Kinetics and Mechanism of the High Temperature Selenidization of Cobalt

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A cobalt sheet was selenidized in selenium vapor of 1.33—13.33 kPa at 823—973 K by means of a sealed-tube method. X-Ray diffraction patterns and an electron probe microanalysis of the product films showed that double layers composed of thin outer $CoSe_2$ and thick inner Co_3Se_4 were formed under all the reaction conditions employed. All the selenidizations obeyed a parabolic rate law and therefore the rate-determining step was apparently a diffusion process. The parabolic rate constant, K_p, was expressed as a function of the absolute temperature. The pressure dependence of K_p was not clearly recognized. A marker experiment indicated that cobalt was the component which diffused.

The metal selenides become important as fine inorganic materials. Particularly noteworthy is the zinc monoselenide as a blue LED (Light Emitting Diode). Studies of cobalt selenides have been published concerning magnetic properties,[1,2] thermodynamic quantities,[3—5] and others. The authors reported an article entitled "Kinetics of the Reaction between Cobalt and Selenium Vapor at High Temperatures" as a letter.[6] The details of its subsequent investigation are described in the present paper.

Experimental

1. Materials. A cobalt sheet 0.5 mm thick with a purity of 99.9 wt% was cut into rectangles of 6 mm×25 mm. According to an analysis by the supplier (The Nilaco Corporation), the impurity level of this sheet was as follows: Ni=0.066, C=0.033, Fe=0.004, Cu=0.001 wt%. These were vacuum-annealed at 1273 K for 7 h. They were abraded with emery papers (#400, #1000, and #1500), then polished with wet fine chromium(III) oxide powder on a buffing cloth, and rinsed in a refined toluene. Their geometric surface areas and weights were measured. Selenium shots with a purity of 99.999 wt%, made by Wako Pure Chemical Industries, Ltd., were used as such for this investigation.

2. Preparation of the Sealed Cobalt Specimen and Selenium. After an excess of selenium shots was introduced into a one-side-closed silica tube (inside diameter: 7 mm) and some clean quartz wool was packed, the cobalt specimen was put in this tube. This tube was evacuated to 10^{-2} Torr (1 Torr= 133.322 Pa) at room temperature, then was filled to 1 atm with argon gas purified by passing through diphosphorus pentaoxide and heated active copper, and finally was reevacuated. The evacuating and the filling were repeated five times at 473 K in order to remove moisture, oxygen, and other gaseous impurities adsorbed on the selenium shots, the quartz wool, and the inner wall of the tube. In this case, only the cobalt specimen placed near the entrance end of the tube was not heated. After these operations this tube was sealed under vacuum.

3. Apparatus and Procedures. A schematic drawing of a selenidization apparatus employed is represented in Fig. 1. It consists simply of two furnaces. The selenidization temperature (T_1) was given by one furnace. Selenium vapor pressure is governed by the minimum temperature in the closed system. The minimum temperature (T_2) in the neighborhood of the contact part of the two furnaces was controlled by adjustment of temperature of the other furnace. The selenium vapor pressure, p in Torr, is given as a function of the Celsius temperature by the following expression:[7]

$$\log(p/\text{Torr}) = 7.6316 - 4213.0/(202.0 + t/^\circ\text{C}).$$

The experiment was carried out under the conditions of (i) a selenium vapor pressure of 4.53 kPa at reaction temperatures of 823, 873, 923, and 973 K and (ii) a temperature of 873 K at 1.33 kPa (10 Torr), 4.53 kPa (34 Torr), and 13.33 kPa (100 Torr).

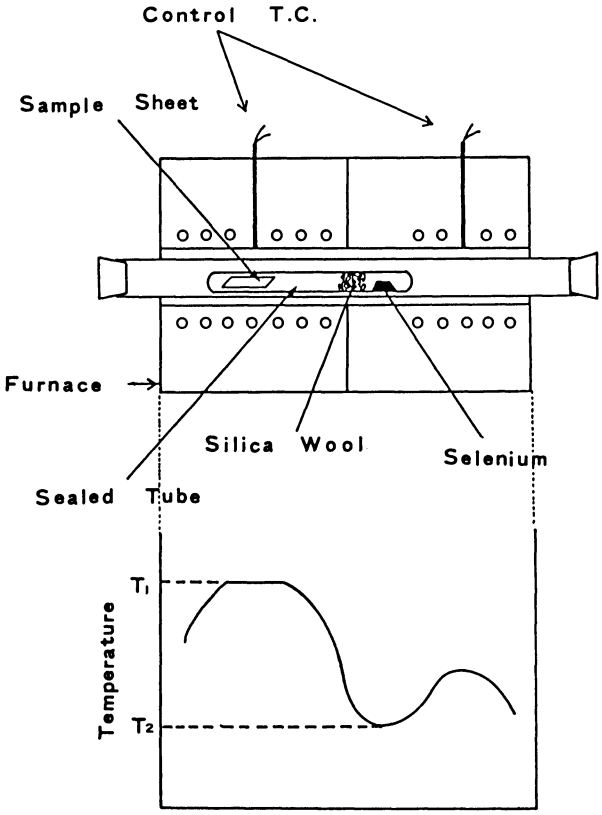

Fig. 1. The selenidization apparatus and the temperature distribution of the furnaces.

Results and Discussion

1. Composition of Product Films. The products were gray films under all the selenidization conditions employed in this experiment. The six cobalt selenides are known in the literature: $CoSe_2$,[2,8] Co_2Se_3,[9] Co_3Se_4,[4,8] CoSe,[3,8] Co_9Se_8,[2] and Co_2Se.[9]

Figure 2 illustrates the X-ray diffraction patterns, employing nickel-filtered copper radiation, for the surface side of selenide films. The diffraction patterns of Fig. 2 were drawn in accord with the positions of diffraction peaks and their heights in the actual diffraction charts. The peak of 2θ=ca. 44.0° belonging to $CoSe_2$[2,10] is observed in the reaction at 823 K (Fig. 2A), whereas this peak disapears completely at 873—973 K. At the further elevated temperatures one or two new diffraction peaks (2θ=45.3°, 46.3°) belonging to the lower selenide Co_3Se_4[8,10] are observed.

The specimen selenidized at 823 K and 4.53 kPa for 0.25 h was embeded in a methyl methacrylate polymer and its cross section was polished with 0.5 μm diameter diamond paste. Figure 3 shows the composition image of its cross section, by means of electron probe microanalyzer (EPMA), which prove thoroughly the selenide film to be dense and to have a double layer structure from a difference in brightness. The film was isolated from the cobalt substrate. This isolation took place naturally on cooling to room temperature, owing to the difference between the thermal expansion coefficients of the selenide and this metal.

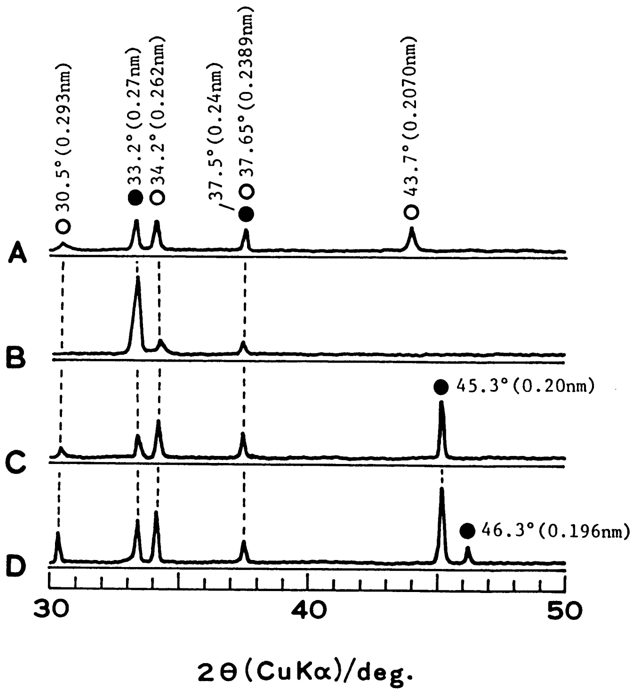

Fig. 2. X-Ray diffraction patterns for surface side of cobalt selenides formed at 823—973 K under a selenium pressure of 4.53 kPa. Parentheses denote the interplanar spacings cited from references.[2,8,10]
A-823 K, 2.25 h; B-873 K, 0.25 h; C-923 K, 1 h; D-973 K, 2. 25 h. ○ : $CoSe_2$, ● : Co_3Se_4.

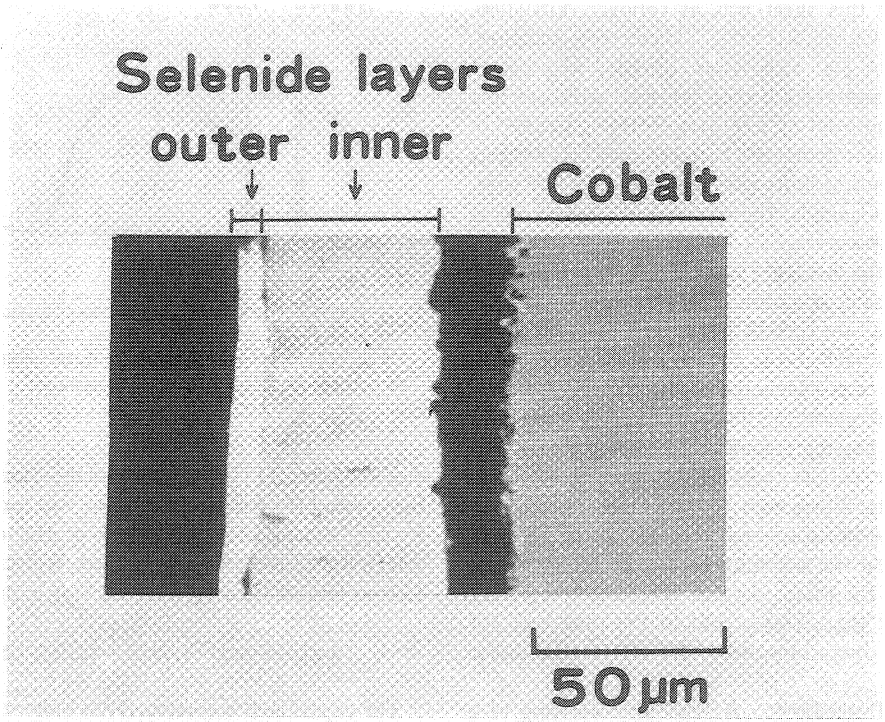

Fig. 3. Composition image of cross sections of the isolated cobalt selenide film (left) formed at 823 K for 0. 25 h in selenium vapor at 4. 53 kPa and of unaltered cobalt substrate (right) by EPMA. The two black regions mean resin.

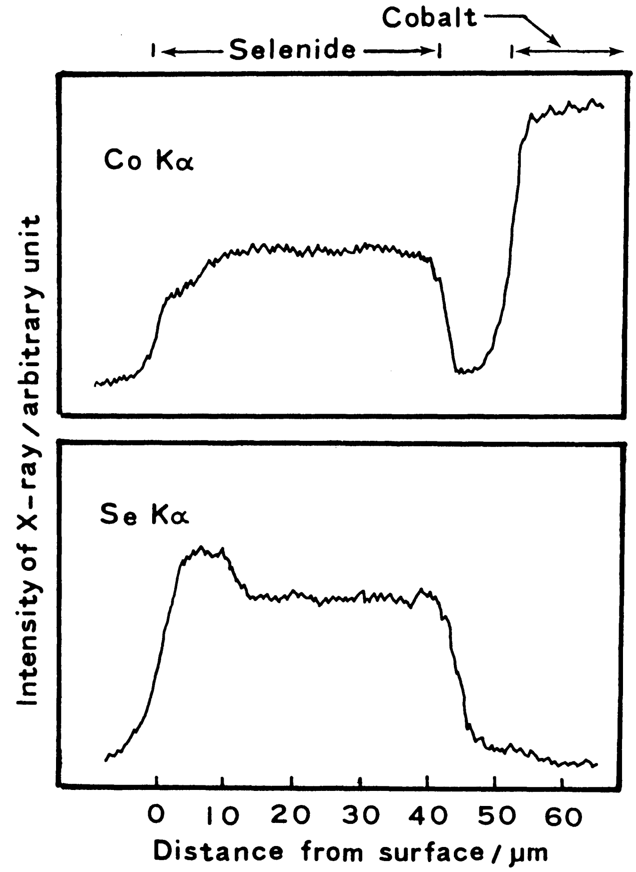

Fig. 4. Distribution profiles of cobalt and selenium in the selenide film formed at 823 K and 4.53 kPa for 0.25 h, which was shown in Fig. 3.

Composition variations through the cross section of the selenide film given in Fig. 3 were examined by EPMA and are shown in Fig. 4, with the intensities of Co *Kα* and Se *Kα* as ordinate and the distance from surface as abscissa. It is clear from Fig. 4 that two plateaus having nearly constant intensity of Se *Kα* or Co *Kα* are present in the bulk selenide. The composition of the outer plateau should correspond to $CoSe_2$ and the inner plateau should correspond to Co_3Se_4 from the X-ray diffraction patterns (Fig. 2). This double layer structure was seen also in Fig. 3, as mentioned already.

2. Kinetics. The weight change with time, caused by selenidization, cannot be measured continuously using the sealed-tube method, but kinetic results obtained by weighing before and after exposure to selenium vapor are shown in Fig. 5 . It should be noted that each data point was obtained from an individual specimen. All the plots yield straight lines, showing that the weight gains followed a parabolic rate law which is based on metal or nonmetal diffusion through a plane parallel scaling film. Values of the parabolic rate constants, K_p, obtained from the slopes of these straight lines are summarized in Table 1.

A semilogarithmic plot of K_p vs. the reciprocal of the

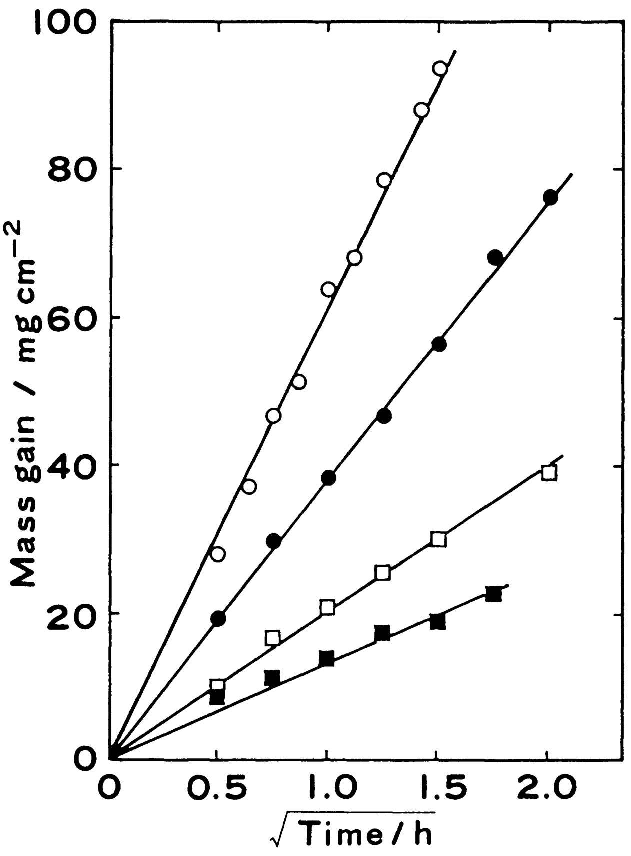

Fig. 5. Selenidization of cobalt in selenium vapor at 4.53 kPa. ○: 973 K, ●: 923 K, □: 873 K, ■: 823 K.

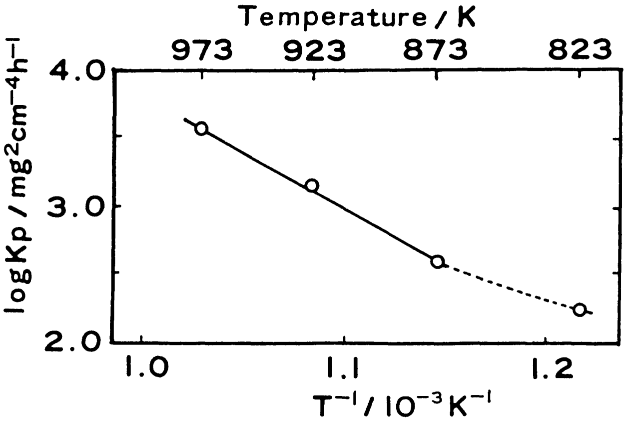

Fig. 6. Temperature dependence of K_p for selenidization of cobalt in selenium vapor at 4.53 kPa.

Table 1. Values of the Parabolic Rate Constants for Selenidization of Cobalt

Temperature/K	Selenium pressure/kPa	K_p/mg^{2}cm^{-4}h^{-1}
823	4.53	$(1.80\pm0.11)\times10^2$
873	1.33	$(4.12\pm0.41)\times10^2$
873	4.53	$(4.07\pm0.43)\times10^2$
873	13.33	$(4.41\pm0.27)\times10^2$
923	4.53	$(1.47\pm0.10)\times10^3$
973	4.53	$(3.83\pm0.32)\times10^3$

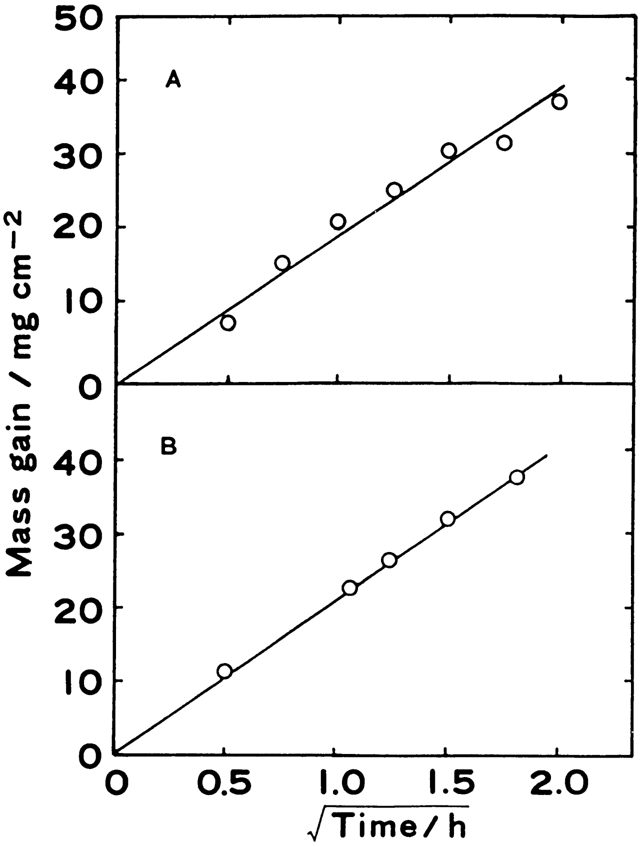

Fig. 7. Selenidization of cobalt at 873 K in selenium vapor at (A) 1.33 kPa and (B) 13.33 kPa.

absolute temperature is shown in Fig. 6. This relationship gives a straight line in the temperature range of 873—973 K, which was approximately expressed as follows:

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

Figure 7 represents the findings of selenidization of coblat at 873 K under the selenium vapor pressures of 1.33 and 13.33 kPa, and shows that both the selenidizations obey parabolic behavior. The rate constants obtained from these slopes are given in Table 1. No vapor pressure dependence of K_p at 873 K was recognized in the pressure range of 1.33—13.33 kPa.

3. Diffusing Species. Since in the selenide growth the rate-determining step seemed to be a diffusion process, a marker experiment relating to the diffusion process[11] was carried out for the selenidization of cobalt by use of silica fiber as a marker. Figure 8A shows the composition image of the cross section of the specimen selenidized at 923 K and 4.53 kPa for 1 h and shows the positions of the silica fiber markers, which was examined by EPMA. Four black portions indicated by four arrows were confirmed to be the silica fiber markers by the Si $K\alpha$ image shown in Fig. 8B.

Since the markers are situated near the selenide/metal interface, the reaction can be regarded as controlled by diffusion of cobalt through the selenide film.

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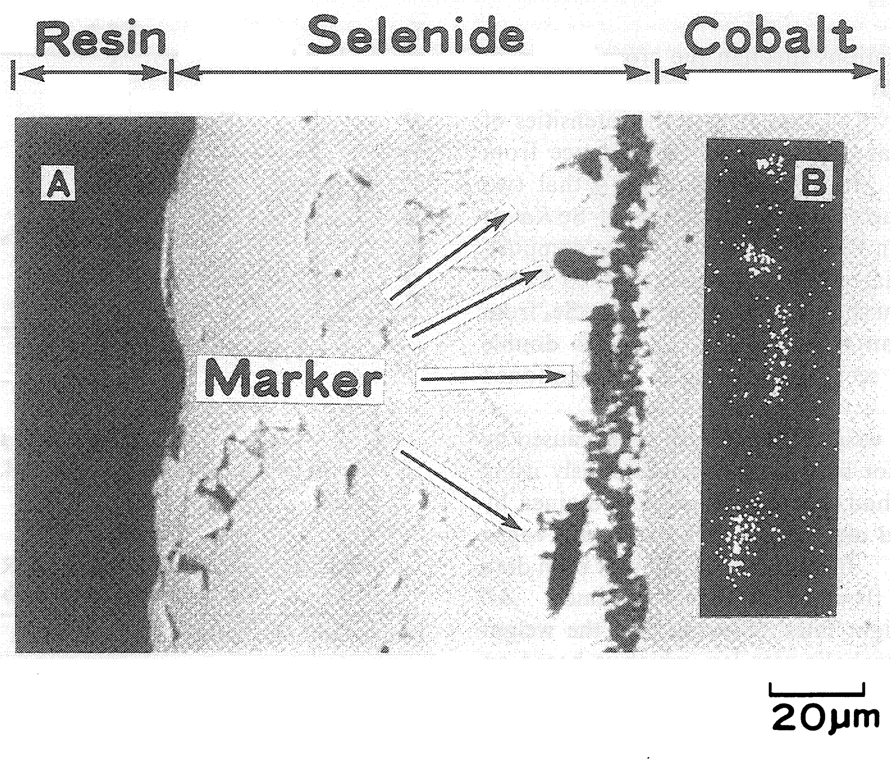

Fig. 8. Cross section of the cobalt selenide film formed at 923 K for 1 h in selenium vapor at 4.53 kPa and positions of silica fiber markers by EPMA. A-Composition image, B-Si $K\alpha$ image.

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