

State University of New York at Stony Brook

THERMODYNAMIC PROPERTIES OF INTERSTITIAL ELEMENTS IN  
THE REFRACTORY METALS

P. P. Bansal, N.C. Birla, A. C. Huang, and  
L. Seigle

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## ABSTRACT

Major effort has been devoted in this report period to assembling and testing the high temperature galvanic cell for experimental measurement of the thermodynamic properties of the interstitial elements by the emf method. The cell has been operated with a solid  $ZrO_2 + CaO$  electrolyte, and electrodes of  $Ni + NiO$  and  $Cu + Cu_2O$ , yielding values for the free energy, enthalpy, and entropy of the reaction  $Ni + Cu_2O = 2 Cu + NiO$  at  $900^\circ C$  in good agreement with those in the literature.

## I. INTRODUCTION

The interstitial elements, C, O, and N strongly influence the properties of the refractory metals, Mo, W, Cb, and Ta. This is due to the tendency of these elements to precipitate from solid solution at, or segregate to, grain boundaries, dislocations, or other lattice defects, thereby inhibiting plastic flow and inducing brittle behavior. The thermodynamic properties of the interstitial elements are therefore of some importance. The purpose of this work is to determine the thermodynamic properties of C, O, and N in the four refractory metals, and relate these properties to the nature and behavior of the interstitial solid solutions.

## II. DERIVATION OF THE THERMODYNAMIC PROPERTIES FROM PHASE EQUILIBRIUM DIAGRAMS

A continuing effort is being made to calculate the thermodynamic properties of the interstitial elements from a knowledge of the location of the solvus lines, and the free energies of formation of the compounds inequilibrium with the terminal solid solutions. The methods have been discussed in previous reports<sup>(1,2)</sup>. Free energies, entropies, and enthalpies of solution of C in the four refractory metals have been calculated by several methods,

and compared with expectations from theory<sup>(2)</sup>. The calculations for the metal-carbon systems have been extended in order to clarify the precise influence of possible errors in the phase diagrams, as well as variations in the method of calculation upon the derived thermodynamic properties. It is felt important to complete this exercise in order to be sure of the methods when they are extended to the metal-oxygen and metal-nitrogen systems. Calculations for the metal-carbon systems are nearly finished, and necessary data have been collected for the other systems, prior to calculating the thermodynamic properties of the oxygen and nitrogen in solution.

At the same time, an effort is being made to interpret the thermodynamic properties in terms of atomic interactions and distributions in the solid solutions. Both atom misfit and chemical bonding effects are important in these systems. Internal energy and entropy effects arising from atom misfit have been treated by the continuum theory of lattice defects<sup>(2)</sup>, with good results, but the chemical bonding factor has not yet been systematically dealt with. A theoretical study of bonding in these metal-carbon, oxygen, and nitrogen systems is now under way.

### III. EXPERIMENTAL MEASUREMENTS

Although calculations of the thermodynamic properties

from the phase diagrams are of unquestionable value, it would be desirable to confirm these by a direct experimental measurement, if possible. For this reason, a phase of the program is devoted to the development of experimental methods suitable for measuring the thermodynamic properties of the interstitial elements in the refractory metals. Because of its simplicity, the emf method is being explored first, and the metal-oxygen systems considered for initial investigation.

It was shown some time ago by Kiukkola and Wagner<sup>(3)</sup> that the free energy of formation of oxides could be determined with the aid of galvanic cells using solid ( $ZrO_2 + CaO$ ) as the electrolyte. Due to the presence of anionic vacancies, ( $ZrO_2 + CaO$ ) is an ionic conductor, the current being transported essentially by oxygen ions<sup>(3,4,5)</sup>. Therefore cells of the type



can be used, providing the mutual solubilities of the electrolyte and the oxides are low.

The emf of the above cell is a measure of the difference in oxygen potential over  $Me + MeO$  and  $Me' + Me'O$ , with

$$\mu_{O_2} - \mu'_{O_2} = -nLE \quad (1)$$

where  $n = 2$  is the charge on the oxygen ions by means of which current is transported,  $L =$  Faradays constant,

23,070 cal.volt<sup>-1</sup>gm equiv<sup>-1</sup>, and E is the cell potential in volts. If the standard free energy of formation of Me'O is known, the unknown chemical potential  $\mu_{O_2}$  can be determined from the cell potential, since, for the reaction  $Me' + 1/2 O_2 = Me'O$ ,

$$\Delta G'^{\circ} = -Rt \ln K' = 1/2 \mu'_{O_2} \quad (2)$$

The unknown potential,  $\mu_{O_2}$ , is the chemical potential of oxygen in equilibrium with a mixture of the metal and its oxide, and is related to the equilibrium pressure and activity of oxygen,  $\mu_{O_2} = Rt \ln p_{O_2} = Rt \ln a_{O_2}$  taking oxygen at one atm. pressure as the standard state of unit activity, and assuming ideal gas behavior. If metal and oxide are mutually insoluble,  $\mu_{O_2}$  is related to the standard free energy of formation as shown in equ.(2). This is not exactly true if a degree of mutual solubility exists, as is often the case for the refractory metal-interstitial element systems under consideration. However,  $\mu_{O_2}$ , determined from the cell potential is, in any event, the chemical potential of oxygen dissolved in the refractory metal at the composition in equilibrium with the oxide, and is a quantity therefore directly comparable to that obtained from the phase equilibrium diagram.

The electrolytic cell used in the following experiments was quite similar in design to that used by Rapp and Maak<sup>(6)</sup>, and is shown in detail in Fig.1 (dimensions

are given in cm.). All of the connections were taken out through the brass head in order to avoid the use of quartz-metal seals.

The electrodes and electrolyte were in the form of discs of approximately 1 cm diameter, and 3 mm thickness prepared as follows:

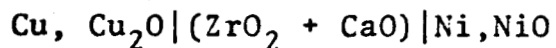
ZrO<sub>2</sub> + CaO: Following the method used by Kiukkola and Wagner<sup>(3)</sup>, Rapp and Maak<sup>(6)</sup>, and Barbi<sup>(7)</sup>, chemically pure ZrO(NO<sub>3</sub>)<sub>2</sub> and CaCO<sub>3</sub> were dissolved together in HNO<sub>3</sub> in correct proportion to ultimately form a mixture of .85ZrO<sub>2</sub>, .15CaO molar composition. The solution was slowly evaporated to dryness, the residue ground by mortar and pestle, decomposed to the oxides at 500°C, and then fired in air at 1200°C for 22 hours. The oxide so formed was ground, mixed with 2% of camphor, and pressed into pellets of the correct size in a tool steel die at 6.5 tons/cm<sup>2</sup> pressure. The camphor was removed by heating at 150°C in vacuum for one hour, after which the pellets were sintered at 1700°C for 20 hours in air.

Ni + NiO: Discs of 90 wt. % Ni and 10 wt. % NiO were formed from powders of 99.99% purity by mixing in a mortar and pestle, pressing with 2 wt. % of camphor at 6.5 tons/cm<sup>2</sup>, then heating for one hour in vacuum at 150°C to remove the camphor, and two hours at 600°C in argon to sinter the compact.

Cu + Cu<sub>2</sub>O: Copper powder of 99.98% purity and pure cuprous oxide (Fisher certified) were mixed, pressed, and sintered as with Ni + NiO.

Mo + MoO<sub>2</sub>: Mo powder of 99.95% purity, -325 mesh, was mixed with pure MoO<sub>3</sub> (Fisher certified, ACS) in a mortar and pestle. After adding camphor, as previously, the mixture was pressed at 6.5 tons/cm<sup>2</sup>, the camphor removed, and the compact sintered in argon at 600°C for two hours. In order to convert the MoO<sub>3</sub> to MoO<sub>2</sub>, the pellet was heated in vacuum at 900°C, but excessive evaporation of MoO<sub>3</sub> occurred. Further attempts are being made to form the Mo + MoO<sub>2</sub> electrode.

In order to test the cell and electrolyte, the system

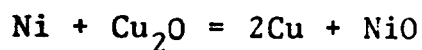


was studied. The cell was assembled as shown in Fig.1, with the electrodes in contact with Pt foils spot-welded to the lead wires. Temperatures were measured with a calibrated Pt - Pt, 10% Rh thermocouple and the cell potentials with a type K-3 L. & N. potentiometer using a galvanometer with a sensitivity of 0.003  $\mu\text{a/mm}$ . The cell was operated in an atmosphere of prepurified argon of 99.998% purity.

Values of the cell emf recorded upon increasing and decreasing temperature are given in Fig.2. The agreement between the two sets of values indicates that equilibrium



was quickly established at temperatures above 800°C. The emf vs temperature plot is closely linear in the range 800 - 1050°C, yielding the values -16,000 cal, and -3.24 cal/degree for the enthalpy and entropy changes of the reaction



A comparison of the values obtained from this cell with those calculated from the data of U. S. Bureau of Mines Bulletin 605<sup>(8)</sup> is given below

	<u>Cell</u>	<u>Bulletin 605</u>
$\Delta F(900^\circ\text{C})$	-12,200	-12,100 cal
$\Delta H(900^\circ\text{C})$	-16,000	-17,000 cal
$\Delta S(900^\circ\text{C})$	-3.24	-4.14 cal/degree

The agreement is good and indicates that the cell is operating satisfactorily.

#### IV. FUTURE WORK

It is expected that work in the future will continue along the lines discussed above, namely, calculations of the thermodynamic properties from the phase equilibrium diagrams will be extended to the oxygen and nitrogen containing systems, the theory of interstitial solid solutions will be further developed, and the high-temperature galvanic cell will be utilized to study the interstitial element-refractory metal systems, beginning with the oxide-metal systems.

One departure from the original plan of work under consideration is the incorporation of some experimental investigation of the solubilities of the interstitial elements in the terminal solid solutions for a few systems where these are in particular doubt. The feasibility of such a study depends upon being able to reach very high temperatures, and thought is being given to the equipment and methods involved, before committing ourselves to such an effort.



CELL Ni, NiO | ZrO<sub>2</sub> + CaO | Cu, Cu<sub>2</sub>O

x increasing temperature  
o decreasing temperature

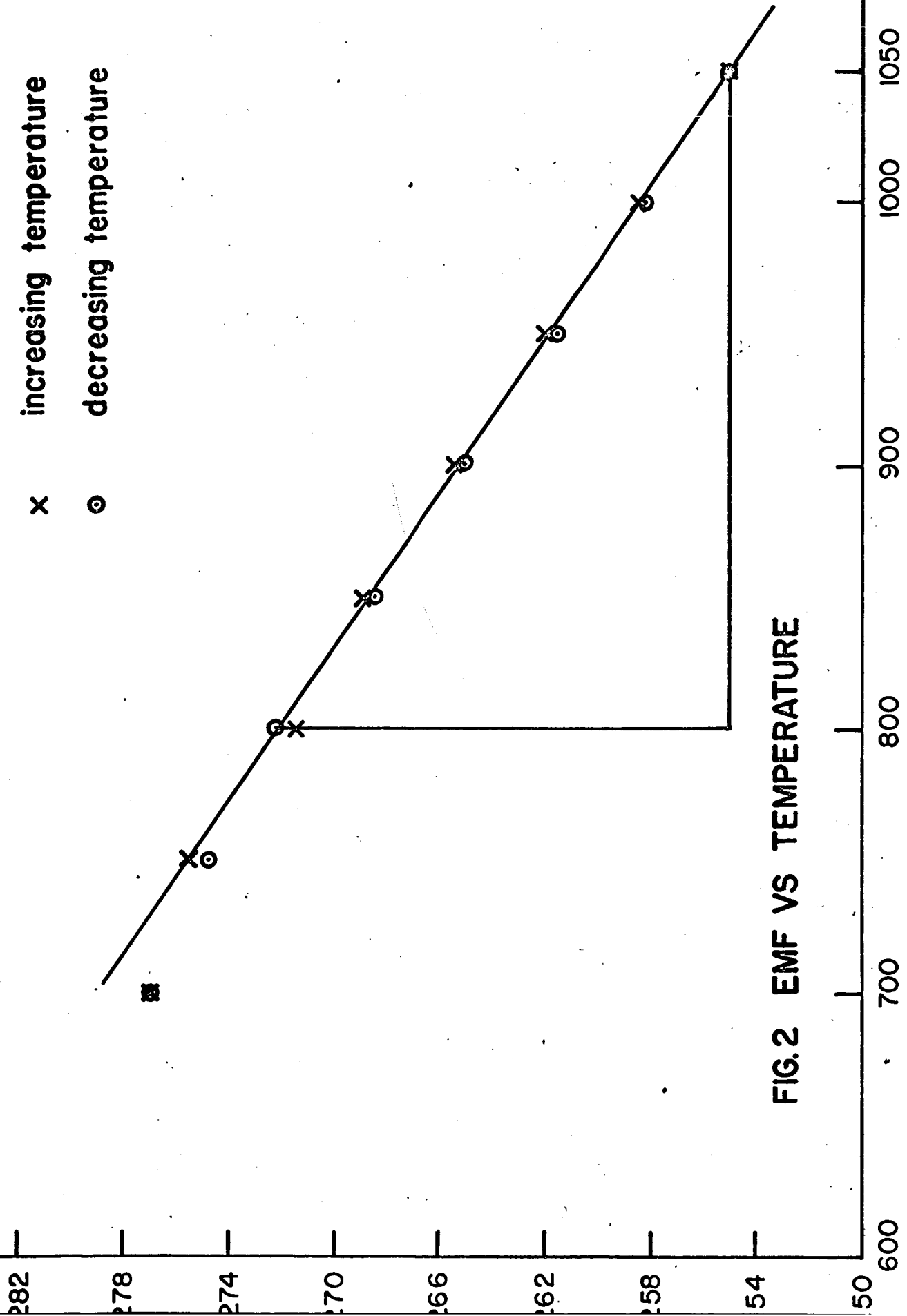


FIG.2 EMF VS TEMPERATURE

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