surface covered, the lower the intensity of the peak of Mo 3d (peak area or the height of the peak) is. So the content of La_2O_3 on the molybdenum surface increases with the increase of the content of doped La_2O_3. With the coverage of the surface (K) increasing, the peak area of Mo 3d should be decreased. However, the analysis result (Table 2) shows that the area of the peak of Mo 3d increases with the increase of the content of the La_2O_3. The abnormal phenomena can be explained by the average length of inelastic scattering of free electrons in molybdenum. Plasma is the main inelastic scattering of photoelectrons. The average length of inelastic scattering of photoelectrons and the photoelectron escaping depth (λ_e) are related to the property of the sample and the kinetic energy of the photoelectrons. As for a certain sample, the relationship between the kinetic energy of the photoelectron and λ_e is shown as:

$$\lambda_e = KE_k^n \quad (2)$$

where K is a constant, n can be got by experiment and its value is 0.5 approximately.

Table 2 Effect of La_2O_3 content on peak area for Mo 3d

$w(La_2O_3)/\%$	0.53	2	4
Peak area/ Counts	6016	7684	8140

The larger the value of λ_e, the larger the kinetic energy of the photoelectron (E_K) is. The above analysis shows that the attraction of the La_2O_3 nanoparticles on the valence electrons of molybdenum is increased with the increase of content of La_2O_3. The loss energy of the plasma in the substrate and on the surface is decreased with the increase of content of La_2O_3, so the kinetic energy of the photoelectron is increased and λ_e is increased too. By Eqn. (1), we know that the intensity of the peak of Mo 3d increases with increasing λ_e. Because the effect of λ_e on the increase of the intensity of Mo peak is larger than the effect of the content of Mo on the decrease of intensity of Mo peak, the intensity of the Mo peak is increased with increasing the content of La_2O_3.

Fig. 2 shows the X-ray photoelectron spectra from La_2O_3-doped molybdenum after being exposed to atmosphere for six months. It is shown that the intensity of Mo $3d_{5/2}$ peak in metallic state increases and the intensity of Mo $3d_{3/2}$ peak in oxidized state decreases with increasing the content of La_2O_3. The X-ray photoelectron peak between Mo $3d_{5/2}$ in metallic state and Mo $3d_{3/2}$ in oxidized state becomes wide obviously. Peak separation shows that molybdenum exists in two chemical states: metallic molybdenum Mo^0 and oxidized Mo^{6+}. The X-ray photoelectron peaks of Mo 3d are Mo $3d_{5/2}$-228.50, Mo $3d_{3/2}$-231.65, and that of Mo^{6+} 3d in MoO_3 are Mo $3d_{5/2}$-232.10, Mo $3d_{3/2}$-236.25. The quantitative calculation results are shown in Table 3.

As shown in Table 3 and Fig. 2, the percentage of the X-ray photoelectron peak of Mo 3d increases and that of Mo^{6+} 3d in MoO_3 decreases with increasing the content of La_2O_3. Because the intensity of the peak is in proportion to its content (as for the same element, the intensity of the peak can show the content of the element), it shows that the anti-oxidation property of molybdenum has been improved after being doped with La_2O_3. The former SEM observation of La_2O_3-doped molybdenum shows that the surface

Table 3 Peak area for Mo 3d with different chemical states

Binding energy	0% La_2O_3		0.53% La_2O_3		2% La_2O_3		4% La_2O_3	
	Peak area	Peak percentage	Peak area	Peak percentage	Peak area	Peak percentage	Peak area	Peak percentage
228.50	556	31.22	478	34.31	432	40.49	793	40.55
231.65	637	35.77	548	39.34	495	46.39	927	47.47
232.10	259	14.54	162	11.63	62	5.81	103	5.27
236.25	329	18.47	205	14.72	78	7.31	131	6.71

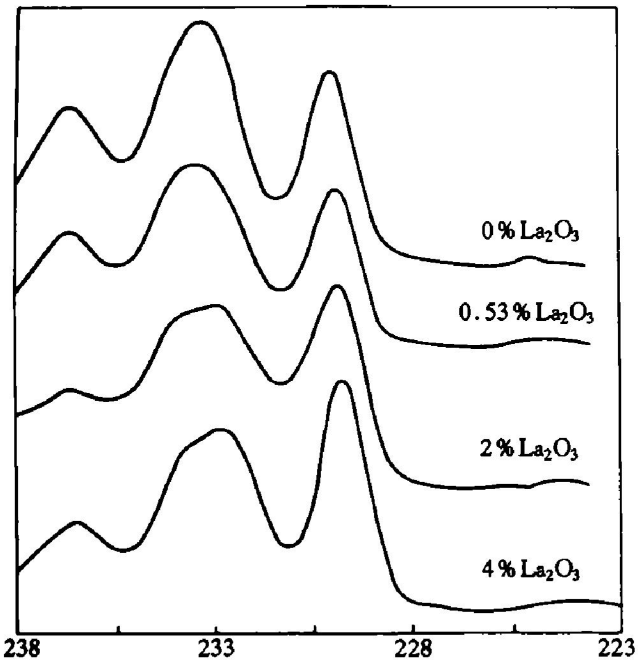

Fig. 2 X-ray photoelectron spectra from doped molybdenum after being exposed to atmosphere

of molybdenum powder is mainly covered with La_2O_3[11], so the area of molybdenum exposed to the atmosphere can be reduced and the anti-oxidation property of the molybdenum is improved.

4 CONCLUSIONS

1) The existence of La_2O_3 nanoparticles on the surface of molybdenum powder increases the inelastic scattering average length of photoelectrons. The intensity of X-ray photoelectron peak of Mo 3d is increased with the increase of the content of La_2O_3; but the intensity of the feature energy loss peak of Mo is decreased with the increase of the content of La_2O_3.

2) The La_2O_3 nanoparticles deposited during the reduction of La_2O_3-doped molybdenum oxide exist on the surface of molybdenum, so the area of molybdenum exposed to the atmosphere can be reduced and the anti-oxidation property of molybdenum is improved.

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