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MASTER

LITERATURE SURVEY OF GASES
IN BERYLLIUM

REPORT TO
WRIGHT AIR DEVELOPMENT DIVISION

J. P. Pemsler and R. W. Anderson

nuclear metals, inc.
concord, massachusetts

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Literature Survey of Gases in Beryllium

Report to
Wright Air Development Division
J. P. Pemsler and R. W. Anderson

January 17, 1961

Nuclear Metals, Inc.
Concord, Massachusetts

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A. R. Kaufmann
Technical Director

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INTRODUCTION

This literature survey was prepared in conjunction with a study of the interaction of the gases oxygen, nitrogen, and hydrogen with the metal beryllium. References were chosen and data organized to aid in the planning of experiments designed to obtain information concerning the solubility and diffusion of the aforementioned gases in beryllium.

I. BERYLLIUM

A. Structure and Thermodynamics

Beryllium has a close-packed hexagonal structure at room temperature. The metal is reported to undergo a phase transformation at 1260°C ⁽¹⁾ to a body-centered cubic structure. The melting point is given as $1283 \pm 1^{\circ}\text{C}$, and the boiling point is calculated as 2480°C .⁽²⁾ The heat of fusion is listed as 2800 ± 50 cal/g-atom,⁽³⁾ the heat of vaporization is calculated to be 70,400 cal/g-atom, and the heat of sublimation at 298°K is 77,900 cal/g-atom.⁽²⁾

Thermodynamic functions for beryllium have been calculated by Stull and Sinke⁽²⁾ using energy levels given by Moore.⁽⁴⁾

Hill and Smith⁽⁵⁾ measured the heat capacity of the solid from -269 to 27°C , and Ginnings, Douglas and Ball⁽⁶⁾ measured the heat capacity from 100 to 900°C . Calculations based on the experimental data lead to an entropy of 2.28 e.u. and enthalpy of 468 cal/g-atom at 25°C .

Kelley⁽⁷⁾ reports values of the heat content of the solid as

$$H_T - H_{298} \text{ cal/g-atom} = 4.58T + 1.06 \times 10^{-3} T^2 + 1.14 \times 10^5 T^{-1} - 1,842$$

$$(0.4\% \text{ accuracy; } 298 - 1556^{\circ}\text{K}) \quad (1)$$

and the heat capacity of the solid as

$$C_p \text{ cal/degrees/g-atom} = 4.58 + 2.12 \times 10^{-3} T - 1.14 \times 10^5 T^{-2} \quad (2)$$

The heat content and heat capacity of the liquid are given as

$$H_T - H_{298} \text{ cal/g-atom} = 7.50 T - 950 \quad (3)$$

(0.1% accuracy; 1556 -2700°K)

and

$$C_p \text{ cal/degrees/g-atom} = 7.50 \quad (4)$$

respectively.

B. Vapor Pressure

The vapor pressure of beryllium was measured by Holden, Speiser and Johnston⁽⁸⁾ between 900 and 1280°C by observing the rate of evaporation into a vacuum and the rate of effusion of saturated metal through an orifice. The data fit the equation

$$\log P(\text{atm}) = 6.186 + 1.454 \times 10^{-4} T - (16,734 \pm 80)/T. \quad (5)$$

A value of $\Delta H_o^\circ = 76,560 \pm 370$ cal/g-atom was calculated. Gulbransen and Andrew⁽⁹⁾ report a vapor pressure equation as

$$\log P(\text{atm}) = 6.186 + 1.454 \times 10^{-4} T - (16,800 \pm 48)/T \quad (6)$$

in excellent agreement with the data of Holden. It was found that the presence of an oxide film, and to a lesser extent a nitride film, greatly reduced the vapor pressure.

II. BERYLLIUM-OXYGEN SYSTEM

A. Compounds

Beryllium is known to form the oxide BeO, which has a wurtzite structure. Recently the existence of a second oxide, Be₂O, has been pos-

tulated on the basis of mass spectrographic and X-ray evidence.⁽¹⁰⁾ The compound, which is reported to distill from beryllium in contact with BeO at temperatures above 1300°C, has a cubic lattice of the CaF₂ type, whose parameter is $a = 5.402 \pm 0.001$ kx.

B. Thermodynamics

Kelley⁽⁷⁾ reports the heat content of BeO as

$$H_T - H_{298} \text{ cal/mole} = 8.45 T + 2.00 \times 10^{-3} T^2 + 3.17 \times 10^5 T^{-1} - 3,760 \quad (7)$$

(3% accuracy; 298 - 1200°K)

and the heat capacity as

$$C_p \text{ cal/degrees-mole} = 8.45 + 4.00 \times 10^{-3} T - 3.17 \times 10^5 T^{-2} \quad (8)$$

Cosgrove and Snyder⁽¹¹⁾ measured the heat of formation of BeO in a precision oxygen bomb calorimeter and obtained a value of $-\Delta H = 143.1 \pm 0.1$ kcal/mole. Coughlin⁽¹²⁾ lists value of the heat and free energy of formation of BeO between 298 and 2000°K.

Glassner⁽¹³⁾ extrapolated the free energy data beyond the melting point of beryllium and reports values for the free energy of formation of BeO up to 2500°K.

The boiling point of BeO was estimated as $4120 \pm 170^\circ\text{C}$, and the entropy of vaporization at the boiling point as 25.6 ± 2.7 e.u.⁽¹⁴⁾

An upper limit of the heat of dissociation of BeO of 125 kcal/mole was calculated by Brewer,⁽¹⁵⁾ assuming that the BeO molecule is almost as important a vaporizing specie as the elements. Earlier spectroscopic determinations by Herzberg,⁽¹⁶⁾ Gaydon,⁽¹⁷⁾ and Lagerquist⁽¹⁸⁾ gave the somewhat lower values 85, 101 and 110 kcal/mole respectively. Chupka, Berkowitz and Giese,⁽¹⁹⁾ on the basis of vaporization studies, report the dissociation energy of BeO as 106 ± 3 kcal/mole. The heats of vaporization of the trimer (BeO)₃ and tetramer (BeO)₄ at 2100°K were reported as 164 and 181 kcal/mole, respectively.

C. Vapor Pressure

The vaporization of BeO was studied by Erway and Seifert⁽¹⁴⁾ by observing the rate of effusion from a Knudsen cell, using radioactive beryllium as a tracer. In the temperature range 1950 to 2150°C, the vapor pressure is given by the equation

$$\log P(\text{mm}) = 18.50 - (34,230)/T - 2 \log T \quad (9)$$

Using the entropy data of Kelley⁽²⁰⁾ and the spectroscopic heat of dissociation of BeO(g), Brewer⁽¹⁵⁾ concluded that molecular BeO is unimportant as a vaporizing specie, and the vapor pressure data of Erway and Seifert⁽¹⁴⁾ agree with those to be expected for dissociation to the elements.

Livey and Murray⁽²¹⁾ sought to determine the principal volatile species over BeO by measuring weight losses of BeO under varying oxygen pressure. Their results indicate that volatilization of the BeO molecule is significant and that, therefore, the data of Erway and Seifert are low, since they account only for dissociation. Pollock, Saul, and Milne⁽²²⁾ suggest that an error on the low side could have been obtained in the data of Erway and Seifert as a result of a non-uniform temperature in the Knudsen cell used by the latter authors.

Chupka, Berkowitz and Giese⁽¹⁹⁾ studied the vapor effusing from a tungsten Knudsen cell containing BeO at temperatures from 1900 to 2400°K. They used a mass spectrometer to identify the volatile species; Be, O, O₂, (BeO)₃ and (BeO)₄ were the principal species, with lesser amounts of BeO, (BeO)₂, (BeO)₅, (BeO)₆, WO₂ and WO₃. Mixed oxides of the type WO_n · (BeO)_m in which n = 2 and 3, and m = 1, 2 or 3 were found.

Pollock, Saul and Milne⁽²²⁾ measured the vapor pressure of BeO by observing the rate of effusion from a tungsten cell. They conclude that, at 2242°K in high vacuum, loss of BeO molecules is somewhat less than that due to dissociation, while at 2474°K the reverse is true. In an inert atmosphere, loss as molecules is about twice that of dissociation, while in oxygen, volatility is determined essentially by the partial pressures of the molecular species.

D. Diffusion

The self-diffusion of beryllium in polycrystalline BeO was measured with the aid of radioactive Be⁷ at temperatures between 1570 and 1934°C.⁽²³⁾ Data can be fitted by two straight lines on a log D vs 1/T plot. Values of the diffusion coefficients are:

$$D, \text{cm}^2/\text{sec} = 5.56 \times 10^{-3} \exp (-111,600/RT) \text{ between } 1570 \text{ and } 1730^\circ\text{C} \quad (10)$$

and

$$D, \text{cm}^2/\text{sec} = 6.14 \times 10^{-2} \exp (-66,100/RT) \text{ between } 1730 \text{ and } 1934^\circ\text{C}. \quad (11)$$

No evidence of grain boundary diffusion was found.

The effect of impurities, microstructure, or other material characteristics on the diffusion coefficient is not known, so the data reported should not be applied directly to other BeO materials.

E. Reaction Kinetics

1. Oxidation of Beryllium

The rate of oxidation of beryllium was measured by Cubicciotti⁽²⁴⁾ in the temperature range 840 to 970°C at 100 mm Hg pressure of oxygen, and at 885°C from 100 to 720 mm Hg pressure of oxygen. The oxidation rates were found to be parabolic over the first 100 minutes, after which at some temperatures a more rapid attack ensued. The latter deviation from parabolic behavior is attributed to film cracking. The energy of activation for the oxidation was 62 kcal/mole. Gulbransen and Andrew⁽⁹⁾ studied the short-time oxidation over a wide range of temperatures (350 to 950°C). The data were fitted by a parabolic equation with deviations noted in the early stages of the reaction. An activation energy of 50.3 kcal/mole was calculated.

Aylmore, Gregg and Jepson⁽²⁵⁾ extended the observation time on the oxidation of beryllium up to 300 hours in the temperature range 500 to

700°C. A decreasing reaction rate with time was noted in temperatures up to 650°C, indicating the protective nature of the oxide. At 750°C the rate initially decreased but was followed by an increasing rate with time, indicating a breakaway reaction resulting from a nonprotective film.

The oxidation of beryllium in air at near atmospheric pressure and temperatures between 930 and 1295°C was investigated by Bradshaw and Wright.⁽²⁶⁾ The reaction followed a linear law, and activation energies of 110 kcal/mole in the range 930 to 1065°C and 10.6 kcal/mole in the range 1065 to 1295°C were observed. The reaction rates in air were faster than would be predicted from the rates in pure oxygen or pure nitrogen. An induction period was observed in all the high-temperature air oxidation studies.

2. Reaction of BeO With Water Vapor

Hutchison and Malm⁽²⁷⁾ reported the volatilization of BeO in the presence of water vapor at temperatures of 1250°C or higher. Elston and Caillat⁽²⁸⁾ reported slight attack on sintered BeO by water vapor at 1300°C.

Grossweiner and Seifert⁽²⁹⁾ made quantitative measurements of the volatility of BeO in the presence of H₂O vapor. The loss of BeO was attributed to the formation of Be(OH)₂(g). The equilibrium constant for the reaction

is given by

$$\log K_p = 1.63 - (9060)/T. \quad (13)$$

Thermodynamic data for the reaction

were calculated as

$$\Delta H^{\circ} = -108.5 \text{ kcal/mole} \quad (15)$$

$$\Delta F^{\circ} = -57.5 \text{ kcal/mole} \quad (16)$$

$$\Delta S^{\circ} = -30 \text{ e.u.} \quad (17)$$

Young⁽³⁰⁾ studied the reaction of water vapor with BeO in the range 1300 to 1575°C using a transpiration technique. The equilibrium constant for the reaction

is given by the equation

$$\log K_p = 1.93 - 9280/T \quad (19)$$

The following thermodynamic data were calculated:

$$\Delta H^{\circ} = 42.5 \text{ kcal} \quad (20)$$

$$\Delta F_{1673^{\circ}\text{K}} = 27.7 \pm 0.7 \text{ kcal} \quad (21)$$

$$\Delta S^{\circ} = 8.8 \text{ e.u.} \quad (22)$$

These data are in good agreement with the results of Grossweiner and Seifert⁽²⁹⁾ calculated for Equation 18.

F. Epitaxy

Kerr and Wilman⁽³¹⁾ first studied the structure and growth of oxide layers formed on beryllium surfaces. Electron diffraction data indicate that polycrystalline surfaces at 300°C and higher develop oxide in

a one-degree orientation which varies with the temperature of formation. Abraded beryllium below 700°C grew BeO in the (001) orientation, but above 700°C in $\{100\}$. Oxide forming on electropolished material at temperatures up to 250°C had a grain size of about $10 \text{ \AA}$; that formed at 300°C and above was $60 \text{ \AA}$ or more, with a preferred (001) orientation up to 700°C . On vacuum-deposited beryllium surfaces the oxide grew epitaxially on the exposed $\{001\}$ and $\{110\}$ metal faces.

Scott⁽³²⁾ studied structure and growth of BeO films on single crystals of beryllium. The (001) planes of BeO were found parallel to (001) beryllium cleavage planes and the [110] BeO direction was parallel to the [100] beryllium. Epitaxial relationships were less well established on electropolished surfaces. One-degree $\{103\}$ -oriented BeO was observed on $\{100\}$ and $\{110\}$ faces of beryllium.

Above 600°C only random growth of oxide was observed in the upper layers. At 800°C a pronounced (001) habit of the randomly-oriented BeO crystals developed.

Saulnier and Mirand⁽³³⁾ studied the form of the BeO second phase particles existing in various beryllium samples. Observations were made on oxide particles extracted onto a replicating film, and direct observations were made on thin metallic sections. Samples prepared from powder with an average grain size of 80μ exhibited a second phase believed to result from the splitting during rolling of the cocoons of BeO surrounding the beryllium particles. Samples prepared with material having an average grain size of 40μ showed some geometric crystals of BeO believed to have resulted from the complete oxidation of the fine particles in the powder. No evidence was found of a continuous network of oxide in the grain boundaries.

III. BERYLLIUM-NITROGEN SYSTEM

A. Compounds

The only compound reported is Be_3N_2 . Stackelberg and Paulus⁽³⁴⁾ determined that Be_3N_2 is a body-centered cubic structure (Mn_2O_3 type) with

a cell size of 8.142 Å. According to Fichter and Brunner⁽³⁵⁾ the nitride sublimes at temperatures above 1850°C, whereas Chiotti⁽³⁶⁾ found the melting point of Be₃N₂ to be 2200°C.

B. Thermodynamics

Sato⁽³⁷⁾ measured the heat content and entropy of Be₃N₂ in the temperature range 298 to 800°K. The heat content and heat capacities may be expressed by the equations:

$$H_T - H_{298} \text{ cal/mole} = 7.32 T + 15.40 \times 10^{-3} T^2 - 3551 \quad (23)$$

(0.6% accuracy; 298-800°K)

$$C_p \text{ cal/degree-mole} = 7.32 + 30.80 \times 10^{-3} T \quad (24)$$

C. Kinetics

Gulbransen and Andrew⁽⁹⁾ and Bradshaw and Wright⁽²⁶⁾ observed that the rate of reaction of nitrogen and beryllium was approximately parabolic for temperatures from 650 to 1070°C. The activation energy of reaction was reported to be 75 kcal/mole and 49.6 kcal/mole by the respective investigators. Langsdorf⁽³⁸⁾ reported that the nitriding rate can be increased by the addition of 2 to 6 % hydrogen into the nitrogen.

IV. BERYLLIUM-HYDROGEN SYSTEM

A. Compounds

The possible formation of beryllium hydride by the reaction of atomic hydrogen and metallic beryllium at 170 to 260°C was reported by Pietsch.⁽³⁹⁾ Holley and Lemmons⁽⁴⁰⁾ were unable to duplicate Pietsch's experiment, but did form what was believed to be either BeH₂ or Be₃N₂ by hydriding at 1300 psi for 26 hours at 600°C. From theoretical considerations, Lemmons and Lewis⁽⁴¹⁾ predicted the existence of a beryllium-hydride phase. The density of the hydride phase would most likely be less than 1.0 g/cc.

Sullivan⁽⁴²⁾ observed no hydride formation when powdered beryllium was reacted with hydrogen at temperatures from 25 to 500°C.

Lemmons and Lewis⁽⁴¹⁾ and Barbaras⁽⁴³⁾ formed BeH_2 in an ether solution. The decomposition temperature of BeH_2 has been reported to be 125°C and 250°C by Barbaras⁽⁴³⁾ and Coates and Glocking⁽⁴⁴⁾ respectively.

B. Thermodynamics

The heat of formation of BeH_2 , should it exist, was predicted to be 54 kcal/mole by Lemmons and Lewis.⁽⁴¹⁾

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