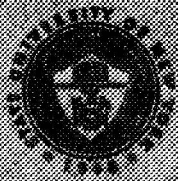


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THERMODYNAMIC PROPERTIES OF INTERSTITIAL ELEMENTS  
IN THE REFRACTORY METALS

by

D. K. Gupta, S. C. Srivastava, and L. Seigle

Seventh and Eighth Progress Reports for the periods  
June 1, 1969 - August 31, 1969, and September 1, 1969 -  
November 30, 1969.

NASA Research Grant NGR-33-015-035



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### ABSTRACT

Details of the experimental techniques for determining the activity of C in Mo and W at the solubility limit by measuring the vapor pressure of Ca over a mixture of Me,  $\text{Me}_2\text{C}$ , and  $\text{CaC}_2$ , and by measuring the emf of a galvanic cell of the type  $\text{Me} + \text{Me}_2\text{C} \mid \text{CaCl}_2 + \text{CaC}_2 \mid \text{C}$  are reviewed. It is concluded that the emf method would be simpler to apply, and work has been started to construct a cell. Work has also begun to obtain missing information about the solubility of oxygen in Mo by equilibrating Mo rods in a mixture of  $\text{Mo} + \text{MoO}_2$ .

## I. INTRODUCTION

Calculation of the thermodynamic properties of C, O, and N dissolved in solid Mo, W, Nb, and Ta from existing phase equilibrium data has proven to be a useful first step in obtaining free energies, enthalpies, and entropies of solution of the interstitial elements in the refractory metals. However, it has become clear in carrying out this work that additional experimental data are required for some of the systems in order to obtain a complete and reliable set of thermodynamic parameters for the terminal solid solutions. The gaps and uncertainties in the available data were discussed in recent progress reports.<sup>(1)</sup> The most important are lack of sufficient information concerning the free energies of formation of the lower carbides of the refractory metals, and insufficient knowledge of the solid solubilities of oxygen in Mo and W. Attention therefore has recently been directed to experimental methods for obtaining these data.

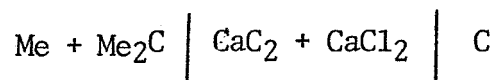
## II. DETERMINATION OF THE FREE ENERGIES OF FORMATION OF THE LOWER CARBIDES

Methods for determining the activity of C in a mixture of Me + Me<sub>2</sub>C were discussed in the last progress report.<sup>(2)</sup> Measurement of the activity of C is equivalent to determination of the free energy of formation of Me<sub>2</sub>C of the specific composition in equilibrium with the terminal solid solution,\* since the solubilities of C in the refractory metals are quite low. At the same time, the measurements give directly the chemical potential of C in the terminal solid sol-

\* The lower carbides are of variable composition

ution at the solubility limit.

In the last progress report it was concluded that an attractive method for determining the free energy of formation of the lower carbides, or the activity of C in the Mo-C and W-C systems, was measurement of the Ca (or Ba) vapor pressure over a mixture of Me + Me<sub>2</sub>C + CaC<sub>2</sub> (or BaC<sub>2</sub>). This vapor pressure was estimated to be 10<sup>-6</sup> to 1 atm. between approximately 1000 and 1800°K. Use of such a method was felt to have an advantage over determination of carbon activities by equilibration with CO-CO<sub>2</sub> mixtures, inasmuch as it avoids possible complications due to the formation of oxycarbides. Another possible method with the same advantage is measurement of the emf of a galvanic cell of the type



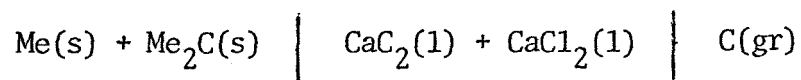
During the current report period a study has been made of the details of apparatus and technique involved in both of the above methods. The conclusions derived from this study can be briefly summarized as follows: First, with regard to measurement of the Ca vapor pressures, it was judged that the dynamic methods<sup>(3,4)</sup> most commonly used to determine vapor pressures at elevated temperatures, such as the transpiration method, the method of Bodhansky and Schins, and even the effusion method\* would be doubtful for the systems of interest, because they all require the transport of an appreciable quantity of Ca from the powder mixture to the vapor phase. It is not certain that diffusion and reaction rates in this mixture of refractory materials,

\* The vapor pressures are also too high for the effusion method over most of the temperature range.

at temperatures far below their melting points, would be rapid enough to maintain equilibrium in the presence of a substantial removal of Ca. Attention was therefore directed toward the static methods of vapor pressure measurement.

There are a number of static methods described in the literature which at first glance seem attractive. (3, 4) On closer inspection, however, it is seen that none of these would be easy to apply to measurement of Ca vapor pressures at high temperatures. For example, the reactivity of Ca vapor rules out the use of silica glass windows in the dew point method. A similar problem arises in the application of light absorption techniques. Direct manometric methods suffer from the difficulty of finding a fluid useful in contact with Ca vapor at very high temperatures. Methods involving weight measurements, or electrical conductivity measurements at high temperatures also are burdened with experimental difficulties. Finally, a method involving the use of radioactive Ca, in which the vapor pressure is determined by counting through the walls of the reaction vessel (3) seemed appealing, but since this called for the use of radiotracer techniques and apparatus it was decided not to act on it until the emf method, which, as previously mentioned, is an alternative to the vapor pressure methods, was more closely examined.

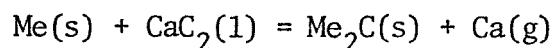
The emf method involves the use of a galvanic cell such as



Electrolytic conduction in the fused salt electrolyte takes place via the acetylide ion,  $\text{C}_2^-$ , and the chemical potential of C in the  $\text{Me} + \text{Me}_2\text{C}$

mixture is proportional to the cell potential. A cell of this type was recently used successfully by Hawkes and Morris <sup>(5)</sup> to determine the activity of C in austenite up to 1000<sup>o</sup> C. Furthermore, Salzano, et al., <sup>(6)</sup> of the Brookhaven National Laboratories report good results in their use of similar cells.

A limitation to the use of these cells is the occurrence of the side reaction



which determines the Ca vapor pressure above the cell. This pressure must be low in order to minimize the extent of the side reaction. An idea of the order of magnitude of this pressure can be obtained from the Ca pressures calculated to be in equilibrium with a mixture of solid  $\text{Me} + \text{Me}_2\text{C} + \text{CaC}_2$ , given in Table 5 of the last progress report. <sup>(6)</sup> At 1000<sup>o</sup>K these are of the order of  $10^{-3} - 10^{-5}$  for the Mo and W systems, and  $10^{11} - 10^{12}$  for the Nb and Ta systems. In the cells the  $\text{CaC}_2$  will be present in dilute liquid solution and therefore the pressures in Table 5 represent an upper limit to the expected Ca vapor pressures. From these values it may be concluded that such cells are feasible for the Mo-C and W-C systems, but not for the Nb-C and Ta-C systems.

Another limitation is imposed by the volatility of the  $\text{CaCl}_2$  in the electrolyte. Evaporation of this constituent limited Hawkes and Morris to a temperature of 1000<sup>o</sup>C in their experiments. However, the boiling point of  $\text{CaCl}_2$  is about 2000<sup>o</sup>C, and it would seem that temperatures could be extended above 1000<sup>o</sup>C by the use of closed cells or perhaps admixture of  $\text{CaCl}_2$  with a less volatile salt, such as  $\text{CaF}_2$ .



Details of the experimental apparatus and technique have been discussed with Salzano. (6) Calcium vapor attacks ceramics such as  $Al_2O_3$ , but this difficulty is easily avoided by utilizing metal, e.g., Ni or Inconel crucibles and furnace tubes. The calcium halides used in the electrolyte must be free of water and oxygen. Highly purified salts are, however, commercially available.

Considering all of the available information, after careful study it has been concluded that although a static vapor pressure method could probably be developed for the Mo-C and W-C systems, it would be simpler to utilize the emf technique described above, and at the present time supplies are being obtained to proceed with this approach.

Since the carbide cell method is not suitable for the Nb-C and Ta-C systems, another technique must be found. Measurement of the CO pressures over a mixture of  $Me + Me_2C + MeO_n$  by the effusion method is a possibility, as mentioned in the last progress report. (2) However, this possibility requires further study.

### III. DETERMINATION OF THE SOLUBILITY OF OXYGEN IN Mo AND W.

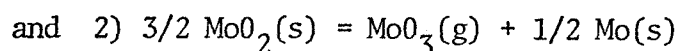
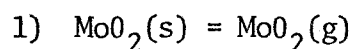
Knowledge of the solid solubilities of the interstitial elements in the terminal solutions is essential to calculation of the thermodynamic properties from the phase diagrams. The solubility of oxygen in Mo was determined by Few and Manning (7) using a technique in which the sample was equilibrated at high temperatures, quenched, and examined metallographically for residual oxide. Oxygen solubilities ranging from 0.004 wt. % at  $1000^{\circ}C$  to 0.006 wt. % at

1600°C were determined in this way. These results are questionable for several reasons. First, experiments with the refractory metal-carbon systems indicate that it is difficult to retain the interstitial element in solution upon quenching from high temperatures. Second, the purity of the Mo used by Few and Manning was not specified. Third, the oxygen solubilities determined vary linearly, rather than exponentially with temperature, and extrapolate to a non-zero solubility at absolute zero. For these reasons it is felt that Few and Manning's data are not reliable, and a new determination of the solubility of oxygen in Mo should be undertaken. Only one value for the solubility of oxygen in W has been reported, <sup>(8)</sup> i.e., 0.005 wt. % at 1700°C, and the need for additional data here is obvious.

The solubility of oxygen in Mo and W cannot easily be obtained by direct equilibration of the metal with gaseous oxygen at a known pressure, due to complications arising from the high vapor pressures of Mo and W oxides. Therefore, the method of equilibrating with solid MoO<sub>2</sub> or WO<sub>2</sub> has been selected as that most likely to succeed. In this method, a small specimen of solid Mo, for example, is embedded in a mixture of powdered Mo + MoO<sub>2</sub> contained in a sealed capsule. The whole is held at temperature for a long enough time to saturate the solid Mo with oxygen. After cooling rapidly to room temperature, the solid Mo is removed from the powder, cleaned and analyzed for oxygen. The analogous method of equilibrating thin Mo rods in a mixture of Mo + Mo<sub>2</sub>C powders was recently used by Rudman <sup>(9)</sup> to determine the solid solubility of C in Mo.

Certain conditions must be fulfilled in order to assure the

success of this method. First the oxide pressure above the Me + MeO<sub>2</sub> mixture must not be too high. Blackburn<sup>(10)</sup> and Burns, et al.,<sup>(11)</sup> have studied the Mo-O system and report that the evaporation of solid MoO<sub>2</sub> is governed by two reactions



Polymers of the trioxide, such as (MoO<sub>3</sub>)<sub>2</sub> (g) and (MoO<sub>3</sub>)<sub>3</sub> (g) also occur in the gas above solid MoO<sub>2</sub>.

The pressures of oxide species above MoO<sub>2</sub> are given in Table 1. From these values, it is evident that there should be no problem in containing a mixture of Mo(s) + MoO<sub>2</sub>(s).

Table 1. PARTIAL PRESSURES OF SPECIES IN EQUILIBRIUM WITH SOLID MoO<sub>2</sub>

T <sup>o</sup> K	Pressure - atm			
	MoO <sub>2</sub>	MoO <sub>3</sub>	(MoO <sub>3</sub> ) <sub>2</sub>	(MoO <sub>3</sub> ) <sub>3</sub>
1566	4.9 x 10 <sup>-9</sup>	1.4 x 10 <sup>-7</sup>	2.9 x 10 <sup>-8</sup>	-----
1632	4.1 x 10 <sup>-8</sup>	6.5 x 10 <sup>-7</sup>	1.4 x 10 <sup>-7</sup>	6.9 x 10 <sup>-9</sup>
1675	1.6 x 10 <sup>-7</sup>	2.0 x 10 <sup>-6</sup>	5.7 x 10 <sup>-7</sup>	-----
1716	2.7 x 10 <sup>-7</sup>	4.1 x 10 <sup>-6</sup>	1.3 x 10 <sup>-6</sup>	7.1 x 10 <sup>-8</sup>
1732	3.7 x 10 <sup>-7</sup>	5.4 x 10 <sup>-6</sup>	1.6 x 10 <sup>-6</sup>	1.4 x 10 <sup>-7</sup>
1777	1.0 x 10 <sup>-6</sup>	1.4 x 10 <sup>-5</sup>	3.7 x 10 <sup>-6</sup>	3.1 x 10 <sup>-7</sup>
*1905	2.8 x 10 <sup>-4</sup>	6.4 x 10 <sup>-4</sup>	-----	-----
*2028	1.5 x 10 <sup>-3</sup>	3.5 x 10 <sup>-3</sup>	-----	-----

\* From Blackburn, et al.<sup>(10)</sup> The rest of the data is from Burns, et al.<sup>(11)</sup>

Blackburn, et al., also studied the evaporation of  $WO_2$ . It was concluded that this oxide evaporates almost completely to  $(WO_3)_3$ , according to the reaction

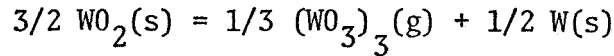


Table 2 gives the pressures of  $(WO_3)_3$  above a mixture of  $W(s)$  and  $WO_2(s)$

Table 2. PRESSURE OF  $(WO_3)_3$  ABOVE SOLID  $W + WO_2$

T <sup>o</sup> K	Pressure - atm
1324	$7.4 \times 10^{-7}$
1375	$4.0 \times 10^{-6}$
1507	$1.0 \times 10^{-4}$
1603	$3.4 \times 10^{-4}$
1658	$1.3 \times 10^{-3}$

A second condition which must be fulfilled in order for the given method to work, is that the diffusion of oxygen into the solid specimens must occur rapidly enough to achieve saturation in a reasonable time. The diffusion coefficients of oxygen in Mo and W are not known, but if we assume that they are of the same order of magnitude as the diffusion coefficients of C in these metals, then we can estimate the times for saturation. Rudman gives for the diffusion coefficient of C in Mo,

$$D(C \text{ in Mo}) = 0.034 \exp \left( - \frac{41,000}{RT} \right) \text{ cm}^2/\text{sec}$$

while Pivani and Sandor <sup>(12)</sup> give for C in W

$$D(C \text{ in W}) = 0.31 \exp \left( - \frac{59,000}{RT} \right) \text{ cm}^2/\text{sec}$$



Using these D values the estimated times for saturation of a 1/8" diameter rod are given in the following table:

Table 3. ESTIMATED TIMES FOR 90% SATURATION OF A 1/8" DIAMETER ROD

Temp. °K	D (cm <sup>2</sup> /sec)		Time	
	Mo	W	Mo	W
1473	2.8 x 10 <sup>-8</sup>		3.5 days	
1673	1.5 x 10 <sup>-7</sup>		16 hrs.	
1800		2.1 x 10 <sup>-8</sup>		4.0 days
1873	5.6 x 10 <sup>-7</sup>		4.2 hrs.	
2000		1.1 x 10 <sup>-7</sup>		18 hrs.
2073	1.6 x 10 <sup>-6</sup>		1.5 hrs.	
2200		4.2 x 10 <sup>-7</sup>		4.8 hrs.

It appears that the method could be feasible for Mo above 1500°K and W above 1800°K.

The success of the proposed method also depends upon use of a highly pure starting material, and ability to determine oxygen content with sufficient precision. Floating zone purified Mo and W rods are commercially available, with an oxygen content of < 4 ppm. According to the supplier these may be even further purified if necessary, and no problem is foreseen in obtaining sufficiently pure starting material. Oxygen contents in the ppm range may be determined by vacuum fusion analysis to a sensitivity of ± 2 micrograms. With a sample size of 2 grams it should be possible to obtain oxygen contents with accuracy down to at least 10 ppm.

Since the described method was judged to be feasible, work has been started to procure materials and set up equipment for determination of the solubility of oxygen in Mo. A molybdenum wound muffle furnace which can reach a temperature of  $1800^{\circ}\text{C}$  in inert atmosphere is available. Crucibles, thermocouples, and other accessories are being made ready.

#### FUTURE WORK

Work in the immediate future will be concentrated on completing the data for the binary systems, in order to obtain a complete and reliable set of thermodynamic parameters for carbon, oxygen, and nitrogen in all four refractory metals.

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