AD-A162 285 CONGRUENT VAPORIZATION IN THE V-SI SYSTEM AS STUDIED BY 1/1
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BINGHAMTON DEPT OF CHEMISTRY C E MYERS ET AL.
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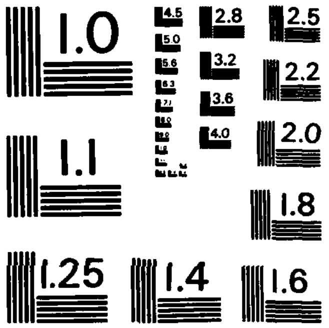

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The vaporization behavior of vanadium silicides has been investigated by Knudsen cell mass spectrometry in the temperature range 1800-2000K. It was demonstrated that at about 1900-2000K the congruently vaporizing composition is within the V_3Si single phase region. Thermodynamic activities relative to the solid elements were obtained by direct comparison. Free energies and enthalpies of phase formation for $V_3Si(s)$ and $V_5Si_3(s)$ were calculated from the experimental data and were found to be in good agreement with data obtained elsewhere.

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TECHNICAL REPORT NO. 4

CONGRUENT VAPORIZATION IN THE V-Si SYSTEM AS STUDIED BY HIGH TEMPERATURE KNUDSEN CELL MASS SPECTROMETRY

by

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CONGRUENT VAPORIZATION IN THE V-Si SYSTEM AS STUDIED BY HIGH TEMPERATURE KNUDSEN CELL MASS SPECTROMETRY*

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The vanadium silicides are of interest as corrosion resistant materials and for their potential applications in the electronics industry. In addition, their cohesive energies may be used, together with those of other silicides and related compounds, to assess factors affecting the strengths of chemical bonds in these compounds. The compounds in the V-Si system (1) are V_3Si, V_5Si_3, V_6Si_5, and VSi_2. Of these, only V_3Si has any significant range of homogeneity; V_6Si_5 is only stable above about 1160K (2). Several authors (1,3,4,5) have reviewed critically the published thermochemical data for the system. These reviews do not include a recent study (2) which employed Knudsen cell-mass spectrometry. One result of this last work was a plot of log activity _vs_ composition (activities relative to the respective pure solid elements) for both V and Si at 1650K. The activities of V and Si were observed to cross within the V_5Si_3 phase region which, in consideration of the vapor pressures of pure V and Si at this temperature, led to the tentative conclusion that V_5Si_3 vaporized congruently (i.e. vapor and condensed phase have same composition). The goal of the present work was to test this conclusion.

EXPERIMENTAL

The samples were prepared by arc melting weighed mixtures of the elements and were characterized by X-ray powder diffraction.

Selected residues were analyzed by wet chemical techniques, and these results agreed closely with the compositions inferred from the original weights of V and Si. The mass spectrometer used was a 90° sector, single focusing, high resolution magnetic deflection instrument manufactured by Nuclide Corporation. The sample was placed in a tungsten metal cup within a tungsten metal effusion cell which was heated by radiation from a tungsten helix resistance heating element. The entire furnace assembly was surrounded by tungsten and tantalum radiation shields within a water cooled vacuum enclosure. Temperatures were measured with a tungsten-rhenium thermocouple inserted into the base of the effusion cell; the thermocouple was calibrated by means of an optical pyrometer sighted through the orifice into the interior of the effusion cell. The design of the mass spectrometer was such that the molecular beam from the effusion cell, the path of the ionizing electrons, and the ion beam were all mutually perpendicular. Silicon signals were obtained with ionizing electron energies of 12.5 eV in order to minimize the effects of the mass 28 background. An ionizing energy of 30.0 eV was used for the vanadium data.

RESULTS

Thermodynamic activities relative to the pure solid elements were obtained as follows. The partial pressure of a species in a Knudsen cell-mass spectrometry experiment is proportional to IT, where I is the ion current due to that species and T is the temperature of the effusing vapor. Hence the thermodynamic activity of a species in the sample is given by $a = I/I^{\circ}$, where I is measured for the element above the sample and I° is measured above the pure element under the same experimental conditions of temperature, orifice area, and electron energy (2). Although I and I° are measured in different experiments, the mass spectrometer is sufficiently stable that reproducible results are obtained. In practice, activities at a given temperature were calculated from slopes and intercepts of log IT and log I°T vs 1/T plots. The activities at a given composition and temperature were used to calculate the free energies of phase formation:

$$(1-x)V(s) \;+\; xSi(s) \;=\; V_{1-x}Si_x(s)$$

$$\Delta G_f^o/R \;=\; 2.303\ T\ \text{Log}\ a_V^{(1-x)} a_{Si}^x$$

where x is the atom fraction of Si. Entropy and heat capacity data for the silicides cited or estimated by Smith (1) were used, together with Smith's data (6) for V and data from the JANAF Tables (7), to calculate $\Delta G_f^o/R$ as a function of temperature and $\Delta H_{f,298.15}^o/R$ from the experimental data. As shown in Table 1, agreement with the results of the earlier mass spectrometric study (2) is quite good. Samples richer in Si than V_5Si_3 were found preferentially to lose Si and samples richer in V than V_3Si were found preferentially to lose V. Hence there is at least one congruently vaporizing composition in the V_3Si-V_5Si_3 composition range. The results from X-ray powder diffraction were ambiguous in that it was very difficult to identify lines attributable to V_3Si, even in samples which were well within the V_3Si-V_5Si_3 two-phase region. However, wet chemical analysis before and after vaporization of a significant fraction (19-58%) showed clearly that, at about 1900-2000K, there is only one congruently vaporizing composition which is within the V_3Si single-phase region. The precise composition is difficult to fix since, near the congruently vaporizing composition, the partial pressures of V and Si differ only very slightly from those at congruency. Hence, to reach congruency it is necessary to vaporize a major fraction of the sample. It should be noted that this congruent vaporization is for effusion conditions. Hence partial pressures differ from those under static conditions since Si effuses more rapidly than V. It is not yet clear whether the congruently vaporizing composition under static conditions lies within V_3Si or V_5Si_3.

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TABLE 1

THERMODYNAMIC DATA FOR VANADIUM SILICIDES

	ΔG^{o}_{f},1650K/R (kK)	
1/4 V_3Si	3.63	Si and V activities (22 a/o Si)
	4.35	Si and V activities, V_5Si_3 + V_3Si
	4.40	Storms and Myers (2), V_5Si_3 + V_3Si
1/8 V_5Si_3	5.49	Si and V activities, V_5Si_3 + V_3Si
	5.47	Storms and Myers (2), V_5Si_3 + V_3Si
	ΔH^{o}_{f},298.15/R (kK)	
1/4 V_3Si	5.35	Si and V activities, V_5Si_3 + V_3Si
	5.40	Storms and Myers (2), V_5Si_3 + V_3Si
	5.18	Smith (1)
1/8 V_5Si_3	6.33	Si and V activities, V_5Si_3 + V_3Si
	6.31	Storms and Myers (2), V_5Si_3 + V_3Si
	6.47	Smith (1)

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