High Temperature Selenidization of Metallic Zirconium

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1 INTRODUCTION

The metal selenides become important as functional inorganic materials. For example, molybdenum selenides are used as solid lubricants. Particularly noteworthy is the zinc monoselenide as a blue LED (Light Emitting Diode).

As part of a series of studies on the formation reactions of metal selenides, the selenidization of zirconium at high temperatures was investigated.

2 EXPERIMENTAL

A zirconium sheet 1 mm thick with a purity of 99.8 wt%, supplied by The Nilaco corporation, was cut into rectangular pieces of approximately 6 mm $\times$ 25 mm. These pieces were vacuum-annealed at 850°C for 4h 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 placed at each end of a one-side closed silica tube. This tube was sealed under vacuum. The selenidizations of zirconium were carried out at temperatures of 500 to 650°C. During the selenidization, the lowest temperature zone was kept at 433°C, so the vapor pressure of selenium was held at 10 Torr (1.33 kPa)¹⁾. The apparatus and experimental procedures employed in this study have been described in detail in a previous paper²⁾.

3 EXPERIMENTAL RESULTS

3.1 Kinetic rates

Plots of the mass gain per unit area against a square root of the reaction time are shown in Fig. 1. Each datum point represents the selenidization of individual specimens. At all the reaction temperatures the plots yield straight lines, showing that these selenidizations obeyed a parabolic rate law; hence the rate-determining step is apparently a diffusion process in the selenide layers. The parabolic rate constants obtained from the slopes of these straight lines are listed in Table 1. An only report³⁾ of the rates of selenidization of zirconium has been presented at 534°C under selenium vapor pressures of 0.026–17.59 kPa, using a silica-spring thermogravimetric apparatus, in which the selenidizations were revealed to obey a parabolic rate law at comparatively lower pressures but not to do at higher pressures. Their apparatus and reaction conditions differ widely from those in the present study.

3.2 Compositions of zirconium selenide films

The x-ray diffraction peaks of powders of the selenide films obtained under all the reaction conditions employed, using nickel-filtered copper radiation, belonged mainly to ZrSe₂ (hexagonal)^{4–6)}.

Table 1 Parabolic rate constants K_p for selenidization of zirconium under the selenium vapor pressure of 10 Torr.

Temperature/°C	$K_p/\text{mg}^2\text{cm}^{-4}\text{h}^{-1}$
500	0.41 ± 0.04
550	1.18 ± 0.08
600	3.56 ± 0.22
650	11.0 ± 0.7

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Fig. 1 Parabolic plots of selenidization of zirconium under the selenium vapor pressure of 10 Torr: ○ 650°C; ● 600°C; □ 550°C; ■ 500°C.

Fig. 2 Distribution profiles of selenium and zirconium in the selenide films (650°C–10 Torr–25h).

Composition variations through the selenide films were examined by an electron probe micro-analyzer. The specimen selenidized at 650°C was embedded in an acrylic resin, and then the cross section was polished with 0.5 μm diameter diamond paste. The results of line analysis across the cross section of this film for each element are illustrated in Fig. 2. It is clear that the intensities of ZrL α and SeL α are nearly constant through the selenide film. The somewhat higher intensity of SeL α in the neighborhood of the surface is assumed to represent a dissolution of Se in the ZrSe₂ matrix and/or a penetration of Se into the crystal grain boundaries of ZrSe₂. It was also confirmed that the molar ratio of Se/Zr, obtained from the selenium weight gained and the weight loss of metal zirconium with respect to the selenide film shown in Fig. 2, was 2.06.

From these facts, the selenide films were concluded to have been mainly composed of ZrSe₂.

4 CONCLUSIONS

Zirconium sheet samples were selenidized at 500–650°C under the selenium vapor pressure of 10 Torr by a sealed-tube method. These selenidizations proceeded according to a parabolic rate law under all the reaction conditions employed. X-ray diffraction patterns and an electron probe microanalysis of product films indicated the selenide films to have been mainly composed of ZrSe₂.

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