CHEMISTRY LETTERS, pp. 863-864, 1993.

Kinetics and Diffusing Species in the Reaction between Molybdenum and Selenium Vapor

Yoshinori SASAKI* and Noboru WAKATSUKI
Department of Applied Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Inage-ku, Chiba 263

Metallic molybdenum was selenidized at temperatures of 773-873 K in selenium vapor at 1.33 kPa. The reaction products were identified to be $MoSe_2$ alone under all the experimental conditions. All the selenidizations obeyed a parabolic rate law. A marker experiment indicated that selenium was the component which diffused.

The molybdenum selenides become important as solid lubricants and semiconductors. The kinetics1,2) of the reactions of molybdenum with selenium vapor have been investigated by means of a quartz spring balance method. The present study was undertaken to elucidate the kinetics of the reaction of molybdenum with selenium vapor and its diffusing species. The reaction conditions employed in this study are completely different from those in the above studies.

A molybdenum sheet 1 mm thick with a purity of 99.95 wt% was cut into rectangles of 6 mm × 20 mm. These were vacuum-annealed at 1273 K for 24 h, abraded with emery papers, and then polished with wet fine chromium(III) oxide powder on a buffing cloth. A sample sheet and an excess of selenium shots with a purity of 99.999 wt% were each placed at ends of a silica tube. This tube was sealed under vacuum. The apparatus and experimental methods employed in this study have been described in greater detail in a previous paper.3)

An existence of $MoSe_2$,4) Mo_3Se_4,4) $Mo_{15}Se_{19}$,5) Mo_9Se_{11},6) MoSe,7) Mo_2Se_5,8) and $MoSe_3$9) has been known as molybdenum selenides in the literature. The reaction products under all the experimental conditions were identified to be $MoSe_2$ alone by X-ray diffraction. An electron probe microanalysis also showed all the selenide films to have been composed of a single layer.

Plots of the mass gain per unit area vs. a square root of time are shown in Fig. 1. Each point represents the selenidization of individual specimens. At all the reaction temperatures, the plots yield straight lines, showing that the selenidization obeyed a parabolic rate law; hence, the rate-determining step is apparently a diffusion process of molybdenum or selenium in the selenide layers. Values of the parabolic rate constants, K_p, obtained from the slopes of these straight lines were as follows: $(2.65\pm0.39)\times10^{-3}$ at 773 K, $(3.37\pm0.24)\times10^{-3}$ at 798 K, $(4.28\pm0.25)\times10^{-3}$ at 823 K, $(4.84\pm0.25)\times10^{-3}$ at 848 K, $(6.47\pm0.23)\times10^{-3}$ $\mathrm{mg^2cm^{-4}s^{-1}}$ at 873 K. In the range of 773-873 K, an Arrhenius plot of K_p gave a straight line;

$$K_p=4.72\exp(-48.1\ \mathrm{kJ\ mol^{-1}}/RT)\ \mathrm{mg^2cm^{-4}s^{-1}}.$$

A marker experiment was carried out with silica fiber as a marker. Figure 2A shows the secondary electron image of the cross section of the selenidized specimen by an electron probe microanalyzer(EPMA). The position of silica marker was confirmed by SiKα image shown in Fig. 2B. Since the marker is situated at the gas/selenide interface, the rate can be regarded as limited by inward diffusion of selenium through the selenide layer.

References

1) J. E. Dutrizac, *Can. Met. Quart.*, **10**, 115(1971).
2) A. N. Zelikman, T. A. Lobova, Yu. O. Kolchin, and P. S. Al'tman, *Izv. Akad. Nauk SSSR, Neorg. Mater.*, **14**, 29(1978).
3) K. Takahashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, **65**, 329(1992).
4) M. Spiesser, J. Rouxel, M. Kerriou, and M. G. Goureaux, *Bull. Soc. Chim. Fr.*, **1969**, 1427.
5) JCPDS X-ray Powder Data File, card 39-786.
6) JCPDS X-ray Powder Data File, card 40-908.
7) J. M. Tarascon, *J. Electrochem. Soc.*, **132**, 2089(1985).
8) D. Schleich, PCT Int. Appl. WO 88 00,172 (1988); *Chem. Abstr.*, **109**, 58180u(1988).
9) E. Diemann, *Z. Anorg. Allg. Chem.*, **432**, 127(1977).

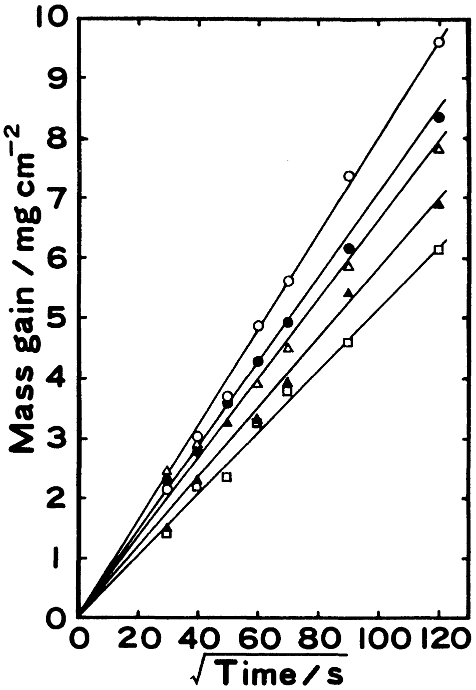

Fig. 1. Selenidization of molybdenum in selenium vapor at 1.33 kPa. ○ 873 K, ● 848 K, △ 823 K, ▲ 798 K, □ 773 K

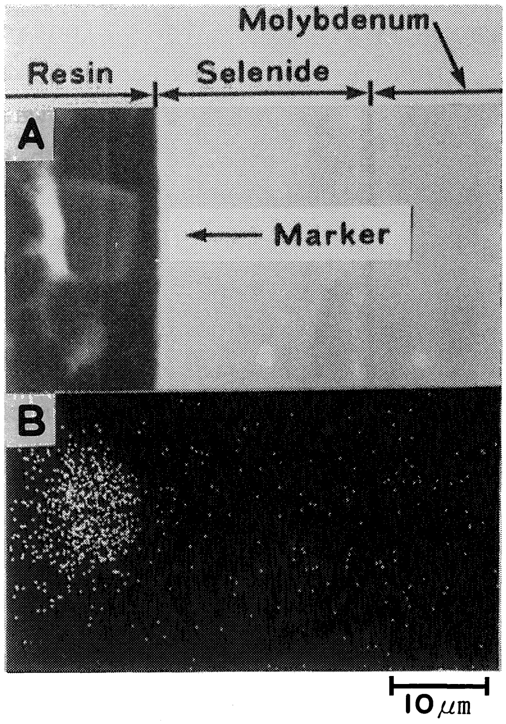

Fig. 2. Cross section of molybdenum selenide film formed at 848 K for 14.4 ks in selenium vapor at 1.33 kPa and position of a silica fiber marker by EPMA. A-Secondary electron image, B-SiKα image.

(Received January 27, 1993)