THERMODYNAMIC PROPERTIES OF CALCIUM AND BARIUM PHOSPHIDES

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The thermodynamic properties of calcium and barium phosphides have been determined in the temperature range 1178–1537 K by a Knudsen effusion technique combined with mass-spectral analysis of the evaporation products.

The specific heats of calcium and barium phosphides in the temperature range 118–863 K have been measured by means of a Mettler differential scanning calorimeter, TA-4000.

The thermodynamic functions obtained in the present work can be recommended for thermodynamic calculations for the compounds studied in the present work.

Keywords: calcium and barium phosphides, specific heat

Introduction

In order to obtain ferroalloys and alloyed steels of high quality it is necessary to reduce the phosphorus content to 0.005%. This problem cannot be solved by means of oxidizing dephosphorization because of the oxidation and loss of expensive alloying elements, having higher affinity for oxygen than iron. A treatment of metallic melts with fluxes and alloys containing alkaline earth elements was found to be promising. By this treatment the concentrations of nonmetallic and some harmful metallic impurities are considerably reduced. However, the interaction between alkaline earth metals and phosphorus has not been studied yet, and the thermodynamic functions of the formation of calcium and barium phosphides - key compounds in the processes of reducing dephosphorization - have not been determined with the required precision.
Experimental

In the present work the thermodynamic properties of calcium and barium phosphides have been determined in the temperature range 1178–1537 K by a Knudsen effusion technique combined with mass-spectral analysis of the evaporation products.

The specific heats of calcium and barium phosphides in the temperature range 118–863 K have been measured too by means of a Mettler Differential Scanning Calorimeter TA-4000.

The preparation method, data on the vapour composition and thermodynamic functions of the formation of calcium phosphides, received by means of high-temperature mass-spectral technique have been reported previously [1]. The preparation method for barium phosphide was the same. Measurements and calculations of the vapour pressures of the components over barium-phosphorus alloys were the same as reported in [1]. Strontium fluoride served as a reference substance. The orifice diameter varied from 0.36 to 0.404 mm while the effusion-cell diameter was 6 mm. No influence of the cell material (niobium, molybdenum, tantalum) and of the area of the effusion orifice on the composition of vapour over barium-phosphorus alloys has been detected.

A survey of the experimental results for the specific heats of calcium phosphide is given in Fig. 1. It can be seen that the specific heat vs. temperature function is almost linear at temperatures exceeding 298 K. The calculations performed by the method of least-squares yielded:

\[ C_\text{p} / \text{J/K} \cdot \text{mol}^{-1} = \begin{cases} 
7_0 & 150 \\
50 & 100 \\
0 & \text{at } T = 1 \text{ K} 
\end{cases} \]

![Fig. 1 Temperature dependence of the specific heat of Ca3P2 in the temperature range 118 to 863 K. Points — experimental data; line — approximated curve](image)

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