Thermodynamic Measurement for Cr-P Alloy with Double Knudsen Cell Mass Spectrometry

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[Background]

De-phosphorization reaction in steel making $2\underline{P}(\text{in Fe}) + \frac{5}{2}O_2(g) = P_2O_5(\text{in slag})$

Product of de-phosphorization reaction $3CaO \cdot P_2O_5$ $4CaO \cdot P_2O_5$

Accurate thermodynamic properties of these compounds are needed to develop this process.

[Experimental]

Double Knudsen cell mass spectrometry equipment

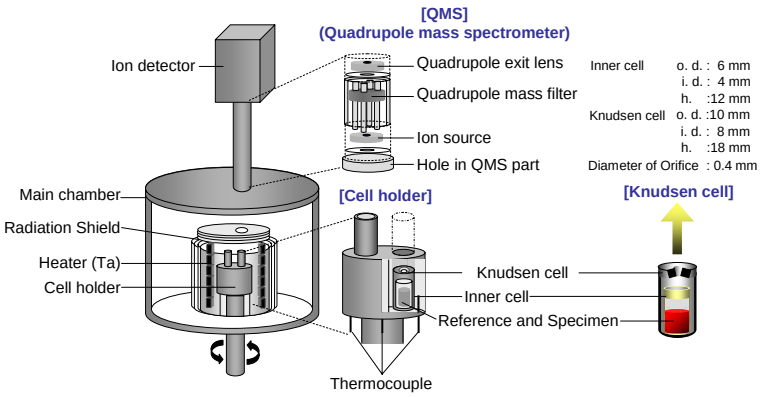

Fig. Schematic view of double Knudsen cell mass spectrometric equipment.

Experimental method

Mass spectrometry

$$p_i = b\frac{I_i}{\sigma_i}T$$

p_i : Partial pressure of i
T : Temperature
b : Device constant
σ_i : Ionized cross section of i
I_i : Ion current of i

Detect vapor pressures as ion current which is proportional to vapor pressure

Device constant influences Results
Device constant changes in each measurements

➡ Decreasing accuracy of measurement

Double Knudsen cell mass spectrometry

$$\frac{p_{P_2\text{ in sample}}}{p_{P_2\text{ in reference}}} = \frac{I_{P_2\text{ for sample}}}{I_{P_2\text{ for reference}}}$$

Compare ion currents from sample and reference substance

➡ Avoid influence of device constant

Exploratory experiment

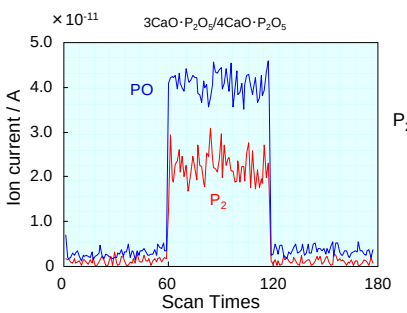

Fig. Ion currents during the measurement

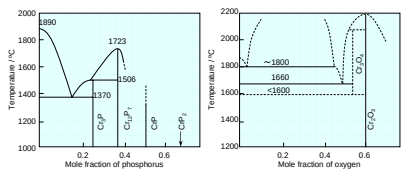

Fig. Phase diagrams of Cr-P and Cr-O systems

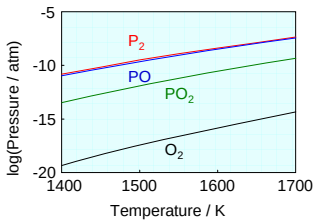

Fig. Calculation of vapor pressure in the mixture

Measurement of $CaO\text{-}P_2O_5$ sample

Ion currents of mass-to-ratio (*e/z*), 47, 62

$^{31}P^{16}O$, $^{31}P_2$

P_2O_5 in slag is in equilibrium with P_2 and PO

$$P_2O_5(\text{in slag}) + \frac{3}{2}P_2 = 5PO \quad a_{P_2O_5} = \frac{p_{PO}^5}{K \cdot p_{P_2}^{\frac{3}{2}}}$$

Reference substance to determine the vapor pressures of P_2 and PO

Mixture of Cr, Cr_3P, and Cr_2O_3

The solubility phosphorus and oxygen to chromium is insignificant.

Cr_3P and Cr_2O_3 are stoichiometric compound .

Calculation of vapor pressure using free energy of formation of Cr_3P and Cr_2O_3

Mixture of Cr, Cr_3P, and Cr_2O_3 can be used as a reference substance of PO and P_2

Free energy of formation of Cr_3P in literature

$\Delta G_f^0 = -244000 + 71.0T$ J/mol[1]

$\Delta G_f^0 = -132000 + 40.5T$ J/mol[2]

[1] A. I. Zaitsev, N. E. Shelkova, A. D. Litvina B. M. Mogutnov, and Zh. V. Dobrokhotova; J. Phase Equilib., 19 (1998) p. 191.
[2] C. E. Myers, G. A. Kisacky, and J. K. Klingert; J. Electrochem. Soc., 132 (1985), p. 236.

Significant difference

$$3Cr(s) + \frac{1}{2}P_2(g) = Cr_3P(s) \quad \Delta G_f^0 = -RT\ln\left(\frac{a_{Cr_3P}}{a_{Cr} \cdot p_{P_2}^{\frac{1}{2}}}\right)$$

Preparation of Cr_3P

Material : Pure Cr (3N), Red Phosphorus(3N)
Temperature, Time (Sample end) : 973 K 30 hr, 1173 K 7 hr, 873 K 30 hr
Temperature (The other end) : 673 K

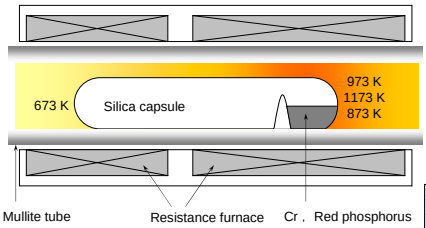

Fig. Schematic configuration of the experimental apparatus

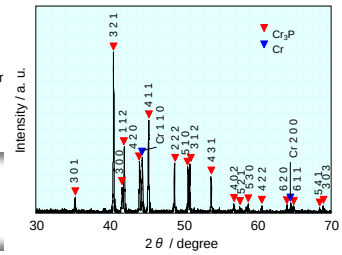

Fig. X-ray diffraction pattern of the annealed sample

Cubical crystal (Ni_3P-type)
a = 9.1887 Å
c = 4.5593 Å
Cu-K_α
r = 1.5406 Å

Diffraction lines of Cr, Cr_3P

➡ **Mixture of Cr and Cr_3P**

[Results and Discussion]

Cr-P system

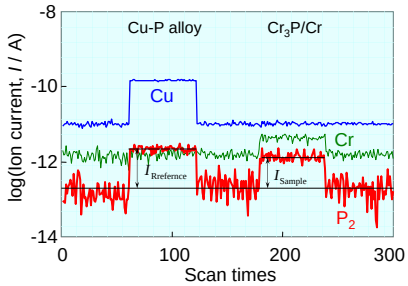

Fig. Ion currents during the measurement

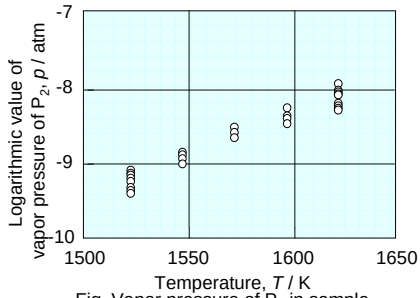

Fig. Vapor pressure of P_2 in sample

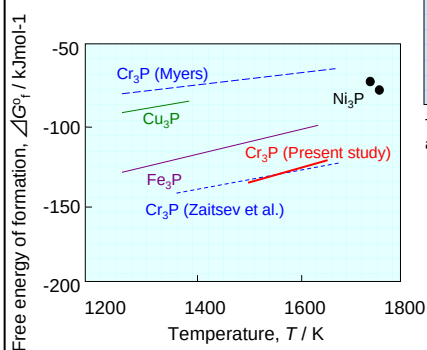

Fig. Free energy change of formation of Me_3P.

Mixture of Cr, Cr_3P, and Cr_2O_3

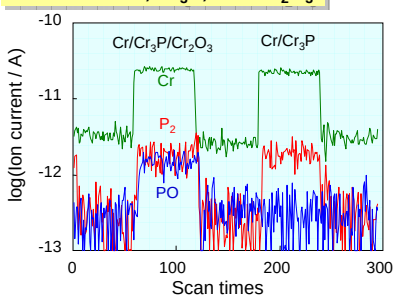

Fig. Ion currents during the measurement

Detection of Ion Currents

Sample (mixture of Cr and Cr_3P)

Ion currents of mass-to-ratio (*e/z*), 52, 62

^{52}Cr, $^{31}P_2$

Reference (Cu-0.90wt%P alloy)

Ion currents of mass-to-ratio (*e/z*), 62, 63, 65

$^{31}P_2$, ^{63}Cu, ^{65}Cu

P_2 pressure in Cu-P alloy was calculated by following data.

$$\frac{1}{2}P_2(g) = P(1\text{wt\% in Cu})$$

$$\Delta G^0 = -125000 + 0.54T \quad \text{Ref}$$

Ref M. Iwase, E. Ichise, N. Yamada, Process metallurgy 65(1985), 319-326.

Obtain vapor pressure of P_2 by comparison of ion currents

$$\frac{p_{P_2\text{ in sample}}}{p_{P_2\text{ in reference}}} = \frac{I_{P_2\text{ for sample}}}{I_{P_2\text{ for reference}}}$$

Free energy of formation of Cr_3P

$$3Cr + \frac{1}{2}P_2 = Cr_3P$$

$$\Delta G_f^0 = -261000(\pm 6800) + 83.0(\pm 4.3)T \text{ J/mol}$$

The free energy of formation of Cr_3P is good agreement with Zaitsev's data.

$\Delta G_f^0 = -244000 + 71.0T$ J/mol[1]

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[2] C. E. Myers, G. A. Kisacky, and J. K. Klingert; J. Electrochem. Soc., 132 (1985), p. 236.

Comparing with phosphides of Cu, Fe, and Ni

Cr_3P is stable compound.

Mixture of Cr, Cr_3P, and Cr_2O_3

Ion currents of mass-to-ratio (*e/z*), 47, 52, 62

$^{31}P^{16}O$, ^{52}Cr, $^{31}P_2$

The intensities of ion currents of Cr and P_2 are good agreement with those from mixture of Cr and Cr_2O_3.

The vapor pressure of PO calculated by ion current and ionized cross section is largely similar to that calculated by thermodynamic data.

The vapors of PO and P_2 from the mixture were detected appropriately.

[Future work]

Measurement of $CaO\text{-}P_2O_5$ samples using a mixture of Cr, Cr_3P, and Cr_2O_3

Determination of free energy of formation of $CaO\text{-}P_2O_5$ compounds