MASS SPECTROMETRIC STUDY OF SOLID SOLUTION REGION OF SPINEL $MgAl_2O_4$

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The information on thermodynamic properties of spinel $MgAl_2O_4$ is of great importance in geochemistry and petrology since it is usually considered as a component of complex systems, which determine the mechanisms of geological processes. The high melting point and chemical stability along with some specific physicochemical properties of spinel [1] are the background of its wide application in various technologies.

In the present work vaporization of spinel from molybdenum cells was studied by the mass spectrometric Knudsen effusion method. Thermodynamic properties of $MgAl_2O_4$ were determined in the temperature range 1850-2250 K on an MI 1201 commercial mass spectrometer with the ion source modified for high temperature measurements. The details of the experimental technique and sample synthesis were described earlier in [2].

The identification of the gas phase composition over the $MgAl_2O_4$ samples shows that the predominant evaporation processes are heterogeneous reactions similar to those of individual oxides:

$$[MgO] = (Mg) + (O), \quad (1)$$
$$[Al_2O_3] = 2(Al) + 3(O). \quad (2)$$

(Square and round brackets denote the components of the condensed and gas phases, respectively).

Due to the difference in the reaction (1) and (2) rates, the composition of the condensed phase during the evaporation changed up to the compositions at the boundary of the concentration range of $MgAl_2O_4$ solid solutions (a typical example is presented in Fig. 1). On the other hand, the evaporation of the boundary compositions took place at a constant concentration. Hence, different temperature regimes in the experiments made it possible to establish the concentration boundaries of the region of spinel solid solutions in the $MgAl_2O_4$-Al_2O_3 system. The peak Al_2O_3 mole fraction for this concentration range was estimated to be 83.02±0.18 mole % Al_2O_3 at 2179±10 K. Comparing the phase diagrams obtained by Berezhnoi [1] and computed by Hallstedt [3] with our experimental data (see Fig. 1) shows the closeness of our data with the same of Berezhnoi.

The values of the MgO and Al_2O_3 activities as well as the Gibbs energy of the spinel formation $\Delta_f G_T(MgAl_2O_4)$ were calculated using the data on the partial pressures of the vapor species in reactions (1) and (2) according to the Hertz-Knudsen equation. The values of the enthalpy and entropy of $MgAl_2O_4$ formation were estimated from the $\Delta_f G_T(MgAl_2O_4)$ temperature dependence in the temperature range 1851-2089 K. These values recalculated for 1 mole of the system compound were found to be –13.3±1.2 kJ/mole and 4.4±1.0 J/(mole · K), respectively. The accurate determination of the thermodynamic properties of stoichiometric spinel at more high temperatures was hampered due to the above-mentioned variations of the condensed phase composition.

Fig. 2 compares the results obtained in the present work with the reference data. One can see that our data on the $MgAl_2O_4$ thermodynamic properties agree with the values determined by Hallstedt [3] and Jacob *et al*. [4] and recommended by Chase Tables [5], and shows the insignificant deviations from the ideality. On the contrary, Kalyanram and Bell [6] and Rein and Chipman [7] consider the system as being ideal. These discrepancies may be due to the crude approximation procedure of the Schuhmann method used in [6, 7]. The values of $\Delta_f G_T(MgAl_2O_4)$ obtained by Grjotheim *et al*. [8] using the data on heterogeneous equilibrium

$$4[MgO] + 2[Al] = [MgAl_2O_4] + 3(Mg) \quad (3)$$

are not usually recommended due to the significant errors, which are the result of the usage of the additional thermodynamic information.

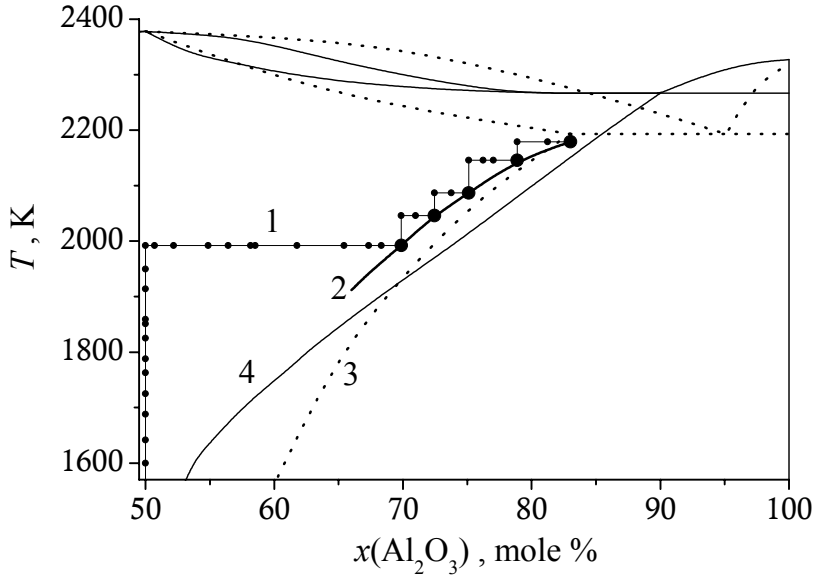

Fig.1. Temperature dependence of the condensed phase composition during $MgAl_2O_4$ evaporation (1) and the boundaries of spinel solid solution region obtained: 2 – in the present study; 3 and 4 – according to the data [1] and [3], respectively.

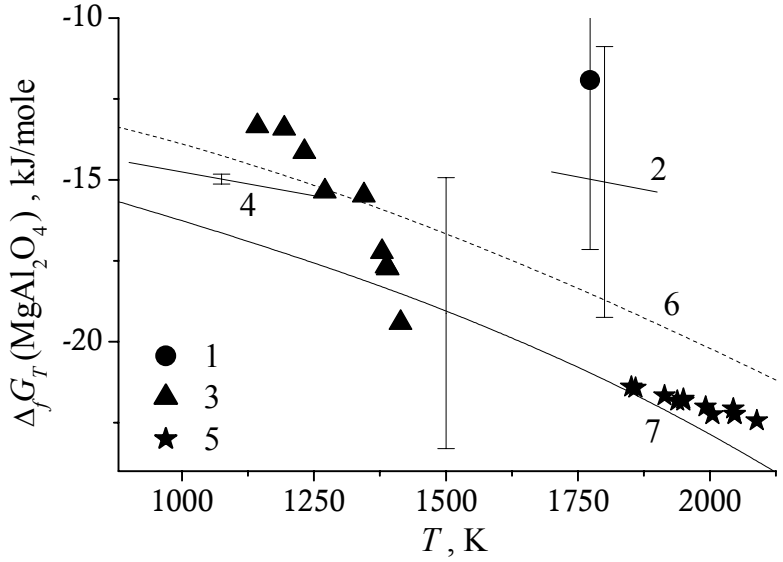

Fig.2. Values of the Gibbs energy of formation of $MgAl_2O_4$ determined: 1-3 – the heterogeneous equilibria [6-8]; 4 – EMF method [4]; 5 – present study, mass spectrometric Knudsen effusion method; 6 – the compound energy model [3]; and 7 – recommended values [5].

References

1. *Berezhnoi A.S.* (1970) Mnogokomponentnye sistemy okislov // Naukova Dumka, Kiev. 1970. 554p.
2. *Shornikov S.I., Archakov I.Yu.Chemekova T.Yu.* (2000) // Russ. J. Phys. Chem. V.74. P.677
3. *Hallstedt B.* (1992) // J. Amer. Ceram. Soc. V.75. P.1497.
4. *Jacob K.T., Jayadevan K.P., Waseda Y.* (1998) // J. Amer. Ceram. Soc. V.81. P.209.
5. *Chase M.W.* (1998). NIST-JANAF Thermochemical Tables.
6. *Kalyanram M.R., Bell H.B.* (1961) // Trans. Brit. Ceram. Soc. V.60. P.135.
7. *Rein R.H., Chipman J.* (1965) // Trans. Met. Soc. AIME. V.233. P.415.
8. *Grjotheim K., Herstad O., Toguri J.M.* (1961) // Can. J. Chem. V.39. P.443.