Journal of Nuclear Materials 451 (2014) 24–27

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Comparison of liquid metal solution model predictions with compatibility data of niobium with liquid sodium

V.P. Krasin [*], S.I. Soyustova

Moscow State Industrial University, 16 Avtozavodskay ulica, Moscow 115280, Russia

HIGHLIGHTS

- The activity coefficient of niobium in ternary melt can be obtained by means of integrating the Gibbs–Duhem equation.
- Effect of oxygen on niobium saturation concentration in sodium is more pronounced at low temperatures.
- At the initial stage of the process of interaction niobium with sodium containing oxygen, a decisive role is played by the mechanism, based on the significant increase of solubility of niobium in sodium.

ARTICLE INFO

Article history:
Received 30 September 2013
Accepted 14 March 2014
Available online 22 March 2014

ABSTRACT

Theoretical correlations based on the coordination cluster model have been used to obtain the solubility of niobium in liquid sodium as a function of oxygen content. It is shown that the derived equations are useful to provide understanding of a relationship between thermodynamic properties and local ordering in the Na–Nb–O melt. The effect of oxygen in sodium on the compatibility niobium with liquid sodium is discussed in terms of two processes: (1) oxygen level increases the solubility of niobium in liquid sodium, and (2) oxygen enhanced dissolution by liquid sodium has been explained by taking into account the formation of ternary oxide of the alkali metal and niobium.

1. Introduction

The use of liquid low melting point metals as coolants for nuclear reactors, particularly sodium, has led to a growing interest in the solution chemistry of these liquids to further the understanding of many of corrosion problems encountered in their use. One of the basic criterions of compatibility liquid metals with structural materials may be the equilibrium solubility of structural metals in a liquid phase. Most of the experimental data [1,2] are shown that oxygen is the most undesirable impurity in liquid sodium and potassium, it increases mass transfer of refractory metals in these mediums, however, mechanism of this phenomenon is a concern. Several investigators [3] consider that nonmetal impurity elements increase the equilibrium solubility of solid metals in these liquid mediums, other researchers [4,5] suppose that processes at solid–liquid interface are crucial. In particular, in some circumstances the formation of ternary compounds with alkali metals and nonmetallic elements on the interface of solid metals may be dominating.

In our work the Na–Nb–O system was chosen because the processes in it are typical for many systems containing refractory metals. Particularly, in terms of corrosion processes in liquid alkali metals, there are many common features in the behavior of niobium and vanadium alloys. In addition, the Na–Nb–O system has been extensively studied [6,7] and niobium solubility data are available as a function of oxygen concentration in liquid sodium.

The purpose of present study is to answer two questions. The first has been concerned with a possibility to apply the coordination cluster model (CCM) of metallic solutions for analyzing the interactions in Na–Nb–O melts. The second has involved a predictions of temperature dependence of the niobium solubility in sodium at various concentrations of oxygen in sodium for the temperature range 300–800 °C and a comparison of the results of calculation with the available experimental data.

The CCM, which has been shown to provide a good presentation of the activity coefficients of nonmetallic solute in binary solvent, is extended for calculations of the solubility of constructional materials in liquid melts in the presence of nonmetallic impurity.

2. Thermodynamic considerations

It was shown in earlier papers [8,9] that application of the CCM which was proposed Blander et al. [10] leads to theoretical values being in satisfactory agreement with the experimental data.

---

[*] Corresponding author.
E-mail address: vkrasin@rambler.ru (V.P. Krasin).

http://dx.doi.org/10.1016/j.jnucmat.2014.03.023
0022-3115/

In view of comparison of the atomic radii elements forming Na–Nb–O system it is assumed that an oxygen atom in the melt of two metals Na and Nb is surrounded by an average six atoms of metals ($z = 6$). Using of the conception "interstitial position" is not quite correct in relation to liquid metals which exist at the temperatures over the melting point. However, the values of the coordination numbers for sodium atoms which were obtained by the X-ray diffaction study of liquid sodium [11] and also methods of molecular dynamics [12] in the temperatures range from 100 to 550 °C indicate that the short-range order in liquids and solids has some common features. However, diffusive mechanisms in solids and liquids are significantly different. In solids the mechanism of diffusion is activation. The analysis of movement of particles in models of simple liquids has showed that the activated jumps of atoms on distances of an order interatomic practically are not observed, and the mechanism of diffusion is drift. Total displacement of a particle is the sum of a large number of small displacements on distances much less interatomic ones [13]. Since in the present work dynamic properties of melt are not considered, the approach based on use of CCM is valid for calculation of coefficients of thermodynamic activity of components of melt.

In the CCM it is supposed that each oxygen atom in the melt has i Nb atoms and $(z - i)$ Na atoms as the nearest neighbors, where i changes from 0 to z. The melt contains $(z + 1)$ kinds of such configurations, which are called clucters and denoted by $\mathrm{O}[(\mathrm{Na})_{z-i}(\mathrm{Nb})_i]$. It should be borne in mind that in the melt atoms are in constant motion, so it makes sense to talk about the average for some time t the configuration of atoms. For clusters the reasonable assessment of time of averaging falls in the range $\tau_0 < t < \tau_D$ (τ_0 is a period of oscillations in the equilibrium position; τ_D is time of the "settled life" of an atom. According to [11] in this paper is used following estimations: $\tau_0 \approx 10^{-13}$ s and $\tau_D \approx 10^{-11}$ s.

Since the oxygen concentration in the Na–Nb–O melt is low (less than 2 mol%) we can neglect of the possibility of O–O bonds existing.

The thermodynamic properties of the solution depend on the distribution of the oxygen atoms among the clusters and are connected with affinity of the metal atoms of each type for oxygen and, also, depend on the thermodynamic parameters of the solvent. According to CCM, the activity coefficient of oxygen in Na–Nb–O alloy is defined by the equation:

$$\gamma_{\mathrm{O}}^{-1} = \sum_{i=0}^{z} \frac{z!}{i!(z-i)!} \left[\frac{x_{\mathrm{Nb}} \gamma^{t}_{\mathrm{Nb(Na-Nb)}}}{\gamma^{1/z}_{\mathrm{O(Nb)}}} \right]^{i} \cdot \left[\frac{x_{\mathrm{Na}} \gamma^{t}_{\mathrm{Na(Na-Nb)}}}{\gamma^{1/z}_{\mathrm{O(Na)}}} \right]^{z-i} \cdot \exp\left(\frac{i(z-i)h_{\mathrm{B}}}{2RT} \right), \quad (1)$$

where $\gamma_{\mathrm{O(Nb)}}$ and $\gamma_{\mathrm{O(Na)}}$ are the activity coefficients of oxygen in binary Nb–O and Na–O systems, respectively; $\gamma_{\mathrm{Nb(Na-Nb)}}$ and $\gamma_{\mathrm{Na(Na-Nb)}}$ are the activity coefficients of Nb and Na in binary Na–Nb system; x_{Nb} and x_{Na} are the mole fractions of Nb and Na in Na–Nb–O melt; T is the absolute temperature; R is the universal gas constant; t is the parameter taking into account the relative weakening of metallic bond between atoms in the first coordination shell around the oxygen atom and h_{B} is an energy parameter.

The energy parameter h_{B} has a physical meaning because it takes into account the tendency of electron transfer from the atom Na or Nb to the atom O in the first solvation shell of oxygen atom.

Parameter h_{B} is introduced from the following assumptions. The transition of the oxygen atom from the cluster $\mathrm{O(Na}_{z-i}\mathrm{Nb}_i)$ to the cluster $\mathrm{O(Na}_{z-i-1}\mathrm{Nb}_{i+1})$ can be represented by the following equation:

$$\mathrm{O(Na}_{z-i}\mathrm{Nb}_i) + V(\mathrm{Na}_{z-i-1}\mathrm{Nb}_{i+1}) = V(\mathrm{Na}_{z-i}\mathrm{Nb}_i) + \mathrm{O(Na}_{z-i-1}\mathrm{Nb}_{i+1}), \quad (2)$$

where the symbol $V(\mathrm{Na}_{z-i}\mathrm{Nb}_i)$ denotes a corresponding vacant "quasi-interstitial" site.

The enthalpy change for this reaction is equal to $\Delta H(i \to i + 1)$.

Parameter h_{B} is expressed as the difference between the enthalpies of reactions at two consecutive transitions so that

$$\Delta H(i \to i+1) - \Delta H(i+1 \to i+2) = h_{\mathrm{B}}. \quad (3)$$

The energy parameter h_{B} can be calculated from the following equation:

$$h_{\mathrm{B}} = \frac{2RT}{z-1} \left[\ln\left(\frac{z - \varepsilon_{\mathrm{O}}^{\mathrm{Nb}}}{z} \right) - \frac{1}{z} \left(\ln \frac{\gamma_{\mathrm{O(Na)}}}{\gamma_{\mathrm{O(Nb)}}} \right) - t \ln \gamma_{\mathrm{Nb(Na)}} \right], \quad (4)$$

where $\varepsilon_{\mathrm{O}}^{\mathrm{Nb}} = (\partial \ln \gamma_{\mathrm{O}} / \partial x_{\mathrm{Nb}})_{x_{\mathrm{Nb}} \to 0}$ is the interaction parameter between Nb and O in ternary system Na–Nb–O.

The value of h_{B} calculated using this assumption was 7150 J/mole (the best accordance $\varepsilon_{\mathrm{O}}^{\mathrm{Nb}}$ with the experimental data [6]).

The parameter t describes the fractional loss of the interactions of the Na and Nb atoms in the cluster $\mathrm{O(Na}_{z-i}\mathrm{Nb}_i)$ (these Na and Nb atoms are labeled Na′ and Nb′ below) with other Na and Nb metallic atoms in the bulk solvent. If the fractional loss is equal to the average fraction of bonds between an Na′ and Nb′ with other solvent atoms which are part of the polyhedron forming the coordination shell around the oxygen atom, then a geometric argument may be used to calculate t. For example, if the Na′ and Nb′ atoms form an octahedron about O, then each Na′ or Nb′ atom has three bonds to other Na′ or Nb′ atoms. If the coordination numbers of Na′ and Nb′ are in the range of 6–12, then t would range from 0.5 to 0.25. Of course, since metallic "bonding" is not so simple this geometric interpretation must be used with caution. Since better estimates of t are not yet available, an average value of $t = 0.33$ is used in the present calculations based on the CCM.

It has been reported [10] that the best agreement between calculation and experiments for the ternary metal–oxygen melts is observed for the values $z = 6$.

Sodium does not form solid solution with Nb and thus, the activity of niobium in the sodium melt in equilibrium with solid niobium is unity relative to pure niobium. Accordingly, we have

$$x_{\mathrm{Nb(Na-Nb)}} = 1/\gamma_{\mathrm{Nb\ (Na-Nb)}}, \quad (5)$$

where $x_{\mathrm{Nb\ (Na-Nb)}}$ is the saturation solubility of Nb in Na–Nb system at T (all concentrations are in atom fractions).

The activity coefficient of Nb in ternary melt can be obtained by means of integrating the Gibbs–Duhem equation. The Gibbs–Duhem equation was integrated along the ABC path (Fig. 1)

$$\ln \gamma_{\mathrm{Nb(Na-Nb-O)}} = \ln \gamma_{\mathrm{Nb(Na-Nb)}} + \left[\int_0^{y_{\mathrm{Nb}}} \frac{\partial \ln \gamma_{\mathrm{Nb}}}{\partial y_{\mathrm{Nb}}} \mathrm{d}y_{\mathrm{Nb}} \right]_{y_{\mathrm{O}}=0} + \left[\int_0^{y_{\mathrm{O}}} \frac{\partial \ln \gamma_{\mathrm{Nb}}}{\partial y_{\mathrm{O}}} \mathrm{d}y_{\mathrm{O}} \right]_{y_{\mathrm{Nb}}=y^{*}_{\mathrm{Nb}}}, \quad (6)$$

where $\gamma_{\mathrm{Nb(Na-Nb-O)}}$ is the activity coefficient of Nb in the Na–Nb–O melt containing x_{Nb} and x_{O} mole fraction of niobium and oxygen at

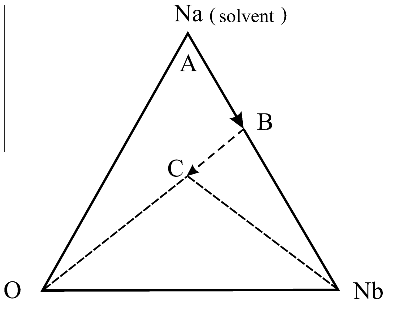

Fig. 1. Path of Gibbs–Duhem integration from infinite dilution AB: from $y_{\mathrm{O}} = 0$, $y_{\mathrm{Nb}} = 0$ to $y_{\mathrm{O}} = 0$, $y_{\mathrm{Nb}} = y^{*}_{\mathrm{Nb}}$, BC: from $y_{\mathrm{O}} = 0$, $y_{\mathrm{Nb}} = y^{*}_{\mathrm{Nb}}$ to $y_{\mathrm{O}} = y^{*}_{\mathrm{O}}$, $y_{\mathrm{Nb}} = y^{*}_{\mathrm{Nb}}$.