CHEMISTRY LETTERS, pp. 2009-2010, 1990.

Kinetics of the Reaction between Cobalt and Selenium Vapor at High Temperatures

Yoshinori SASAKI* and Kazuhiro TAKAHASHI
Department of Applied Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 260

Metallic cobalt was selenidized at temperatures of 550-700 °C in selenium vapor at 4.5 kPa. The products were Co_3Se_4 and $CoSe_2$. All the selenidization reactions proceeded according to a parabolic rate law, and the component which diffused was cobalt.

The metal selenides become important as fine inorganic materials. Particularly noteworthy is the zinc monoselenide as a blue LED(Light Emitting Diode). However, kinetics of the selenidization of cobalt has not been reported up to the present. This study was undertaken to elucidate (1) the relationship between compositions of selenides formed and the conditions in the reaction of cobalt with selenium vapor, (2)its kinetics, and (3)its diffusing species.

A cobalt sheet 0.5 mm thick with a purity of 99.9wt% was cut into rectangles of approximately 6 mm × 25 mm. These rectangles were vacuum-annealed at 1000 °C for 7 h, then polished with emery papers, and finished with finely divided chromium (III) oxide on a wet polishing cloth.

A sample sheet and an excess of selenium shots with a purity of 99.999wt% were each placed at an end of the silica tube. This tube was sealed under vacuum. The apparatus and experimental methods employed in this study were the same as those in phosphidation of metals.[1,2]

An existence of CoSe,[3,4] Co_3Se_4,[3,5] Co_2Se_3,[6] $CoSe_2$,[3,7] Co_2Se,[6] and Co_9Se_8[7] has been known as cobalt selenides in the literature. According to the X-ray diffraction of the product films, all of the diffraction peaks belonged to Co_3Se_4 and $CoSe_2$. By means of the EDTA chelatometric titration of cobalt with xylenol orange as an indicator, it was concluded that generally Co_3Se_4 was the main product and $CoSe_2$ also was slightly formed, and that an amount of $CoSe_2$ decreased with an increase in temperature.

Plots of the mass gain per unit area vs.$\sqrt{\text{time}}$ are shown in Fig. 1. Each point represents the selenidization of individual specimens. At all

of the reaction temperatures, the plots yield straight lines, showing that the selenidization proceeds according to a parabolic rate law; hence, the rate-determining step is apparently a diffusion process of cobalt or selenium in the selenide films.

Values of the parabolic rate constants, K_p, obtained from the slopes of these straight lines were as follows: $(1.80 \pm 0.11)\times10^{2}$ at 550 °C, $(4.07 \pm 0.43)\times10^{2}$ at 600 °C, $(1.47\pm0.10)\times10^{3}$ at 650 °C, $(3.83\pm0.32)\times10^{3}$ $mg^2cm^{-4}h^{-1}$ at 700 °C. An Arrhenius plot of K_p gave a straight line in the range of 600-700 °C, which may be approximately expressed as follows

$$K_p=1.01\times10^{12}\exp(-156.8\ kJ\ mol^{-1}/RT)\ mg^2\ cm^{-4}\ h^{-1}.$$

A marker experiment[8] was carried out with use of silica fiber as a maker. Figure 2A shows the composition image of the cross section of the specimen selenidized, which was examined by an electron probe micro analyzer(EPMA). Four black parts indicated by arrows were confirmed to be the silica makers by SiKα image shown in Fig. 2B. Since the markers are situated near the selenide/metal interface, the reaction can be regarded as limited by diffusion of cobalt.

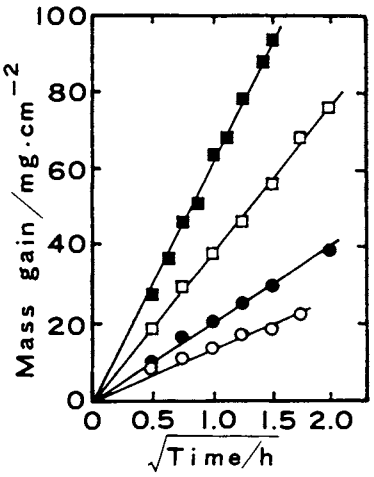

Fig. 1. Selenidization of cobalt in selenium vapor at 4.5 kPa. ○550 °C, ●600 °C, □650 °C, ■700 °C

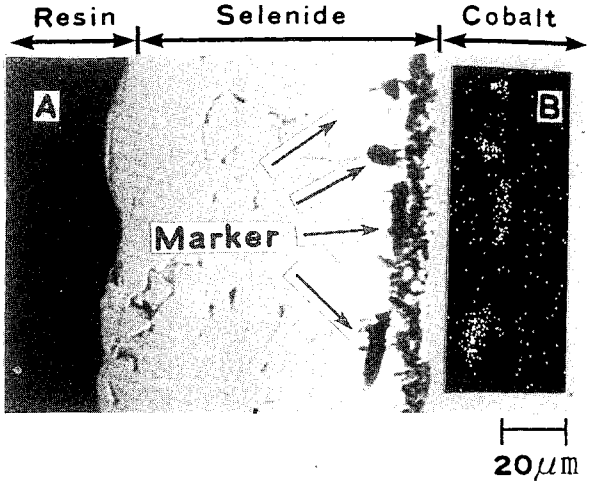

Fig. 2. Cross section of cobalt selenide film formed at 650 °C for 1 h in selenium vapor at 4.5 kPa and position of silica fiber marker by EPMA.
A-Composition image, B-SiKα image

References

1) Y. Sasaki, A. Kato, and S. Ueda, J. Electrochem. Soc., 118, 101(1971).
2) Y. Sasaki and S. Ueda, Bull. Chem. Soc. Jpn., 45, 2977(1972).
3) P. Ramdohr and M. Schmitt, Neues Jahrb. Mineral. Monatsh, 6, 133(1955).
4) M. P. Morozova, V. A. Vladimirova, A. V. Grudetskii, and E. A. Malysheva, Russ. J. Phys. Chem., 51, 927(1977).
5) F. Grønvold, J. Chem. Thermodyn., 8, 757(1976).
6) G. J. Moody and J. D. R. Thomas, J. Chem. Soc., 4, 1417(1964).
7) F. Bøhm, F. Grønvold, H. Haraldsen, and H. Prydz, Acta Chem. Scand., 9, 1510(1955).
8) A. D. Smigelskas and E. O. Kirkendall, Trans. AIME, 171, 130(1947).

(Received August 4, 1990)