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

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Metallic titanium was selenidized at temperatures of 550-700°C in selenium vapor at 4.5 kPa. The reaction product was identified to be $Ti_{1+x}Se_2$ alone under all experimental conditions. Selenide growth rates were parabolic. A marker experiment indicated that the reaction was controlled by inward diffusion of selenium through the selenide layer.

The metal selenides become important as functional inorganic materials. The kinetics of selenidization of titanium was investigated only for 400-550°C under selenium pressures of 0.01-4.3 kPa,$^{1)}$ showing to have obeyed a parabolic rate law. The present study was undertaken concerning the kinetics of selenidization of titanium at 550-700°C under the selenium vapor of 4.5 kPa and concerning its diffusing species.

A titanium sheet 1 mm thick with a purity of 99.5 wt% was cut into rectangles of approximately 6 mm x 25 mm. These rectangles were vacuum-annealed at 800°C for 4 h and polished with emery papers then with finely divided chromium (III) oxide on a wet polishing cloth.

A sample sheet and an excess of selenium shots with a purity of 99.999 wt% were each placed at ends of a silica tube. This tube was sealed under vacuum. The vapor pressure of liquid selenium is given in the literature.$^{2)}$ The apparatus and experimental methods employed in this study were the same as those in phosphidation of metals.$^{3,4)}$

An existence of $TiSe_2$,$^{5,6)}$ Ti_5Se_8,$^{6,7)}$ Ti_2Se_3,$^{6)}$ Ti_3Se_4,$^{6,8)}$ Ti_8Se_9,$^{6,8)}$ TiSe,$^{6)}$ Ti_3Se_2,$^{6)}$ and $Ti_9Se_4$$^{9)}$ has been known as titanium selenides in the literature. The reaction product was identified to be $Ti_{1+x}Se_2$ alone under all the experimental conditions by X-ray diffraction. An electron probe microanalysis also showed all the selenide films to have been composed of a single phase product.

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 obeyed a parabolic rate law; hence, the rate-determining step is apparently a diffusion process of titanium 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: $(0.39\pm0.04)\times10^2$ at 550°C, $(0.66\pm0.05)\times10^2$ at 600°C, $(1.15\pm0.09)\times10^2$ at 650°C, $(1.87\pm0.19)\times10^2$ $\text{mg}^2\text{cm}^{-4}\text{h}^{-1}$ at 700°C. In the range of 550-700°C, an Arrhenius plot of K_p gave a straight line;

$$K_p=1.05\times10^6\exp(-69.9\ \text{kJ mol}^{-1}/RT)\ \text{mg}^2\ \text{cm}^{-4}\ \text{h}^{-1}.$$

A marker experiment was carried out with silica fiber as a marker. Figure 2A shows the composition image of the cross section of the selenidized specimen by an electron probe micro analyzer(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 reaction can be regarded as limited by inward diffusion of selenium through the selenide layer.

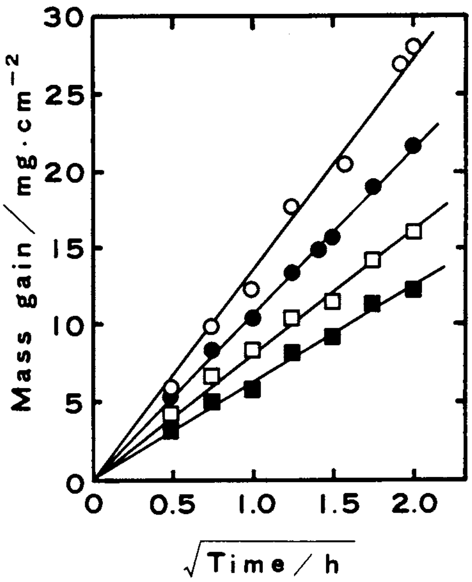

Fig. 1. Selenidization of titanium in selenium vapor at 4.5 kPa.
○700 °C, ●650 °C, □600 °C, ■550 °C

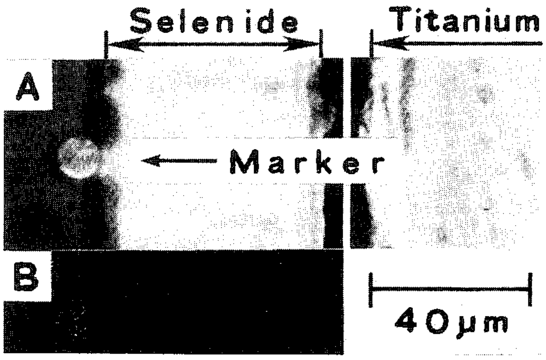

Fig. 2. A - Secondary electron images of cross section of exfoliated titanium selenide scale (left) formed at 650 °C for 4 h in selenium vapor at 4.5 kPa and of unaltered titanium substrate (right) and position of silica fiber marker by EPMA.
B - SiKα image.

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