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Thermodynamic properties of molybdenum silicides by molten electrolyte EMF measurements

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Abstract

EMF measurements on silicon concentration cell were carried out using molten lithium silicate electrolyte in the temperature range 1305–1507 K. Using the EMF–temperature relations, the standard free energies of formation for Mo_3Si, Mo_5Si_3 and $MoSi_2$ have been obtained as functions of temperature: $\Delta_f G^\circ$ (Mo_3Si) (kJ mol^{-1}) = $-122.1 + 0.0027T$ (K) ± 0.15, $\Delta_f G^\circ$ (Mo_5Si_3) (kJ mol^{-1}) = $-312.9 - 0.0064T$ (K) ± 0.26 and $\Delta_f G^\circ$ ($MoSi_2$) (kJ mol^{-1}) = $-146.3 + 0.0096T$ (K) ± 0.22, respectively. Combining the results with thermodynamic data, the standard enthalpies of formation for these silicides at 298 K have been calculated as $\Delta_f H^\circ$ (Mo_3Si, 298) (kJ mol^{-1}) = -122.1 ± 6.0, $\Delta_f H^\circ$ (Mo_5Si_3, 298) (kJ mol^{-1}) = -313.5 ± 12.0 and $\Delta_f H^\circ$ ($MoSi_2$, 298) (kJ mol^{-1}) = -135.8 ± 4.5, respectively.

Keywords: Transition metal alloys and compounds; Electromotive force; EMF; Thermodynamic properties

1. Introduction

Silicides of transition metals are well known for their oxidation resistance. For example, molybdenum disilicide is used as heating element in oxidizing atmosphere for achieving high temperature. Although thermodynamic properties of molybdenum silicides indicate applicability for various practical uses, direct measurements of the standard free energies of formation for molybdenum silicides have been reported only to a limited extent. Chart [1] reported these values for Mo_3Si, Mo_5Si_3 and $MoSi_2$, by measuring the vapor pressure of SiO at temperatures from 1410 to 1675 K by Knudsen effusion method. EMF measurements using zirconia electrolyte were performed by Ohmori et al. [2] and they reported these values for Mo_3Si and Mo_5Si_3 at temperatures 1150–1450 K. However, the results of these works do not agree with each other. Additionally, assessed and calculated values of the standard free energies of formation for these silicides by Hultgren et al. [3], Barin [4] and Tomaszkiewicz et al. [5,6] are also inconsistent. The standard enthalpies of formation at 298 K, $\Delta_f H^\circ$ (298), for these three silicides were reported by Searcy and Tharp [7] and Chart [1]. Searcy and Tharp [7] measured the silicon vapor pressure at temperatures from 1926 to 2261 K by Knudsen effusion method and obtained values by combining the heat capacity data. Robbins and Jenkins [8], Maslov et al. [9], Tomaszkiewicz et al. [5,6], O'Hare [10] and Meschel and Kleppa [11] used calorimetric method for determination of $\Delta_f H^\circ$ (298) values. However, difference in these results is not negligible.

The EMF measurements have been widely used for determination of thermodynamic activity. However, application of these measurements to refractory metal silicide systems has not been so popular, because of high reactivity of silicon and low partial pressure of oxygen determined by Si/SiO_2 equilibrium. In the previous works by the authors [12,13], molten lithium silicate electrolyte was utilized for EMF measurements of the silicon concentration cells for determination of the standard free energies of formation for niobium and tungsten silicides. Because of the potential utility of the method adopted in the previous work, this has been applied for molybdenum silicides in the present study. The temperature range investigated is 1305–1507 K. Based on the results, the standard enthalpies of formation at 298 K for Mo_3Si, Mo_5Si_3 and $MoSi_2$ have also been obtained.

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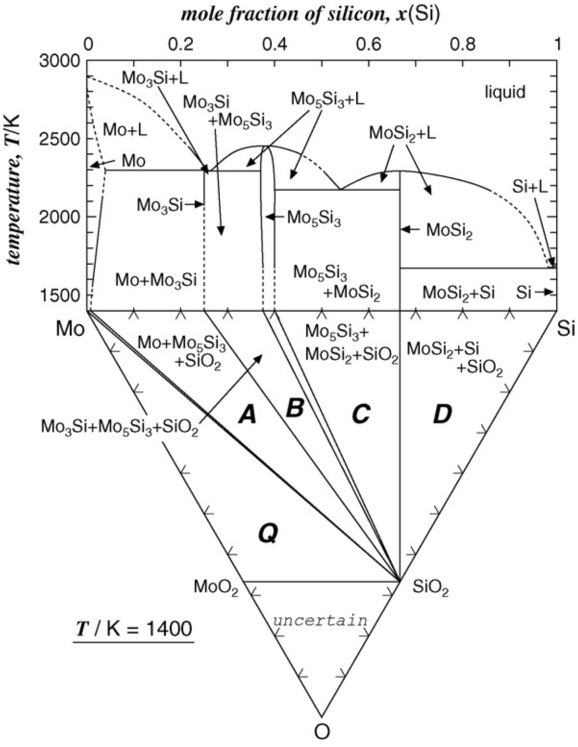

Fig. 1. Phase diagram of the Mo–Si binary system and the isothermal section of the Mo–Si–O ternary system at 1400 K. Each of the three-phase regions of A–D and Q corresponds to the point A–D and Q in Fig. 2.

2. Experimental

2.1. Phase relation and potential diagram

In Fig. 1, phase diagram of the Mo–Si binary system [10] is shown together with the isothermal section of the Mo–Si–O ternary system at 1400 K. According to the binary phase diagram, three molybdenum silicides, i.e., Mo_3Si, Mo_5Si_3 and $MoSi_2$, exist in this system. In this figure, a polymorphic transformation of $MoSi_2$ at high temperature (2173 K) is omitted. The isothermal section is constructed based on the potential diagram shown in Fig. 2. In calculation of the relations in Fig. 2, present results of EMF measurement (Section 3.1) and Barin's [4] data of the standard free energy of formation for oxides were used. The solid lines in Fig. 2 correspond to the two-phase equilibrium except for the lines for SiO_2 and Si (these are represented as gray lines). The points A–D and Q in Fig. 2 correspond to the three-phase triangles A–D and Q in the isothermal section shown in Fig. 1. No ternary compounds have been reported in the literature in the quadrangle Mo–MoO_2–SiO_2–Si for the isothermal section (Fig. 1). In addition to this, the partial pressure of oxygen at point Q is calculated to be much higher than that at point A (Fig. 2). Thus, SiO_2 coexists with each of the phases in the Mo–Si binary system, i.e., Mo, Mo_3Si, Mo_5Si_3 and $MoSi_2$, at this temperature.

In this study, EMF measurements have been carried out, for the three-phase regions of A–C. It should be noted here that solid solubility is estimated to be less than 1 mol.% Si in Mo phase at the present experimental temperatures [14]. In addition to this, non-stoichiometry of Mo_5Si_3 phase is not negligible and this phase is assumed to be stable from the stoichiometric composition of Mo_5Si_3: $x(\mathrm{Si}) = 0.375$ to the silicon rich composition: $x(\mathrm{Si}) = 0.400$ within the experimental temperature range [14], where $x(\mathrm{Si})$ is the mole fraction of silicon in the Mo–Si binary system. Thus, consideration of these phase equilibria has been applied in calculation of the standard free energy of formation for the silicides from the EMF values measured (in Section 3.2).

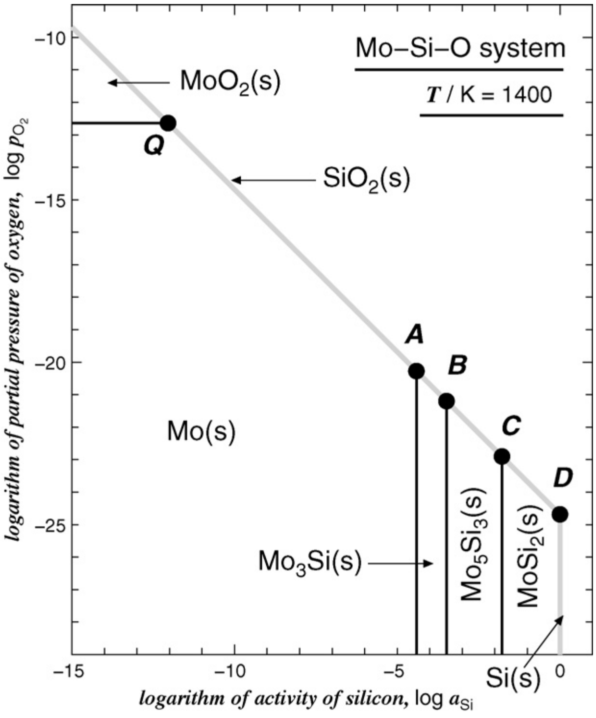

Fig. 2. Potential diagram of Mo–Si–O ternary system at 1400 K. Points A–D and Q correspond to the three-phase regions shown in Fig. 1.

2.2. Configuration of the cells

Three kinds of cells were used for EMF measurements, i.e.,

$$\mathrm{cell(A)}: (-)\mathrm{Mo, Si} + (\mathrm{Ag\ alloy\ or\ MoSi_2}) + \mathrm{SiO_2/electrolyte/Mo} + \mathrm{Mo_3Si} + \mathrm{SiO_2, Mo}(+) \quad (1)$$

$$\mathrm{cell(B)}: (-)\mathrm{Mo, Si} + (\mathrm{Ag\ alloy\ or\ MoSi_2}) + \mathrm{SiO_2/electrolyte/Mo_3Si} + \mathrm{Mo_5Si_3} + \mathrm{SiO_2, Mo}(+) \quad (2)$$

$$\mathrm{cell(C)}: (-)\mathrm{Mo, Si} + (\mathrm{Ag\ alloy\ or\ MoSi_2}) + \mathrm{SiO_2/electrolyte/Mo_5Si_3} + \mathrm{MoSi_2} + \mathrm{SiO_2, Mo}(+) \quad (3)$$

The activity of silicon was fixed as unity in the reference electrode of these cells. For this purpose, liquid silver alloy saturated with Si and SiO_2 was chosen. However, three-phase mixture of Si, SiO_2 and $MoSi_2$ was used for some of the initial experiments [13]. Right-hand sides of the cells (A–C) correspond to the three-phase equilibria of A–C in Figs. 1 and 2, respectively. Oxide melts of the Li_2O–SiO_2 binary system saturated with SiO_2 were used as electrolyte in all the cells. The ionic conductivity of this electrolyte can be assumed unity [15]. The electrolyte composition was 86 mass% SiO_2. This composition corresponds to the SiO_2-liquidus at 1573 K in the Li_2O–SiO_2 binary phase diagram [16].

2.3. Procedure and materials

Details on the experimental procedure have been reported elsewhere [12,13]. Mo_3Si, Mo_5Si_3 and $MoSi_2$ were synthesized by vacuum heating of the compacted mixture of pure elements (Mo powder: 99.9%, less than 74 μm, Si powder: 99.999%, less than 50 μm, Furuuchi Chemical Co.) at 1473 K for 7.2 ks and at 1873 K for 7.2 ks, respectively. Lithium silicate used as electrolyte was prepared from Li_2CO_3 and SiO_2. The mixture of Li_2CO_3 and SiO_2 was decarbonated at 1173 K in platinum crucible for 43.2 ks and pre-melted at 1473 K in graphite crucible. Surface carbon of the pre-melted drop of lithium silicate was eliminated by heating at 1273 K in air.