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Phase relationships in the system Ni-W-O and thermodynamic properties of $NiWO_4$

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The phase diagram of the Ni–W–O system at 1200 K was established by metallographic and X-ray identification of the phases present after equilibration at controlled oxygen potentials. The oxygen partial pressures over the samples were fixed by metered streams of $CO + CO_2$ gas mixtures. There was only one ternary oxide, nickel tungstate ($NiWO_4$), in the Ni–W–O system at a total pressure of 1 atm, and this compound decomposed to a mixture of $Ni + WO_{2.72}$ on lowering the oxygen potential. The Gibbs' free energy of formation of $NiWO_4$ was determined from the measurement of the e.m.f. of the solid oxide galvanic cell,

$$\text{Pt, Ni} + NiWO_4 + WO_{2.72}/CaO\text{–}ZrO_2/\text{Ni} + \text{NiO, Pt}$$

and thermodynamic properties of tungsten and nickel oxides available in the literature. For the reaction,

$$NiO(s) + WO_3(s) \rightarrow NiWO_4(s)$$

$$\Delta G^\circ = -10\,500 - 0.708\,T\ (\pm 250)\ \text{cal mol}^{-1}.$$

1. Introduction

Tungsten-fibre reinforced metal composites with nickel metal or nickel base alloy as a matrix material have recently received considerable attention because of their promising high temperature properties and possible application as structural materials for severe service conditions such as those encountered in turbojet engines [1]. Nickel cladding, a few thousands of an inch thick, of the tungsten fibre has been shown to provide protection from high temperature oxidation. Roy and Pastein [2] have discussed the function of an intermediate oxide coating as a "diffusion barrier" in nickel–tungsten composites. Kvernes and Kofstad [3] have reported on the high temperature stability of nickel–tungsten fibre composites in atmospheres containing oxygen. Their results indicated that while nickel coating improved the oxidation resistance, it did not prevent degradation after long time exposures due to the dissolution of oxygen in the nickel coating and matrix, oxidation of the nickel coating, interdiffusion of tungsten and nickel, and the internal oxidation of tungsten resulting in a mixture of several binary oxides and $NiWO_4$. Woo and Roy [4] have identified $NiWO_4$ as a major constituent of the oxide layer. A meaningful analysis of the oxidation behaviour of this composite material requires a knowledge of the phases that can appear during oxidation as well as their relative stabilities. However, a phase diagram of the ternary system Ni–W–O is not available in the literature.

Navrotsky and Kleppa [5] have measured the heat of formation of $NiWO_4$ from the component oxides, NiO and WO_3, as −10.57 (± 0.28) kcal mol^{-1}, using oxide-melt solution calorimetry. Porshina and Rezukhina [6] report a value of −12.9 kcal mol^{-1}, while Amosse and Mathieu [7] suggest a value of −11.9 (± 0.4) kcal mol^{-1} for the heat of formation, both based on calorimetric measurements. The free energy of formation has not been measured previously. Rezukhina *et al.* [8] have indicated that the reduction of $NiWO_4$ with hydrogen results in the formation of the ternary oxides $NiWO_{2.67}$ and $NiWO_2$, before yielding finally a mixture of $Ni_4W + W$. The stoichiometries of the ternary oxides suggested by Porshina and Rezukhina [6] are not compatible with the present knowledge on the valency states of nickel and tungsten in their oxides. Recently Landee and Westrum [9] have measured the heat capacity of $NiWO_4$ between 5 and 350 K by adiabatic calorimetry. The temperature of maximum heat capacity for the antiferromagnetic anomaly in $NiWO_4$ is 60 K, and the corresponding entropy is $R\ln 3$ ($2.18\,\mathrm{cal\,deg^{-1}\,mol^{-1}}$). A number of studies on the thermodynamic properties and phase relations in the binary Ni–O [10, 11] and W–O [12, 13] systems are reported in the literature, while a phase diagram of the Ni–W binary system is given in the compilation of Hansen and Anderko [14].

By identifying the equilibrium phases in the Ni–W–O system at 1200 K and at different oxygen potentials by metallography and X-ray diffraction, and using information available in the literature on the binary systems, a ternary phase diagram has been developed in this study. It has been shown that three condensed phases, Ni, $NiWO_4$ and $WO_{2.72}$, coexist at a specific oxygen potential at a fixed temperature. The value of this oxygen potential and its variation with temperature have been measured by a solid oxide galvanic cell. From this information the standard free energy of formation of $NiWO_4$, the only ternary oxide in the system, was calculated as a function of temperature. Ternary phase relationships at other temperatures can readily be derived from the thermodynamic data on the condensed phases.

measurements, and the carbon monoxide and dioxide, each 99.9% pure, used in gas equilibrium experiments, were supplied by Matheson of Canada. The argon gas was dried and then deoxidised by passing through copper turnings at 725 K and titanium granules at 1170 K before being passed into the e.m.f. apparatus. Fully stabilised calcia–zirconia solid electrolyte tubes were obtained from "Zircoa".

2. Experimental methods

2.1. Materials

Fine powders of analar nickel, tungsten, nickel oxide (NiO) and tungsten trioxide (WO_3) were obtained from the Fisher Chemical Co. The tungsten trioxide was further dehydrated by heating at 675 K in an alumina boat. The suboxides of tungsten ($WO_{2.72}$ and $WO_{2.9}$) were prepared by reacting mixtures of $W + WO_3$ in the required ratios in sealed quartz capsules at 1050 K for two days. The nickel tungstate was synthesised by heating the component oxides NiO and WO_3 in evacuated quartz capsules at 1050 K for 20 h and then at 1275 K for 30 h. The argon gas, 99.998% pure, used as the atmosphere during the e.m.f.

2.2. Apparatus and Procedure

2.1.1. Phase Relations

Mixtures of fine powders of metals and oxides were compressed into pellets of 5 mm diameter and 2.5 mm thickness by a hydraulic press at a pressure of about $1500\,\mathrm{kg\,cm^{-2}}$. The compositions of the starting materials are shown in Table I. The pellets, suspended on platinum wires, were equilibrated in a gas tight vertical reaction tube with a gas inlet at the bottom and an exit at the top. The

TABLE I The equilibrium phases identified at different oxygen potentials in the Ni–W–O system at 1200 K

Starting materials	Composition* $\eta_{Ni}/\eta_{Ni} + \eta_W$	p_{CO_2}/p_{CO}	$\Delta\mu_{O_2}$ (kcal mol^{-1})	Equilibrium phases identified
Ni + W	0.5	0.37	−90	$W + Ni_4W$
Ni + W	0.5	0.476	−88.8	$Ni_4W + WO_2$
Ni + W	0.5	0.695	−87	$Ni_{ss} + WO_2$
$Ni + WO_2$	0.5	1.06	−85	$Ni_{ss} + WO_2$
$Ni + WO_2$	0.5	1.78	−82.5	$Ni + WO_{2.72}$
$Ni + WO_{2.72}$	0.5	2.45	−81	$NiWO_4$
$Ni + NiWO_4$	0.75	4.59	−78	$Ni + NiWO_4$
$Ni + NiWO_4$	0.75	200	−60	$NiO + NiWO_4$
$NiWO_4 + WO_{2.72}$	0.25	4.59	−78	$NiWO_4 + WO_{2.72}$
$NiWO_4 + WO_{2.72}$	0.25	8.6	−75	$NiWO_4 + WO_{2.9}$

* η_i = moles of i

Kanthal-wound furnace used to heat the pellets had a constant temperature (±2 K) zone of 5 cm. The temperature of the furnace was controlled by a solid state controller and measured by a Pt/Pt–13%Rh thermocouple. The junction of the thermocouple was placed close to the sample. Initial experiments indicated that approximately 40 h were required to attain equilibrium at 1200 K. Equilibration times varying from 50 to 55 h were used in the experiments. The carbon monoxide and dioxide gases were dried, metered by capillary flow meters, and mixed in a tower packed with glass beads. Because of the different molecular weights of carbon monoxide and dioxide, the possibility of thermal segregation had to be considered. Darken and Gurry [15] have demonstrated that linear gas velocities greater than 0.6 cm $\sec^{-1}$ should be employed to avoid thermal segregation in the $CO + CO_2$ gas mixture. A linear velocity of 0.8 cm $\sec^{-1}$ was used in the experiments. At the end of the equilibration period the $CO + CO_2$ mixture in the reaction tube was replaced by argon gas and the sample was quenched in liquid nitrogen. The phases present in each sample were identified by metallographic and X-ray diffraction analysis. Conventional preparatory techniques were used in these analyses.

2.2.2. e.m.f. measurement

From the observation of the phases present at 1200 K as a function of oxygen potential, it appeared that $NiWO_4$ would decompose into a mixture of Ni(s), $WO_{2.72}$ and gaseous oxygen. Since, according to the phase rule, the three condensed phases Ni, $NiWO_4$ and $WO_{2.72}$ could coexist only at unique oxygen potential at each temperature, a pellet containing an equimolar mixture of the three phases was sealed under vacuum in a quartz capsule. The pellet was contained in an alumina crucible placed inside the quartz capsule. The capsule was equilibrated at 1200 K for 90 h and quenched in liquid nitrogen. Examination of the pellet by optical microscopy and X-ray diffraction showed that there was no change in the amount or number of phases present during the heat treatment. This pellet was therefore used as an electrode in the solid oxide galvanic cell,

$$\mathrm{Pt, Ni + NiWO_4 + WO_{2.72} / CaO{-}ZrO_2 / Ni + NiO, Pt.} \qquad (1)$$

The apparatus and procedure used in the measurement of the e.m.f. of this cell were identical to that described earlier [16]. The reversible e.m.f. of the cell was measured as a function of temperature in the range 1025 to 1300 K using a "Keithley" digital voltmeter. The reversibility of the cell was checked by passing small currents through the cell in either direction. In each case the e.m.f. was found to return to the original value. The time required to reach equilibrium varied from 10 to 15 h depending on temperature. The e.m.f. was independent of the flow rate of the argon gas through the cell.

3. Results, analysis and discussion

The phases identified after equilibration of various mixtures of condensed phases with $CO + CO_2$ gas mixtures are summarised in Table I. The lattice parameters of the nickel phases present in the samples containing an equimolar ratio of nickel to tungsten and equilibrated at oxygen potentials of −85 and −87 kcal mol^{-1} indicated that they were solid solutions containing 7(±2) and 16(±4) at.% tungsten respectively. The oxygen potential corresponding to each ratio of p_{CO_2}/p_{CO} at 1200 K was calculated from the standard free energy change for the reaction

$$\mathrm{CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g)}, \qquad (2)$$

obtained from Janaf tables [12]. The uncertainty in the oxygen potential, evaluated according to the statistical procedure of Birge [17], is ±360 cal mol^{-1}. This uncertainty arises mainly from errors in the measurement of flow rates of carbon monoxide and carbon dioxide streams and from errors in temperature measurement.

The tungsten–oxygen system at 1200 K com-

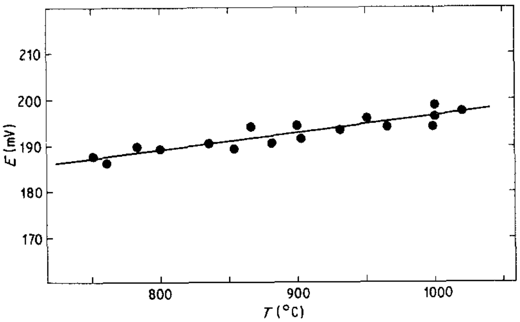

Figure 1 The variation of the e.m.f. of Cell 1 with temperature.

prises the oxides WO_2, $WO_{2.722}$ ($W_{18}O_{49}$), $WO_{2.9}$ ($W_{20}O_{58}$) and WO_3. The oxygen potentials at which WO_2, $WO_{2.72}$ and $WO_{2.9}$ were found to appear in this study are consistent with the known thermodynamic information about the tungsten–oxygen binary system [12, 13]. Only one ternary oxide phase, nickel tungstate ($NiWO_4$), was identified.

The variation of the e.m.f. of the solid oxide galvanic cell with temperature is shown in Fig. 1. The least mean-squares regression analysis suggests the following equation for the temperature dependence of the e.m.f.;

$$E = 154 + 0.0334T(\pm 1.8)\,\text{mV}. \qquad (3)$$

The e.m.f. is related to the difference in the oxygen potential between the two electrodes by the Nernst equation

$$-nFE = \Delta\mu_{O_2}(\text{Ni} + \text{NiWO}_4 + \text{WO}_{2.72}) - \Delta\mu_{O_2}(\text{Ni} + \text{NiO}), \qquad (4)$$

where E is the e.m.f. in volts, $n = 4$, and F is the Faraday's constant (23 063 cal V^{-1} mol^{-1}). The oxygen potential over the Ni + NiO reference electrode is given [10] by

$$\Delta\mu_{O_2} = -111\,930 + 40.58T(\pm 200)\,\text{cal mol}^{-1}. \qquad (5)$$

The oxygen potential corresponding to the three phase equilibria, represented by the equation

$$\text{Ni(s)} + \text{WO}_{2.72}\text{(s)} + 0.64\,\text{O}_2\text{(g)} \rightarrow \text{NiWO}_4\text{(s)}, \qquad (6)$$

calculated from the e.m.f. of the cell is

$$1.563\Delta G^\circ_{(6)} = \Delta\mu_{O_2} = -126\,137 + 37.5T(\pm 250)\,\text{cal mol}^{-1}. \qquad (7)$$

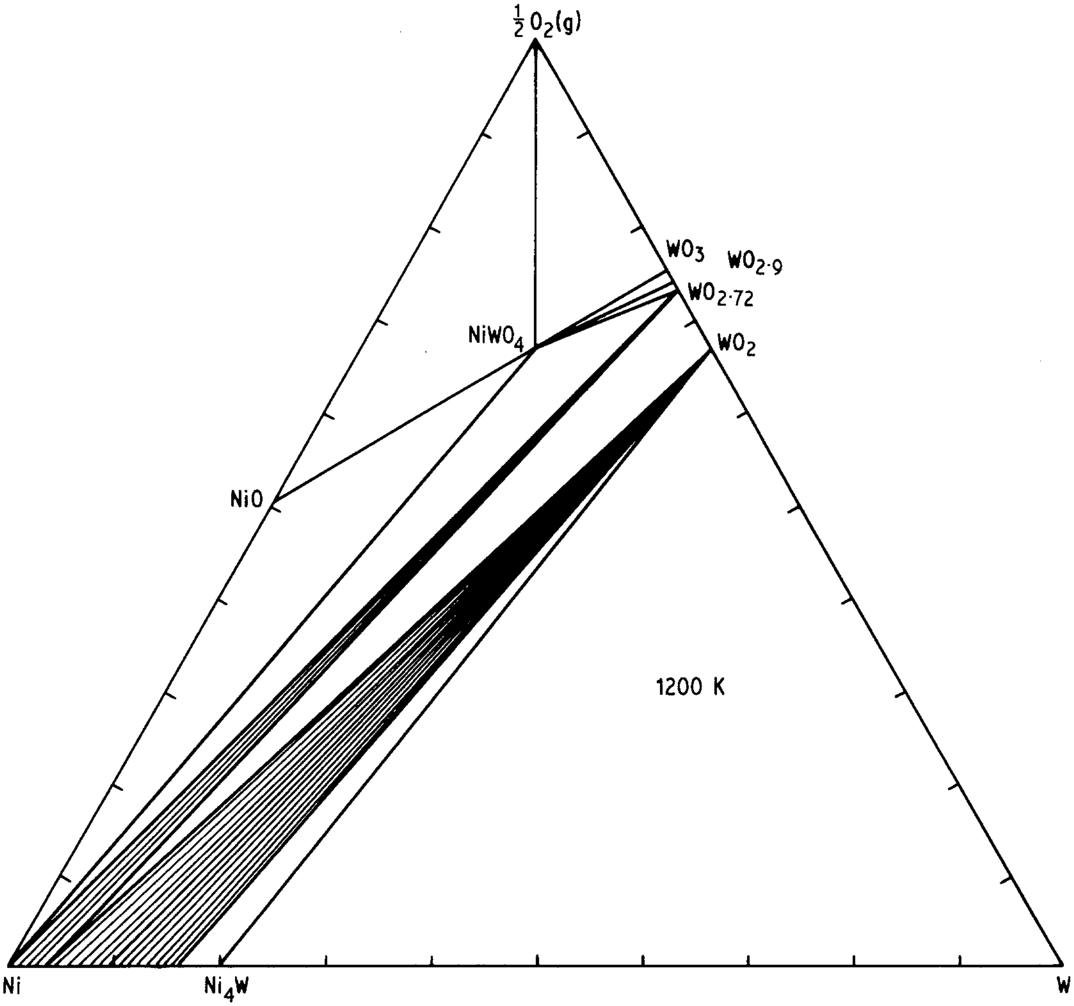

Figure 2 Gibbs triangle representation of phase relations in the Ni–W–O system at 1200 K.

By combining the standard free energy change for reaction 6 with the standard free energy of formation of $WO_{2.72}$ [12], the standard free energy of formation of $NiWO_4$ from elements is obtained:

$$W(s) + Ni(s) + 2O_2(g) \rightarrow NiWO_4(s) \quad (8)$$

$$\Delta G^\circ = -264\,030 + 77.15T(\pm 250)\,\text{cal mol}^{-1}. \quad (9)$$

The standard free energy of formation of $NiWO_4$ from component oxides is obtained by subtracting the free energies of formation of NiO [10] and WO_3 [12] from Equation 9. For the reaction

$$NiO(s) + WO_3(s) \rightarrow NiWO_4(s) \quad (10)$$

$$\Delta G^\circ = -10\,500 - 0.708T(\pm 250)\,\text{cal mol}^{-1} \quad (11)$$

The "second law" heat of formation of $-10.5(\pm 0.8)\,\text{kcal mol}^{-1}$ for $NiWO_4$ from oxides obtained in this study is in excellent agreement with the calorimetric value of $-10.57(\pm 0.28)$ kcal mol^{-1} reported by Navrotsky and Kleppa [5]. The bomb calorimetric determinations of Porshina and Rezukhina [6] suggest a value $2.4\,\text{kcal mol}^{-1}$ more negative, while solution calorimetry by Amosse and Mathieu [7] give a value $1.4\,\text{kcal mol}^{-1}$ more negative than that obtained in this study.

The Gibbs' triangle representation of phase relations in the Ni–W–O system at 1200 K is shown in Fig. 2. The ternary diagram is in agreement with all the information obtained in this study and information available in the literature on the binary systems Ni–O, W–O and Ni–W. Both WO_2 and $WO_{2.72}$ are in equilibrium with nickel-rich solid solutions. By interpolation the tungsten concentration of the solid solution in equilibrium with both WO_2 and $WO_{2.72}$ is estimated as 3.5(±2) at.%.

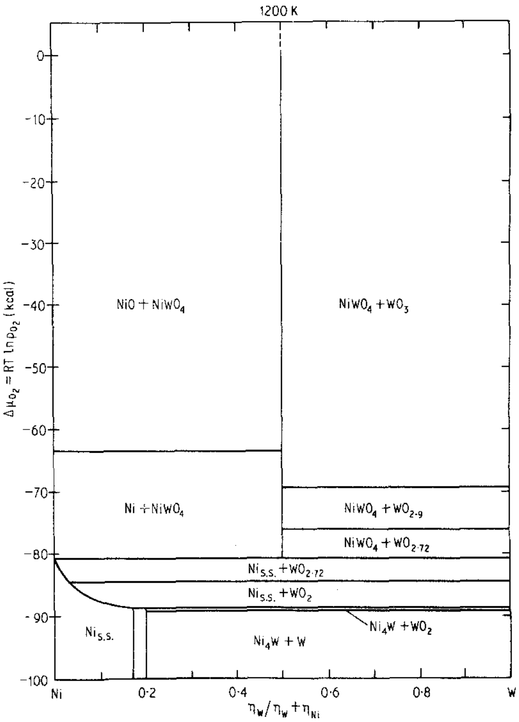

Figure 3 Phase equilibria in the system Ni–W–O as a function of oxygen potential at 1200 K.

From a practical point of view it is more useful to present the phase relations as a function of oxygen potential at a constant temperature (1200 K) as shown in Fig. 3. According to the phase rule, at a constant temperature, three condensed phases can coexist only at a fixed oxygen potential. The various three phase equilibria are therefore represented by horizontal lines on the diagram. It is seen that $NiWO_4$ is a stable phase for a large range of oxygen potentials, ranging from 0 to $-80.5\,\text{kcal mol}^{-1}$. No other phase in the ternary system has a higher range of stability at 1200 K. This fact probably explains the observation of Woo and Roy [4] that $NiWO_4$ is a major constituent of the oxide layer formed during the oxidation of tungsten-fibre reinforced nickel base composite materials. The phase relations at other temperatures can readily be derived from the thermodynamic data on the condensed phases.

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