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INTERACTIONS IN ALKALI METAL SOLUTIONS CONTAINING OXYGEN

I. THE NIOBIUM-OXYGEN-POTASSIUM SYSTEM

R. L. Klueh

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METALS AND CERAMICS DIVISION

INTERACTIONS IN ALKALI METAL SOLUTIONS CONTAINING OXYGEN

I. THE NIOBIUM-OXYGEN-POTASSIUM SYSTEM

R. L. Klueh

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ABSTRACT

Refractory metals are highly resistant to dissolutive corrosion attack by liquid and boiling alkali metals when the alkali metals and refractory metals are free of impurities. Dissolution increases drastically, however, when the alkali metals contain oxygen. This phenomenon has been attributed to the formation of ternary oxides containing atoms of the two metals.

As an alternative to the ternary oxide hypothesis, we have examined the possibility that at equilibrium only two condensed phases are present and that the oxygen affects the solubility of the refractory metal by decreasing the activity coefficient of the refractory metal in the liquid. The interplay between solute species in refractory metal-oxygen-alkali metal systems can be characterized in terms of interaction parameters as developed by Wagner. This approach was evaluated using data from the niobium-oxygen-potassium system at 600°C. The observed solubility of niobium as a function of the oxygen content in potassium was consistent with that expected on the basis of calculated interaction parameters. Analysis of the observed behavior in terms of the phase rule also indicated that only two condensed phases exist at equilibrium.

INTRODUCTION

Since liquid metals are being considered for use as heat transfer and working fluids in nuclear reactors, much work has been directed toward determining the compatibility between possible coolants and structural and cladding materials. These studies have been directed toward the compatibility of the alkali metals lithium, sodium, and potassium with stainless steels and nickel-base alloys at lower temperatures and the refractory metals niobium, tantalum, molybdenum, and their alloys at higher temperatures.

When the system is free of impurities, especially oxygen, attack of refractory metals by alkali metals is negligible. Oxygen, however, can debilitate the compatibility between refractory metals and alkali metals in two ways (1), depending upon whether it is in the refractory metal or the alkali metal:

1. When the oxygen concentration in niobium or tantalum exceeds some threshold level depending upon the alkali metal and temperature, the alkali metal rapidly penetrates the metal (2) (both intergranular and transgranular penetrations are observed).

2. When oxygen is in the alkali metal the "apparent solubility*" of the refractory metal (low in oxygen) in the alkali metal increases with an increase in the oxygen concentration of the alkali metal. The present study is restricted to consideration of the latter effect.

*The term "apparent solubility" is used to indicate that the exact nature of the refractory metal in the alkali metal is unknown.

Litman (3) found that at 600°C an increase of 50 to 100 ppm of oxygen in potassium increased the "apparent solubility" of niobium several hundredfold over that reported for pure potassium. Others have reported oxygen-enhanced dissolution in potassium (4,5), sodium (6), and cesium (7). These observations have been explained by hypothesizing the formation of ternary oxides of the alkali metal and refractory metal (3,4,5,8). Such oxides are viewed by some to be in the form of a condensed phase, but by others to be in the form of a dissolved complex. The existence of oxides of this type at the test temperature has not been demonstrated, although there are indications that the penetration of oxygen-doped tantalum or niobium by alkali metals (first effect discussed above) is accompanied by the formation of a reaction product containing oxygen, alkali metal, and refractory metal.

In the present work, we considered the interactions between solute species in liquid metal solutions and compared predicted solution behavior with that observed for the niobium-potassium-oxygen system at 600°C. The exact atomic (or molecular) state of the species was ignored and the problem was addressed phenomenologically in terms of the activities of the species in solution and the effects of interactions in solution on these activities.

INTERACTION PARAMETERS

For a dilute, multicomponent solution Wagner (9) and Chipman (10) have proposed that the activity coefficient of one of the components can be expressed as a function of concentration by adding to the activity coefficient for that component in the limiting binary terms which

empirically account for interactions between the solutes in the solution.

Accordingly, Wagner used a Taylor series expansion about

$N_2 = N_3 = \dots = N_n = 0$ for the logarithm of the activity coefficient of component 2 in a multicomponent solution and obtained

$$\begin{aligned} \ln \gamma_2 = \ln \gamma_2^0 + \left[N_2 \left(\frac{\partial \ln \gamma_2}{\partial N_2} \right) + N_3 \left(\frac{\partial \ln \gamma_2}{\partial N_3} \right) + \dots + N_n \left(\frac{\partial \ln \gamma_2}{\partial N_n} \right) \right] + \left[\frac{1}{2} N_2^2 \left(\frac{\partial^2 \ln \gamma_2}{\partial N_2^2} \right) \right. \\ \left. + N_2 N_3 \left(\frac{\partial^2 \ln \gamma_2}{\partial N_2 \partial N_3} \right) + \frac{1}{2} N_3^2 \left(\frac{\partial^2 \ln \gamma_2}{\partial N_3^2} \right) + \dots \right] + \dots, \quad (1) \end{aligned}$$

where $N_2, N_3, \dots, N_n$ are the mole fractions of the solutes 2, 3, 4, ..., n in the solvent component 1, γ_2^0 is the limiting value of γ_2 in the pure solvent (i.e., the 1-2 binary), and the derivatives are to be taken for the limiting case of zero concentration for all solutes. Equation (1) is usually written as

$$\begin{aligned} \ln \gamma_2 = \ln \gamma_2^0 + N_2 \epsilon_2^{(2)} + N_3 \epsilon_2^{(3)} + \dots + N_n \epsilon_2^{(n)} \\ + \frac{1}{2} N_2^2 \epsilon_2^{(2,2)} + N_2 N_3 \epsilon_2^{(2,3)} + \frac{1}{2} N_3^2 \epsilon_2^{(3,3)} + \dots \quad (2) \end{aligned}$$

where

$$\epsilon_2^{(2)} = \frac{\partial \ln \gamma_2}{\partial N_2}, \quad \epsilon_2^{(3)} = \frac{\partial \ln \gamma_2}{\partial N_3}, \quad \dots \quad (3)$$

and

$$\epsilon_2^{(2,2)} = \frac{\partial^2 \ln \gamma_2}{\partial N_2^2}, \quad \epsilon_2^{(2,3)} = \frac{\partial^2 \ln \gamma_2}{\partial N_2 \partial N_3}, \quad \dots; \quad (4)$$

the ϵ 's are referred to as interaction parameters to be determined experimentally and which empirically account for the interactions between

the respective solutes (indicated by the subscripts and superscripts).

Similar equations can be written for all components in the solution.

Wagner also showed that

$$\epsilon_i^{(j)} = c_j^{(i)}. \quad (5)$$

Truncating terms higher than first order, Eq. (2) for a ternary solution becomes*

$$\ln \gamma_2^{(1+3)} = \ln \gamma_2^{(1)} + N_2 \epsilon_2^{(2)} + N_3 \epsilon_2^{(3)}. \quad (6)$$

When Henry's law is obeyed by component 2 in the 1-2 binary,

$\ln \gamma_2 = \ln \gamma_2^{(1)} = \text{constant}$ and $\epsilon_2^{(2)} = 0$. A negative value of $\epsilon_2^{(3)}$ then indicates that the addition of component 3 increases the solubility of component 2 and vice versa when $\epsilon_2^{(3)}$ is positive.

EXPERIMENTAL

The effect of oxygen on the solubility of niobium in potassium and the redistribution of oxygen between niobium and potassium at 600°C were studied using the experimental system shown in Fig. 1. The system consists of a niobium specimen in contact with potassium in a niobium container, encapsulated, in turn, in a protective stainless steel container. Oxygen concentrations of both the niobium and potassium were determined before test.

*Examples of the nomenclature used for activities, activity coefficients, and concentrations in the solutions are:

$\gamma_2^{(1)}$ = activity coefficient of component 2 in the binary system 1-2.

$\gamma_2^{(1+3)}$ = activity coefficient of component 2 in the ternary

system 1-2-3.

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Fig. 1. Schematic representation of experimental system for investigation of the effect of oxygen on the solubility of niobium in potassium and the redistribution of oxygen between niobium and potassium.

After an exposure period of 500 hr, the capsule was inverted and quenched in liquid nitrogen. The oxygen concentration of the niobium specimen and capsule was determined by vacuum-fusion analysis, and the concentration of oxygen in the potassium was calculated by a mass balance. The potassium was dissolved in isopropyl alcohol from which it was recovered as potassium fluoride, and the amount of niobium in the potassium fluoride was determined by spectrographic analysis with an accuracy of $\pm 10\%$.

RESULTS AND DISCUSSION

Determination of $\epsilon_{\text{Nb}}^{(O)}$

Table 1 summarizes the experimental results, and in Fig. 2 these results have been plotted to show the effect of oxygen on the solubility of niobium in potassium at 600°C . Extrapolation to 1 ppm O gives a concentration of niobium of between 4 and 5 ppm, which is in reasonable agreement with solubility data (5,11,12) for niobium in "pure" potassium extrapolated to 600°C . (The data point at 10 ppm O was ignored in drawing the curve in Fig. 2 because the level of niobium in potassium is below that at which a precision of $\pm 10\%$ is meaningful.)

If Henry's law applies and only first-order interaction parameters are considered, the activity coefficient in the ternary liquid is given by

$$\ln \gamma_{\text{Nb}}^{(K+O)} = \ln \gamma_{\text{Nb}}^{(K)} + \epsilon_{\text{Nb}}^{(O)} N_{\text{O}}^{(K+\text{Nb})} \quad (7)$$

where $\gamma_{\text{Nb}}^{(K)}$ is the Henry's law constant.

Fig. 2. Effect of Oxygen Content in Potassium on the Solubility of Niobium in Potassium at 600°C.

Table 1. Summary of Experimental Observations in the
Niobium-Oxygen-Potassium System at 600°C

Oxygen in Niobium ppm		Oxygen in Potassium ppm		Niobium in Potassium After ^d ppm	Distribution Coefficient
Before ^a	After ^a	Before ^b	After ^c		
32	45	< 10	~ 10	~ 50	10.7
70	50	~ 10	200	430	0.596
32	57	~ 30	280	680	0.487
70	59	30	280	640	0.500
70	64	100	350	960	0.637
70	68	530	780	1,060	0.208
70	58	1,010	1,260	2,190	0.110
70	67	2,030	2,280	3,380	0.070
70	71	3,900	4,150	3,600	0.041
70	100	19,000	18,000 ^e	13,400	0.013

^aDetermined by vacuum-fusion analysis.

^bLow oxygen levels determined by mercury amalgamation; higher oxygen levels (> 100 ppm) determined by adding weighed amounts of K₂O to the potassium.

^cCalculated by mass balance taking into account the oxygen in the potassium, the niobium specimen, and the capsule.

^dDetermined by spectrographic analysis.

^eThis oxygen concentration, while high, is less than that corresponding to saturation at 600°C in the potassium-oxygen system.

The activity of niobium in the potassium solution in equilibrium with solid niobium is assumed to be unity relative to pure niobium; that is,

$$a_{\text{Nb}}^{(\text{K+O})} = 1 = \gamma_{\text{Nb}}^{(\text{K+O})} N_{\text{Nb}}^{(\text{K+O})} \quad (8)$$

and

$$\gamma_{\text{Nb}}^{(\text{K+O})} = \frac{1}{N_{\text{Nb}}^{(\text{K+O})}} \quad (9)$$

Figure 3 shows $\ln \gamma_{\text{Nb}}^{(\text{K+O})}$, as determined from Eq. (9) and the data of Table 1, plotted as a function of $N_{\text{O}}^{(\text{K+Nb})}$. From Eq. (7), $\epsilon_{\text{Nb}}^{(\text{O})}$ is given by the slope of the curve in Fig. 3 as $N_{\text{O}}^{(\text{K+Nb})}$ approaches zero (extrapolated in line with Fig. 2); that is

$$\epsilon_{\text{Nb}}^{(\text{O})} = \left(\frac{d \ln \gamma_{\text{Nb}}^{(\text{K+O})}}{d N_{\text{O}}^{(\text{K+Nb})}} \right)_{N_{\text{O}}, N_{\text{Nb}} \rightarrow 0} \simeq -4 \times 10^3 \quad (10)$$

It is obvious from Fig. 3 that at oxygen concentrations greater than 0.1 at. % $\ln \gamma_{\text{Nb}}^{(\text{K+O})}$ is no longer accurately described by the first-order parameter. However, since lower oxygen concentrations are more relevant in practice and the data justify only order-of-magnitude comparisons, higher order terms have not been determined.

Distribution Coefficient Discrepancy

In addition to affecting niobium solubility, the oxygen content of the potassium also affects the oxygen concentration of the niobium. Thermodynamic considerations (1,2) have been used to predict the ratio of oxygen concentration in the niobium to that in the potassium at equilibrium. Such predictions have been at odds with experimental findings.

Fig. 3. Effect of Oxygen Content in the Potassium on the Activity Coefficient of Niobium in the Niobium-Oxygen-Potassium System.

The interaction coefficients discussed above, however, lead to certain refinements in the predictions which bring the experimental and calculated oxygen ratios into better accord.

Thermodynamic considerations of the oxygen ratio between niobium and potassium begin with the statement that at equilibrium the fugacities of the oxygen above the two phases must be equal; that is,

$$f_{O_2}^{(Nb)} = f_{O_2}^{(K)} , \quad (11)$$

and, since the oxygen pressure of the system is extremely low,

$$\left(\frac{f_{O_2}^{(Nb)}}{f_{O_2}^{(K)}} \right)^{\frac{1}{2}} = \left(\frac{p_{O_2}^{(Nb)}}{p_{O_2}^{(K)}} \right)^{\frac{1}{2}} = 1 . \quad (12)$$

The pressure of oxygen gas in equilibrium with niobium or potassium saturated with oxygen is given by

$$\left(p_{O_2} \right)_{\text{sat}}^{\frac{1}{2}} = \exp \left(\frac{\Delta G^{\circ}_{\text{oxide}}}{RT} \right) , \quad (13)$$

where $\Delta G^{\circ}_{\text{oxide}}$ is the free energy of formation of the pure oxide (per gram atom of oxygen), NbO, or K₂O, from the pure metal and oxygen gas at 1 atm. Multiplication of Eq. (12) by $\left(p_{O_2}^{(K)} \right)_{\text{sat}}^{\frac{1}{2}} / \left(p_{O_2}^{(Nb)} \right)_{\text{sat}}^{\frac{1}{2}}$ gives

$$\left[\frac{p_{O_2}^{(Nb)} / \left(p_{O_2}^{(Nb)} \right)_{\text{sat}}}{p_{O_2}^{(K)} / \left(p_{O_2}^{(K)} \right)_{\text{sat}}} \right]^{\frac{1}{2}} = \exp \left(\frac{\Delta G^{\circ}_{K_2O} - \Delta G^{\circ}_{NbO}}{RT} \right) \quad (14)$$

and which can be written in terms of activities as

$$\frac{a_O^{(Nb)}}{a_O^{(K)}} = \exp \left(\frac{\Delta G_{K_2O}^\circ - \Delta G_{NbO}^\circ}{RT} \right). \quad (15)$$

In this expression the standard state for oxygen dissolved in niobium and potassium has been taken as that corresponding to saturation in the respective solutions.

In using this activity relationship to predict oxygen concentrations in the two solvents other investigators (1,2) have assumed that Henry's law applies to oxygen in the niobium and potassium up to saturation and that niobium and potassium are completely immiscible. Under these assumptions the theoretical distribution coefficient is defined as

$$\kappa_T \equiv \frac{N_O^{(Nb)}}{N_O^{(K)}} = \frac{\left(N_O^{(Nb)}\right)_{sat}}{\left(N_O^{(K)}\right)_{sat}} \exp \left(\frac{\Delta G_{K_2O}^\circ - \Delta G_{NbO}^\circ}{RT} \right) \quad (16)$$

where $\left(N_O^{(Nb)}\right)_{sat}$ and $\left(N_O^{(K)}\right)_{sat}$ are the saturation solubilities at T and κ_T should be constant.

At 600°C where $N_O^{(K)} \approx 6.1 \times 10^{-2}$ (ref. 13), $N_O^{(Nb)} \approx 5.2 \times 10^{-3}$ (ref. 14), $\Delta G_{K_2O}^\circ \approx 59,000$ kcal (ref. 15), and $\Delta G_{NbO}^\circ \approx 80,000$ kcal (ref. 15), Eq. (16) gives a theoretical distribution coefficient of about 1.5×10^4 . In the present experiments, on the other hand, the distribution coefficient was found to be much less than this (Table 1) and to vary with the oxygen content of the potassium, as shown in Fig. 4. Since, as seen in the preceding section, oxygen in the potassium affects the activity coefficient of niobium in potassium, and since

$$\epsilon_{Nb}^{(O)} = \epsilon_O^{(Nb)}, \quad (17)$$

Fig. 4. Effect of Oxygen Content in the Potassium on the Oxygen Distribution Coefficient in the Niobium-Oxygen-Potassium System.

the assumption of immiscible solvents obviously does not hold in the liquid. Niobium, therefore, must affect the activity coefficient of the oxygen in the potassium.

The distribution coefficient can be rewritten as a function of the oxygen in the liquid* as

$$\kappa_T \left(\frac{N_O^{(K+Nb)}}{N_O^{(K+Nb)}} \right) = \frac{N_O^{(Nb)}}{N_O^{(K+Nb)}} \gamma_O^{(K+Nb)} \left(\frac{N_O^{(Nb)}}{N_O^{(K+Nb)}} \right)_{\text{sat}} \exp \left(\frac{\Delta G_{K_2O}^\circ - \Delta G_{NbO}^\circ}{RT} \right) \quad (18)$$

where

$$\ln \gamma_O^{(K+Nb)} \simeq \ln \gamma_O^{(K)} + \epsilon_O^{(Nb)} N_{Nb}^{(K+O)}, \quad (19)$$

In theory it should be possible to calculate $\gamma_O^{(K+Nb)}$ from Eq. (19) and substitute it into Eq. (18) and show that the distribution coefficient thus calculated agrees with the value determined experimentally. When this is done using available potassium-oxygen solubility data, however, the discrepancy is reduced only by about an order of magnitude (i.e., from about 10^4 to 10^3 at 200 ppm O). Several reasons can be given for this: First, the solubility of oxygen in potassium at 600°C was determined by extrapolation of data obtained at 305°C and below (13); second, the Henry's law approximation used for the binary system is questionable because the solubility may be as large as 10 at. % at 600°C.

*Although Eq. (19) is written explicitly as a function of the concentration of niobium in the potassium, the equilibrium niobium concentration depends upon the oxygen concentration according to the relationship shown in Fig. 3.

On the other hand, if Fig. 3 is extrapolated in accordance with available solubility data for niobium in pure potassium (11,12) (about 1 ppm) the agreement is further improved by about two orders of magnitude.

Determination of $\epsilon_0^{(\text{Nb})}$

Equation (18) can be rearranged to give

$$\gamma_0^{(\text{K+Nb})} = \frac{\kappa_T \left(\frac{N_O^{(\text{K+Nb})}}{N_O^{(\text{Nb})}} \right)}{\left(\frac{N_O^{(\text{Nb})}}{N_O} \right)_{\text{sat}}} \exp - \left(\frac{\Delta G_{\text{K}_2\text{O}}^\circ - \Delta G_{\text{NbO}}^\circ}{RT} \right), \quad (20)$$

which can be used along with Figs. 2 and 4 for an independent determination of $\epsilon_0^{(\text{Nb})}$. The data used for this determination are shown in Table 2, from which $\epsilon_0^{(\text{Nb})}$ was determined as

$$\epsilon_0^{(\text{Nb})} \simeq - 2 \times 10^4, \quad (21)$$

in good agreement with $\epsilon_{\text{Nb}}^{(\text{O})}$ determined above.

If the procedure used to determine $\epsilon_{\text{Nb}}^{(\text{O})}$ is compared with that used to determine $\epsilon_0^{(\text{Nb})}$, the error contributed by experimental procedure is least for the latter because the vacuum-fusion technique used to determine the oxygen concentrations in the niobium is accurate to about $\pm 10\%$ even at the lower oxygen concentrations studied. The major difficulty in the determination of $\epsilon_{\text{Nb}}^{(\text{O})}$ is that the accuracy of the analytical technique for determining niobium in potassium decreases significantly below 100 ppm Nb. Nevertheless, the good agreement between the two methods is encouraging and indicates that the extrapolations employed are reasonable.

Table 2. Data Used for Interaction Parameter Calculations

$c_O^{(K+Nb)}$ ppm	$N_{Nb}^{(K+O)}{}^{(a)}$	$\kappa_T \left(N_O^{(K+Nb)} \right)^{(b)}$	$\ln \gamma_O^{(K+Nb)}$
10	1.4×10^{-5}	10.7	-4.48
100	1.0×10^{-4}	2.5	-5.93

^aTaken from Fig. 2.

^bTaken from Fig. 4.

It is interesting to note that $\epsilon_{\text{Nb}}^{(\text{O})}$ and $\epsilon_0^{(\text{Nb})}$ determined here are larger in absolute magnitude than first-order interaction parameters reported for other systems (16); the effect on solubility, however, also appears much larger than in the other systems investigated. Most of the available data have been obtained in liquid iron alloys where the strongest interaction observed was between aluminum and oxygen (16), $\epsilon_0^{(\text{Al})} \simeq -10^3$.

If $\epsilon_0^{(\text{Nb})}$ of -2×10^4 is accepted as the most accurate value, an interesting extrapolation, which demonstrates the consistency of the solution hypothesis, is possible. It is possible to calculate the Henry's law constant for the potassium-niobium system [i.e., $\gamma_{\text{Nb}}^{(\text{K})}$] by extrapolation to zero oxygen concentration as follows:

$$\epsilon_0^{(\text{Nb})} \simeq -2 \times 10^4 = \frac{9.2 - \ln \gamma_{\text{Nb}}^{(\text{K})}}{2.44 \times 10^{-4}}, \quad (22)$$

where the extrapolation has been made from 100 ppm O in potassium (Table 2). Hence,

$$\gamma_{\text{Nb}}^{(\text{K})} \simeq 1.3 \times 10^6, \quad (23)$$

and if Henry's law applies to saturation

$$N_{\text{Nb}}^{(\text{K})} \simeq 7.7 \times 10^{-7} \text{ at. fract.}, \quad (24)$$

which is about 2 ppm Nb and order-of-magnitude agreement with experiment (11,12).

Phase Rule Analysis

Although the above discussion demonstrates that the niobium-oxygen-potassium system can be characterized phenomenologically in terms of the activity of the niobium and oxygen in the potassium, it does not eliminate the possibility that a ternary oxide phase exists. Information of this nature, however, can be obtained by use of the phase rule, for if the ternary oxide is present at equilibrium, no degrees of freedom remain [i.e., the temperature and the composition of one phase (ternary oxide) have been fixed]. Therefore, there will be no distribution of oxygen between the niobium and potassium when the total oxygen concentration of the system is varied [i.e., the concentration of the oxygen in niobium (and potassium) should remain constant]. Distribution should occur, however, when no third condensed phase exists.

Table 1 shows the change in oxygen concentration of niobium with the addition of oxygen to the potassium (the change in the oxygen concentration in niobium is most significant since it can be determined with the greatest accuracy). The variation of the oxygen in the niobium from 45 to 100 ppm with the simultaneous variation of the oxygen in potassium from 10 to 18,000 ppm is thought to indicate a redistribution of oxygen in the system. The variation of the oxygen in niobium at the lower levels is not believed to indicate the formation of a compound in the system because the level of oxygen in the niobium could not then increase from this level (about 60) to 100 ppm; that is, only more of this compound would form and eventually large amounts of it would be found. Although the specimens exposed to the potassium containing 18,000 ppm O was discolored, no compounds were detected by x-ray diffraction.

Furthermore, any surface reaction products were removed before the oxygen concentration was determined.

The relatively small change in oxygen concentration in the niobium with a much larger change in the oxygen content of the potassium is consistent with the solution hypothesis. This can be seen by rewriting Eq. (18) as

$$\frac{N_O^{(Nb)}}{N_O^{(K+Nb)}} = \gamma_O^{(K+Nb)} \kappa'_T \quad (25)$$

where κ'_T includes all terms that are independent of liquid composition and depends only on temperature. Hence,

$$\frac{\Delta N_O^{(Nb)}}{N_O^{(Nb)}} = \frac{\Delta N_O^{(K+Nb)}}{N_O^{(K+Nb)}} + \frac{\Delta \gamma_O^{(K+Nb)}}{\gamma_O^{(K+Nb)}} , \quad (26)$$

and from Eq. (19)

$$\frac{\Delta \gamma_O^{(K+Nb)}}{\gamma_O^{(K+Nb)}} = \epsilon_O^{(Nb)} \frac{\Delta N_O^{(K+O)}}{N_O^{(K+O)}} + N_O^{(K+O)} \frac{\Delta \epsilon_O^{(Nb)}}{N_O^{(K+O)}} . \quad (27)$$

But since $\Delta \epsilon_O^{(Nb)} \simeq 0$

$$\frac{\Delta N_O^{(Nb)}}{N_O^{(Nb)}} = \frac{\Delta N_O^{(K+Nb)}}{N_O^{(K+Nb)}} + \epsilon_O^{(Nb)} \frac{\Delta N_O^{(K+O)}}{N_O^{(K+O)}} . \quad (28)$$

At the low oxygen levels, where the first-order approximation is applicable, Eq. (28) indicates that a rather large percentage change in the oxygen concentration in potassium results in only a small percentage

change in the concentration of oxygen in the niobium when $c_O^{(Nb)}$ is a large negative number. This is in accord with the present results.

Equilibrium Assumption

All of the calculations used in this analysis presuppose equilibrium for the system. With respect to dissolution and homogenization of niobium by the liquid, comparison of 100- and 500-hr tests indicates that equilibrium is achieved in 500 hr. In the absence of surface reaction products, which characterized all but the highest oxygen level experiments, the slowest step in the approach to equilibrium is the diffusion of oxygen in the niobium.

Diffusion calculations which assume a constant surface concentration indicate that after 500 hr the concentration of oxygen at the center of the niobium specimen is within 2% of its final value; hence, for all practical purposes, the system has reached equilibrium after 500 hr at 600°C. Furthermore, no microhardness gradients could be detected across the width of the specimens (3), indicating that no oxygen gradient existed.

SUMMARY

It is proposed that the effect of oxygen on the "apparent solubility" of refractory metals in alkali metals is a result of the interaction between solutes (oxygen and the refractory metal) in the alkali metal, and that this effect can be characterized in terms of the Wagner interaction parameters.

The niobium-oxygen-potassium system was investigated at 600°C, and the experimental results were characterized in terms of Wagnerian inter-action parameters.

Using this approach, it was possible to explain the often-discussed distribution-coefficient discrepancy. Order-of-magnitude calculations demonstrated that the treatment is consistent with other experimental results.

The phase rule was used to show that at equilibrium at 600°C the niobium-oxygen-potassium system contains only two condensed phases, and thus, no ternary oxide phase, as has often been postulated, exists.

It should be kept in mind that the treatment used in this study applies only under equilibrium conditions; the kinetics by which equilibrium is approached were not considered. Indeed, if a surface reaction is rate controlling, equilibrium might well be approached by an intermediate step involving the formation and dissolution of a ternary oxide phase.

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