

Corrosion phenomena in sodium-potassium coolant resulting from solute interaction in multicomponent solution

V P Krasin and S I Soyustova

Moscow Polytechnic University, 38, Bolshaya Semenovskaya St., Moscow, 107023, Russia

E-mail: vkrasin@rambler.ru

Abstract. The solubility of Fe, Cr, Ni, V, Mn and Mo in sodium-potassium melt has been calculated using the mathematical framework of pseudo-regular solution model. The calculation results are compared with available published experimental data on mass transfer of components of austenitic stainless steel in sodium-potassium loop under non-isothermal conditions. It is shown that the parameters of pair interaction of oxygen with transition metal can be used to predict the corrosion behavior of structural materials in sodium-potassium melt in the presence of oxygen impurity. The results of calculation of threshold concentration of oxygen of ternary oxide formation of sodium with transitional metals (Fe, Cr, Ni, V, Mn, Mo) are given in conditions when pure solid metal comes in contact with sodium-potassium melt.

1. Introduction

Liquid sodium-potassium alloy, because of favorable thermal properties, is attractive as heat transfer media for a nuclear reactor of space power systems [1] and for next generation ground-based power plants [2]. On the other hand, sodium-potassium alloy has remarkable potential as working fluid for heat pipes of higher thermal performances [3]. The main advantages of the Na-K coolant are its low melting point (-12.6°C for the composition of 32 at. % Na and 68 at. % K), and its relatively high thermal conductivity.

The lack of reliable data on the solubility of metals in the NaK melt hinders the authors' ability to predict corrosion behavior of structural materials in this coolant.

The purpose of this paper is to examine metal solution models for numerical determination of the solubility of Fe, Cr, Ni, V, Mn and Mo in sodium-potassium alloy. Also, an attempt is made here to evaluate the liquid metal coolants: sodium and NaK alloy in terms of the influence of oxygen impurity on the compatibility of these coolants with the structural materials.

Simple solution of the solid metal into the liquid metal is the basis of most of the corrosion mechanisms. The initial data for theoretical determination of solubility of transition metals in NaK melt can be divided into two groups. The first group includes the enthalpy of mixing and excess entropy for solutions of transition metals in one-component metallic solvent (liquid sodium and liquid potassium). Thermodynamic parameters of liquid binary solutions of the Na-K system belong to the second group.



2. Thermodynamics of dissolved metal solutes in two-component metallic solvent

A theoretical determination of solubility of transition metal in sodium-potassium alloy has been carried out using equations of the pseudo-regular solution model.

The initial data for these calculations were the partial molar enthalpy of mixing and partial molar excess entropy of metals dissolved in the pure sodium and potassium, given in the previous section.

The method of calculating the thermodynamic activity coefficient of components of the ternary system based on the pseudo-regular solution approximation is described in detail in the monograph [4].

Using the mathematical formalism of the pseudo-regular solution model, the coefficient of thermodynamic activity of metal M in the ternary system Na-K-M can be described by:

$$\ln \gamma_{M(\text{Na-K-M})} = \left[x_K^2 E_{\text{Na-K}} + (1 - x_M)^2 E_{\text{Na-M}} - x_K(1 - x_M)(E_{\text{Na-K}} + E_{\text{Na-M}} - E_{\text{K-M}}) \right] / RT, \quad (1)$$

where $\gamma_{M(\text{Na-K-M})}$ is the activity coefficient of M in a ternary system; x_{Na} , x_{K} and x_{M} are the mole fractions of the components in the ternary liquid metal solution Na-K-M; $E_{\text{Na-K}}$, $E_{\text{Na-M}}$, $E_{\text{K-M}}$ are exchange energies, and it should be noted that the value of each of them is determined by the thermodynamic properties of the corresponding binary system; T is the absolute temperature and R is the universal gas constant.

It should be taken into account that for each of the twelve examined binary systems of type A-M, the solution of metal M in one-component metallic solvent A can be considered as diluted. For dilute solutions the exchange energies are described by the following equations: $E_{\text{Na-M}} = a_{13} + \bar{a}_{13} \cdot T$ and $E_{\text{K-M}} = b_{23} + \bar{b}_{23} \cdot T$, where a_{13} , \bar{a}_{13} , b_{23} , \bar{b}_{23} are constant coefficients.

As for the above-mentioned binary systems Na-M and K-M $x_{M(\text{Na})} \ll 1$ and $x_{M(\text{K})} \ll 1$, parameters $E_{\text{Na-M}}$ and $E_{\text{K-M}}$ can be found from the following expressions:

$$E_{\text{Na-M}} = \frac{RT \ln \gamma_{M(\text{Na})}}{(1 - x_{M(\text{Na})}^{\text{sat}})^2} \approx RT \ln \gamma_{M(\text{Na})}, \quad E_{\text{K-M}} = \frac{RT \ln \gamma_{M(\text{K})}}{(1 - x_{M(\text{K})}^{\text{sat}})^2} \approx RT \ln \gamma_{M(\text{K})},$$

where $x_{M(\text{Na})}^{\text{sat}}$ and $x_{M(\text{K})}^{\text{sat}}$ are the solubility of metal M in pure Na and K, respectively; $\gamma_{M(\text{Na})}$ and $\gamma_{M(\text{K})}$ are the thermodynamic activity coefficients of metal M in liquid Na and K, respectively. In the present work, values $\gamma_{M(\text{Na})}$ and $\gamma_{M(\text{K})}$ have been calculated from the data on the solubility of metal M in pure Na and K.

Based on literature data the exchange energy of a binary solution Na-K of the eutectic composition was written as follows:

$$E_{\text{Na-K}} (\text{J/mol}) = R \cdot T \cdot (-0.1436 + 457.8 / T).$$

Alkali metal A (A = Na or K) does not form solid solution with transition metal M (M = Fe, Cr, Ni, V, Mn, Mo) and thus, the thermodynamic activity of M in the binary solution A-M in equilibrium with solid M is unity relative to pure metal M. Accordingly, there is:

$$x_{M(\text{Na-K-M})}^{\text{sat}} = 1 / \gamma_{M(\text{Na-K-M})}. \quad (2)$$

Eqs. (1) and (2) were used to calculate the solubility of transition metals in $\text{Na}_{0.32}\text{K}_{0.68}$ solvent.

Fig. 1 allows one to compare the calculated temperature dependence of solubility of Ni in liquid $\text{Na}_{0.32}\text{K}_{0.68}$ with the experimental solubility of this element in pure Na and K. Additionally, the nickel solubility in $\text{Na}_{0.32}\text{K}_{0.68}$ was calculated assuming that a binary Na-K solution can be considered as ideal solution. In this case, the nickel solubility was determined as follows:

$$\ln x_{\text{Ni}(\text{Na-K})}^{\text{sat}} = 0.32 \cdot \ln x_{\text{Ni}(\text{Na})}^{\text{sat}} + 0.68 \cdot \ln x_{\text{Ni}(\text{K})}^{\text{sat}}, \quad (3)$$

where $x_{\text{Ni(Na)}}^{\text{sat}}$ and $x_{\text{Ni(K)}}^{\text{sat}}$ are the solubility of Ni in pure Na and K, respectively. As follows from the results of the calculations (Fig. 1), the difference between the values calculated in accordance with Eqs. (1), (2) on the one hand and Eq. (3) does not exceed 7-10 % in the temperature range of 673-1373 K. This result can be considered quite expected, taking into account small positive values $E_{\text{Na-K}}$ which are typical for binary system Na-K. As an example of the systems having significantly different properties compared to the Na-K system, anyone can look at the Li-Pb system, in which calculations based on pseudo-regular solution model and on the ideal solution model leads to significantly different results. The reason for this is that parameter $E_{\text{Li-Pb}}$ accepts only negative values and $|E_{\text{Li-Pb}}| \gg |E_{\text{Na-K}}|$ in the same temperature range.

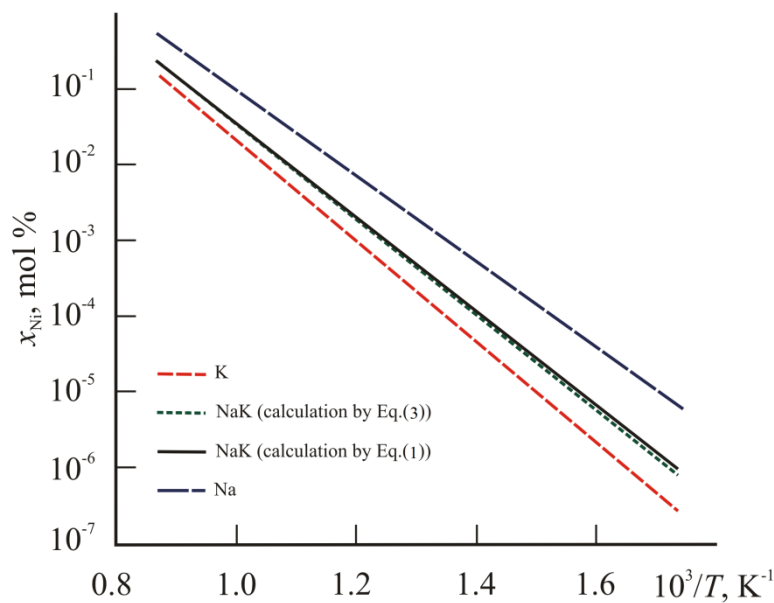


Figure 1. Solubility of nickel in Na, K and NaK alloy.

It should be noted that all six selected transition metals are of interest from the point of view of their use as components of structural materials for liquid-metal heat transfer systems. The knowledge of solubility parameters is essential for prediction of the mass transfer and processes of selective dissolution of components in liquid metal loop systems. If these above-mentioned six metals are arranged in ascending order of their solubility, let us obtain the following sequence: Mo, V, Cr, Fe, Mn, Ni (Table 1).

Table 1. Parameters of temperature dependence $x_{\text{M(Na-K)}}^{\text{sat}}$ (mole fraction) = $\exp(A - B/T)$ of the solubility of elements in $\text{Na}_{0.32}\text{K}_{0.68}$ at 673-1173 K.

solute	Mo	V	Cr	Fe	Mn	Ni
A	11.91	10.21	9.69	8.96	8.92	6.62
$B \cdot 10^{-3}, \text{K}$	39.62	30.63	28.49	24.75	21.37	14.51

Results of the calculation (Table 1) show that there is the same sequence of six solid metal arrangement with regard to their solubility in $\text{Na}_{0.32}\text{K}_{0.68}$ which was observed in the binary systems based on one-component metallic solvent. Also the solubilities of all six of the considered metals ($M = \text{Fe, Cr, Ni, Mo, V, Mn}$) in A satisfy the following inequality:

$$x_{M(K)}^{\text{sat}} < x_{M(\text{Na-K})}^{\text{sat}} < x_{M(\text{Na})}^{\text{sat}}.$$

Polley and Skyrme [5] have offered a detailed theoretical treatment, which allows one to determine the concentration driving force using the experimental data on mass transfer in non-isothermal liquid sodium loop system, in the case where there are no reliable experimental data on the solubility of solid metal in the liquid coolant. The analysis of corrosion data has enabled the authors of [5] to draw a conclusion that the corrosion rate depends critically on the magnitude of the solubility of the corroding species.

In view of this observation, it is of interest to compare the results of experiments on the mass transfer in $\text{Na}_{0.32}\text{K}_{0.68}$ loop with the theoretically defined levels of solubility of metals in this coolant.

The experimental data on the mass transfer study of the components of Type 316 stainless steel (16-18 % Cr, 10-14 % Ni, ≤ 2 % Mn, ≤ 1 % Si, ≤ 0.08 % C) in the sodium-potassium loop at pretest oxygen level < 100 ppm are reported in Ref. [6]. Chemical analysis of cold-leg deposits showed that the chemical elements are distributed in the extracted corrosive product as follows: 4.91 % Fe; 32.5 % Ni; 47.2 % Cr and 15.39 % are other elements, including oxygen and carbon. The results of theoretical determination of solubility in $\text{Na}_{0.32}\text{K}_{0.68}$ can explain the experimental data on the study of cold-leg deposits in the loop. Indeed, higher concentration of nickel and simultaneously with low iron content observed in the deposits confirm authors' theoretical estimates of a higher level of Ni solubility in $\text{Na}_{0.32}\text{K}_{0.68}$ as compared to the solubility of iron in the same temperature range.

Excess chromium content compared with a nickel content in deposits observed in this experiment [6], can be explained by increased oxygen concentration (~ 100 ppm) in $\text{Na}_{0.32}\text{K}_{0.68}$. As is well known oxygen impurity in liquid sodium intensifies the mass transfer of chromium due to the formation of sodium chromite.

3. Effect of oxygen on the solubility of solid metals in liquid sodium and $\text{Na}_{0.32}\text{K}_{0.68}$

It has been noted in Refs. [7, 8] that there are difficulties in establishing the detailed mechanism, which was to be responsible for specific processes acting on the mass transfer rate in sodium loops in the presence of oxygen impurity.

Coordination-cluster model [9] has been selected for the preliminary assessment of the effect of oxygen on the solubility of the six transition metals which are considered in present study. Additionally, a simplified thermodynamic description of the influence of dissolved oxygen on the solubility can be achieved if to use the interaction parameter formalism, which was proposed by Wagner.

As it was shown earlier, in the case of diluted solutions ($x_{\text{O}} \ll 1$, $x_{M(\text{Na})}^{\text{sat}} \ll 1$) the solubility dependence on the oxygen level can be described by the following approximate equation:

$$\ln x_{M(\text{Na-O})}^{\text{sat}} \approx \ln x_{M(\text{Na})}^{\text{sat}} - \epsilon_{\text{M}}^{\text{O}} \cdot x_{\text{O}}, \quad (4)$$

where $\epsilon_{\text{M}}^{\text{O}} = \left(\partial \ln \gamma_{M(\text{Na-M-O})} / \partial x_{\text{O}} \right)_{x_{\text{O}} \rightarrow 0}$ is the interaction parameter between oxygen and metal M in

Na-M-O liquid metal solution (or first order interaction parameter); $x_{M(\text{Na})}^{\text{sat}}$, $x_{M(\text{Na-O})}^{\text{sat}}$ are the solubility of M in Na solvent and $\text{Na}_{0.32}\text{K}_{0.68}$ solvent, respectively; x_{O} is mole fraction of oxygen in the three-component solution.

If oxygen and metal M are contained as two solutes in dilute solution of system $\text{Na}_{0.32}\text{K}_{0.68} - \text{M} - \text{O}$, the following approximate relationship is applicable:

$$\ln x_{M(\text{Na-K-O})}^{\text{sat}} \approx \ln x_{M(\text{Na-K})}^{\text{sat}} - \sigma_{\text{M}}^{\text{O}} \cdot x_{\text{O}}, \quad (5)$$

where $\sigma_{\text{M}}^{\text{O}} = \left(\partial \ln \gamma_{M(\text{Na-K-O})} / \partial x_{\text{O}} \right)_{x_{\text{O}} \rightarrow 0}$ is the specific interaction parameter between oxygen and

metal M in a four-component metallic solution of Na-K-M-O system at $x_{\text{Na}} : x_{\text{K}} = 32 : 68$; $x_{M(\text{Na-K})}^{\text{sat}}$ is

the solubility of metal M in $\text{Na}_{0.32}\text{K}_{0.68}$; $x_{\text{M}(\text{Na-K-O})}^{\text{sat}}$ is the solubility of metal M in $\text{Na}_{0.32}\text{K}_{0.68}$, containing x_{O} mole fractions of oxygen.

Specific interaction parameters defined by the equations of coordination-cluster model [9] for Na-K-M-O systems (M = Fe, Cr, Ni, V, Mn, Mo) are summarized in the Table 2. The calculation results show that the pronounced effect of oxygen on the metal solubility should be observed in systems containing vanadium, iron, chromium, manganese and molybdenum.

Table 2. Calculated interaction parameters and specific interaction parameters of metals with oxygen at 873 K.

	Fe	Cr	Ni	V	Mn	Mo
Parameter $\epsilon_{\text{M}}^{\text{O}}$ for system Na-M-O	-57	-3880	-0.90	-13390	-334	-9840
Parameter $\sigma_{\text{M}}^{\text{O}}$ for system $\text{Na}_{0.32}\text{K}_{0.68}$ -M-O	-45	-3180	-0.84	-12750	-270	-16380

4. Ternary oxides coexisting with the metal in liquid sodium and $\text{Na}_{0.32}\text{K}_{0.68}$

For each ternary oxide there is only one value of threshold concentration at a given temperature. The basic equations required to calculate the threshold oxygen levels in $\text{Na}_{0.32}\text{K}_{0.68}$ for the formation of ternary compound Na_4FeO_3 can be described by the following equation:

$$\ln x_{\text{O, tr}}^{\text{Na}} = \frac{1}{RT} \left[\frac{1}{3} \Delta G_{\text{f}}^{\text{O}}(\text{Na}_4\text{FeO}_3) - \Delta G_{\text{f}}^{\text{O}}(\text{Na}_2\text{O}) \right] + \ln x_{\text{O, sat}}^{\text{Na}}, \quad (6)$$

$$\ln x_{\text{O, tr}}^{\text{NaK}} = \frac{1}{RT} \left[\frac{1}{3} \Delta G_{\text{f}}^{\text{O}}(\text{Na}_4\text{FeO}_3) - \Delta G_{\text{f}}^{\text{O}}(\text{Na}_2\text{O}) \right] + \ln x_{\text{O, sat}}^{\text{NaK}} + \frac{2}{3} \ln a_{\text{Na}}^{(\text{Na}_{0.32}\text{K}_{0.68})}, \quad (7)$$

where $x_{\text{O, tr}}^{\text{Na}}$ is the threshold oxygen level in liquid sodium for the formation of Na_4FeO_3 on the surface of solid iron; $x_{\text{O, tr}}^{\text{NaK}}$ is the threshold oxygen level in liquid $\text{Na}_{0.32}\text{K}_{0.68}$ for the formation of Na_4FeO_3 on the surface of solid iron; $\Delta G_{\text{f}}^{\text{O}}(\text{Na}_2\text{O})$ and $\Delta G_{\text{f}}^{\text{O}}(\text{Na}_4\text{FeO}_3)$ are the free energies of formation of Na_2O and Na_4FeO_3 , respectively; $a_{\text{Na}}^{(\text{Na}_{0.32}\text{K}_{0.68})}$ is the thermodynamic activity of sodium in the $\text{Na}_{0.32}\text{K}_{0.68}$ alloy.

Table 3. Approximate threshold oxygen concentration of the formation of ternary oxides in Na and $\text{Na}_{0.32}\text{K}_{0.68}$, calculated by equation $x_{\text{O, tr}}$ (mole fraction) = $\exp(A + B/T)$

Ternary oxide	Na				$\text{Na}_{0.32}\text{K}_{0.68}$ alloy			
	-A	B, K	500K	1000K	-A	B, K	500K	1000K
Na_4FeO_3	1.82	-3807	Es	$3.59 \cdot 10^{-3}$	4.978	-552	$2.29 \cdot 10^{-3}$	$3.97 \cdot 10^{-3}$
NaCrO_2	5.34	-5502	$7.98 \cdot 10^{-8}$	$1.96 \cdot 10^{-5}$	9.593	-1006	$9.13 \cdot 10^{-6}$	$2.49 \cdot 10^{-5}$
Na_4MoO_5	5.56	-807	Es	$1.72 \cdot 10^{-3}$	9.355	2560	Es	$1.12 \cdot 10^{-3}$
NaMnO_2	6.05	-1882	Es	$3.59 \cdot 10^{-4}$	10.203	1548	$8.19 \cdot 10^{-4}$	$1.74 \cdot 10^{-4}$
NaVO_2	4.59	-4671	$8.9 \cdot 10^{-7}$	$9.51 \cdot 10^{-5}$	8.743	-1240	$1.33 \cdot 10^{-5}$	$4.62 \cdot 10^{-5}$
Saturation solubility of oxygen	-2.59	-6470	$3.19 \cdot 10^{-5}$	0.021	-0.69	-3266	$2.9 \cdot 10^{-3}$	0.076
Es - Exceeds saturation solubility of oxygen in sodium								

Using the values of standard Gibbs energy of formation of ternary oxides [10] approximate threshold concentrations for formation of these compounds in the liquid sodium and $\text{Na}_{0.32}\text{K}_{0.68}$ were calculated (Table 3).

Unfortunately, it cannot be asserted that the threshold oxygen levels are determined in present study so precisely that it is possible to make a reliable comparison between sodium and $\text{Na}_{0.32}\text{K}_{0.68}$ in this parameter.

Taking into account everything that was said about the sources of computational errors, final conclusion has to be given to the following:

the compounds NaCrO_2 and NaVO_2 can be formed on the surface solid metal at very low levels of oxygen in both coolants.

for the existence of the ternary oxides of iron, manganese and molybdenum in the temperature range 573-1073 K, it is necessary that oxygen content in each of these two coolants is at least 0.1 of the saturation concentration.

5. Concluding remarks

Due to the near-complete lack of reliable data on the solubility of metals in NaK melt application of thermodynamic models for the determination of metal solubility allows one to improve one's understanding of the corrosion problems encountered in use of this coolant.

The use of the equations of the pseudo-regular solution model makes it possible to carry out a preliminary assessment of the solubility levels of transition metals in $\text{Na}_{0.32}\text{K}_{0.68}$.

Theoretical predictions by using the pair interaction parameters to estimate the effect of oxygen impurity on the solubility of metals have proved effective in explaining the results of mass transfer in systems where conditions exist for selective dissolution of the components of the structural material.

It has been shown that a reliable determination of the threshold oxygen levels in $\text{Na}_{0.32}\text{K}_{0.68}$ that is required for the formation of ternary oxides of transition metals is impossible due to the scatter and discrepancy of the data on oxygen solubility in NaK coolant.

For practical application of $\text{Na}_{0.32}\text{K}_{0.68}$ as heat transfer media, further studies of various aspects of corrosion phenomena are necessary. It is especially important to propose an approach that would not contain contradictions between the conventional mass transfer theory and the recommended solubility values of metals and nonmetallic impurities in the NaK coolant.

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