Electrochemical Formation of Ca-Si in Molten CaCl₂-KCl

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Electrochemical formation of a Ca-Si film in a molten CaCl₂-KCl at 923 K was investigated. Potentiostatic electrolysis of a Si electrode at –0.10 V for 1 h resulted in the formation of a multiphase Ca-Si film having a thickness of about 30 μm. The Ca-Si film was converted into other alloy phases by anodic potentiostatic electrolysis after the cathodic electrodeposition of Ca metal at –0.10 V. The various transformation reactions and the corresponding equilibrium potentials were clarified. At 923 K, the equilibrium potential was found to be 0.18 V (CaSi₂). Reflectance measurements in the ultraviolet, visible, and near-infrared region clarified that the CaSi₂ film has a direct bandgap of 3.1 eV.

Results and Discussion

Electrochemical window of CaCl₂-KCl.— Figure 1 shows the cyclic voltammograms obtained in CaCl₂-KCl at 923 K. A molybdenum wire and a glassy carbon rod were used as the working electrodes in the negative and positive potential regions, respectively. In the negative potential region, a sharp cathodic current and the corresponding voltage appears. The redox reaction at the Mn⁰/M electrode prepared by the following reaction was calibrated with a reference electrode prepared by the following reaction.

Results and Discussion

Experimental

CaCl₂ (95.0%, Wako Pure Chemical Co. Ltd.) and KCl (99.5%, Wako Pure Chemical Co. Ltd.) were mixed in eutectic composition (CaCl₂:KCl = 38.4:61.6 mol%), and introduced in a high-purity alumina crucible (99.5 wt% Al₂O₃; SSA-S grade, NIKKATO Co. Ltd.), which was then kept under vacuum for more than 24 h at 473 K to ensure complete removal of water. All experiments were performed in the CaCl₂–KCl eutectic melt in a dry argon atmosphere. Temperature measurements were performed using a Chromel-Alumel thermocouple, with an accuracy of ±1 K. To investigate the electrochemical behavior, n-type Si plates (5 mm × 20 mm × 0.5 mm; 99.5%, Nilaco Co. Ltd.) were used as the working electrodes. The reference electrode was a silver wire immersed in CaCl₂-KCl containing 1 mol% of AgCl, placed in an alumina tube with a thin bottom to maintain electrical contact with the melt. The potential of the reference electrode was calibrated with reference to that of a M⁰/M electrode, which was prepared by electrodepositing an alkali metal on Mo wire. All potentials referred to in this paper are expressed with reference to the M⁰/M potential. The counter electrode was a glassy carbon rod (3 mm diameter; Tokai Carbon Co. Ltd.). A potentiostat/galvanostat (Hokuto Denko Co. Ltd. HZ-3000) was used for cyclic voltammetry and chronopotentiometry measurements. The samples were prepared by potentiostatic electrolysis and rinsed with ethylene glycol. The obtained samples were analyzed by X-ray diffractometry (XRD) with a Cu Kα line. The surface and cross-section of the samples were observed by scanning electron microscopy (SEM; JSM-7001, JEOL). For evaluation of the optical properties of the films, ultraviolet-visible-near infrared (UV-VIS-NIR) reflectance spectra were measured using a JASCO V-670 spectrophotometer.

Results and Discussion

Electrochemical window of CaCl₂-KCl.— Figure 1 shows the cyclic voltammograms obtained in CaCl₂-KCl at 923 K. A molybdenum wire and a glassy carbon rod were used as the working electrodes in the negative and positive potential regions, respectively. In the negative potential region, a sharp cathodic current and the corresponding anodic current were observed at about 0.10 V, which were attributable to the deposition of Ca or K metal and dissolution of the deposits, respectively. The current observed at a potential more negative than –0.4 V is due to the formation of Ca metal (activity smaller than 1) and its dissolution in CaCl₂. The potential at the cathodic limit was defined as the potential of the M⁰/M electrode prepared by the following procedure. Galvanostatic electrolysis was conducted at –50 mA cm⁻² using a molybdenum electrode for 20 s, and then, the open-circuit potential was measured, as shown in Figure 2. The potential measured immediately after the electrolysis was the M⁰/M potential.

In the positive potential region of the cyclic voltammogram, the anodic current increased from about 3.40 V, as shown in Figure 3. Because chloride ions were the only anions in this melt, the anodic currents were considered to be due to the oxidation of chloride ions to chlorine gas.

2Cl⁻ → Cl₂ + 2e⁻ [1]

After the potential sweep direction was reversed (to negative), the current constantly decreased, eventually falling to zero at 3.46 V.
This potential was defined as the potential of the anodic limit, since it is regarded as the Cl$_2$/Cl$^{-}$ potential. From the CV results, the electrochemical window was determined to be 3.46 V.

**Cyclic voltammetry.**— In order to investigate the electrochemical behavior of the calcium ions, cyclic voltammetry was conducted in molten CaCl$_2$-KCl at 923 K. Figure 4 shows the cyclic voltammograms for a Si electrode at a scanning rate of 0.1 V s$^{-1}$ at 923 K.

The electrochemical behavior of a Mo electrode was also investigated for comparison, because Mo does not form an alloy with Ca. Figure 4 shows the typical cyclic voltammograms for Mo and Si electrodes at a scanning rate of 0.1 V s$^{-1}$. For the Mo electrode, a sharp increase in the cathodic current was observed at 0.2 V. Since Mo does not form alloys with Ca and K, the cathodic current was considered to be due to Ca or K metal deposition. After reversing the scanning direction at 0.10 V, a large anodic current peak was observed, because of the anodic dissolution of Ca or K metal.

For the Si electrode, cathodic currents were observed from 1.20 V. Since this potential was more positive than the potential for Ca metal deposition, the cathodic currents were attributed to the formation of Ca-Si alloys. The standard formal potentials of Ca$_2$Si, CaSi, and CaSi$_2$ were 0.35, 0.46, and 0.49 V, respectively, as calculated from the corresponding standard Gibbs energies of formation. These results agreed with those deduced from the cyclic voltammogram in Figure 4.

When the potential scan direction was reversed at −0.10 V, several anodic peaks were observed at 0.35, 0.65, and 1.00 V, respectively, indicating Ca dissolution from the different Ca-Si alloy phases.

**Formation of Ca-Si alloy.**— Based on the results of cyclic voltammetry, an alloy sample was prepared by potentiostatic electrolysis on a Si electrode at −0.10 V for 1 h. Figure 5 shows the XRD pattern of the sample. The spectrum showed peaks assignable to CaSi, CaSi$_2$, and the Si substrate, along with several unknown peaks.
Figure 5. XRD pattern of the sample obtained by potentiostatic electrolysis with a Si electrode at $-0.10$ V for 1 h in CaCl$_2$-KCl eutectic at 923 K.

Figure 6 shows a cross-sectional SEM image of the sample and the concentration profiles of Ca and Si obtained by EDS line analysis. The observed alloy layer with a thickness of approximately 30 $\mu$m was considered to comprise CaSi and CaSi$_2$ layers, in accordance with the XRD result.

**Phase control of Ca-Si.**— The phase diagram of the Ca-Si system is shown in Figure 7. Accordinng to this diagram, three Ca-Si intermetallic compounds having Ca concentrations lower than those of CaSi$_2$, CaSi, and Ca$_2$Si should exist at 923 K.

Figure 7. Phase diagram of the Ca-Si system.

Chronopotentiometry measurements were conducted to confirm the possibility of formation of Ca-Si alloy phases.

Open-circuit potentiometry was carried out to further investigate the formation of Ca-Si alloys. Figure 8 shows the open circuit potential transient curve for a Si electrode after the deposition of Ca metal by galvanostatic electrolysis at $-50$ mA cm$^{-2}$ for 60 s, in molten CaCl$_2$-KCl at 923 K.

As can be seen in the chronopotentiogram, the potential remained at 0 V for the initial 10 s, probably because of the presence of the deposited Ca metal on the electrode. Subsequently, plateaus were observed at 0.18, 0.47, and 0.57 V, which were possibly due to different coexisting Ca-Si phases. Based on this result, samples were prepared by potentiostatic electrolysis.

First, potentiostatic electrolysis was conducted at $-0.10$ V for 30 min. Then, anodic dissolutions of Ca were conducted for 30 min.
The phases of the samples were analyzed by XRD, and the cross sections of the samples were observed by SEM.

Figure 9a shows the XRD pattern of sample 1 (obtained at 0.10 V). The alloy phase was identified as CaSi. Figure 9b shows the cross-sectional SEM of sample 1, indicating that the thickness of the CaSi film is about 10 μm. Figure 10a shows the XRD patterns of sample 2 (obtained at 0.37 V). The alloy phase was identified as CaSi₂. From the cross-sectional SEM image (Figure 10b), the thickness of the CaSi₂ film was determined to be about 20 μm.

Therefore, the potential plateau at 0.18 V was considered to correspond to the following reaction:

\[ \text{CaSi}_2 + \text{Ca}^{(II)} + 2e^- \rightarrow 2\text{CaSi} \]

Figure 11a shows the XRD pattern of sample 3 (obtained at 0.50 V), indicating Si and CaSi₂ phases. The cross-sectional SEM image in Figure 11b shows the film thickness to be about 20 μm. Figure 12a shows the XRD patterns of sample 4 (obtained at 0.78 V), revealing only Si peaks. Figure 12b shows the cross-sectional SEM image of sample 4, indicating that the transformed film is about 20 μm thick with a porous structure. Thus, the potential plateau at 0.57 V was considered to correspond to the following reaction:

\[ 2\text{Si} + \text{Ca}^{(II)} + 2e^- \rightarrow \text{CaSi}_2 \]

These results suggested that phase control of the Ca-Si alloys is possible by appropriately adjusting the applied potential.

Optical properties of Ca-Si film.— The optical properties of the Ca-Si film, such as reflectance and absorption coefficient, were investigated as a function of wavelength by UV-VIS-NIR reflectance measurements. The reflection spectrum of the Ca-Si product in the
wavelength range 300–600 nm is shown in Figure 13, which reveals reflectance changes in the UV region. In the UV region, the Kubelka-Munk function was used to convert the diffuse reflectance:

\[
\frac{\alpha}{S} = \frac{(1 - R)^2}{2R} \tag{4}
\]

where \(\alpha\) is the absorption coefficient, \(S\) is the scattering coefficient, which is assumed to be constant and equal to 1, and \(R\) is the reflectance.

For determining the absorption edge of the semiconductors, the following equation applicable to a direct-band-gap semiconductor was used.

\[
(h\nu\alpha)^2 = C (h\nu - E_g) \tag{5}
\]

The band-gap energy was determined from the plot of \((h\nu\alpha)^2\) versus \(h\nu\), which was linear, as illustrated in Figure 14. The band-gap value was obtained by extrapolating the straight portion of the graph on the \(h\nu\) axis to \((h\nu\alpha)^2 = 0\), as indicated by the dotted line in the figure. Thus, the direct absorption edge was found to be located at 3.1 eV.
From the present measurements, the bandgap of CaSi₂ was confirmed to be in the ultraviolet region.

Conclusions

The electrochemical formation of a Ca-Si alloy was investigated in CaCl₂-KCl at 923 K. The electrochemical window of CaCl₂-KCl was found to be 3.46 V at 923 K. Potentiostatic electrolysis of a Si electrode at $-0.10 \text{ V}$ resulted in the formation of a multiphase Ca-Si film having a thickness of about 30 $\mu$m. The multiphase Ca-Si film was converted into a CaSi, CaSi₂, or Si phase by anodic potentiostatic electrolysis depending on the potential. The various transformation reactions and the corresponding equilibrium potentials were clarified. UV-VIS-NIR reflectance measurements confirmed that the bandgap of CaSi₂ is 3.1 eV with a direct absorption edge.

References