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Thermodynamic and experimental study of corrosion behavior of vanadium-based alloy in liquid sodium-potassium coolant

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HIGHLIGHTS

- The mass transfer of vanadium was interpreted in terms of theoretical approach based on oxygen effect.
- –The oxygen effect can be considered as the result of short-range ordering in liquid metal solution.
- Ternary oxide $NaVO_2$ should be formed at higher oxygen concentration in $Na_{0.32}K_{0.68}$ coolant.

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ABSTRACT

A preliminary assessment of oxygen effect on vanadium solubility in Na–K melt eutectic composition has been carried out using mathematical framework of the subregular solution model and equations of coordination-cluster model. The effect of oxygen on the solubility of vanadium in the Na–K alloy can be considered as the result of short-range ordering in liquid metal solution. The negative deviations from the ideality for dilute oxygen solutions in Na–K solvent is one reason that explains the quantitative differences between Na and Na–K coolants, when we need to estimate the threshold oxygen concentration for the formation of ternary oxide $NaVO_2$ on the surface of the solid vanadium in liquid sodium and in Na–K alloy. Isothermal capsule experiments qualitatively confirmed the results of calculations of vanadium solubility in $Na_{0.32}K_{0.68}$ alloy.

1. Introduction

It is known that vanadium-based alloys are highly compatible with high purity liquid metal coolants (Li, Na, K). However, pure vanadium in sodium and in Na–K alloy does not have sufficient corrosion resistance without providing high degree of purity of liquid metal. The results of the various corrosion studies on vanadium alloys show that compatibility is strongly dependent on the oxygen concentration in the sodium and in sodium-potassium eutectic alloy. It is generally found that increasing the oxygen concentration of alkali metal leads to change in the chemical composition of the surface layers of a structural material, and rapid penetration of interstitial impurity into the material by reaction-controlled diffusion [1].

Vanadium-based alloys, in particular, the well-known V–4Ti–4Cr alloy, are attractive for use in space nuclear power systems because of their considerable high -temperature strength, a low induced radioactivity (a high resistance to activation), a fairly low specific density, and a potentially high corrosion resistance in liquid metal coolants (if requirements to purity of the coolant are fulfilled).

As it was mentioned in Ref. [2], in contrast to the sodium coolant a systematic analysis of the effect of oxygen on the corrosion processes in molten Na–K eutectic has not been carried out. The reliability of this assessment is confirmed by the significant scatter of oxygen solubility data for Na–K alloy, which have been reported by various authors.

The corrosion studies of V–4 Ti–4 Cr alloy in thermal convection loop of eutectic Na–K alloy have been described in detail previously [3]. The early work on the corrosion behavior of materials in the same coolant demonstrated that V – 4 Ti – 4 Cr alloy has a high corrosion resistance in Na – K alloy in the static isothermal conditions [4]. It is known that the main effect of corrosion was to

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produce a hardened surface zone of high interstitial concentration at the surface of vanadium-based alloy [3,5]. The V–Ti–Cr alloys, not very different in composition, were examined after corrosion tests in liquid sodium [5] and in Na–K alloy [3]. Despite the similarity of conditions of corrosion tests (coolant temperature, and duration of exposure) a hardened surface zones of high oxygen concentration vary significantly with depth in both coolants. In particular, after exposure to sodium it has been found that hardened surface layer depth exceeds 200 μm for the alloy containing 5% titanium and more than 500 μm for alloys with low titanium content [5]. It should be noted that corrosion study of vanadium-based alloy with 4% titanium in Na–K coolant showed that the depth of internal oxidation layer does not exceed 120 μm [3].

Since the thermodynamic parameters of the oxygen in the Na–O and Na–K–O systems differ, this fact should influence the characteristics of corrosion processes in the two coolants. The purpose of this paper is to study of the features of corrosion processes in the vanadium-based alloy – $Na_{0.32}K_{0.68}$ system[1] in the concentration range from $1 \cdot 10^{-3}$ to 1.0% of oxygen. In addition, selected aspects of the corrosion behavior of vanadium alloys in liquid metal coolants will be compared for sodium and Na–K environments. This comparison is important for the practice to make use of already acquired knowledge of liquid metal corrosion of vanadium alloys in sodium coolant, which is more studied, as compared with Na–K coolant. Corrosion effects associated with the formation of a hardened surface zone of high interstitial concentration are discussed in detail in Ref. [3]. The studies of the surface layer of V–4 Ti–4 Cr alloy samples showed that the oxygen concentration gradients were of the same form as the microhardness gradients. The X-ray diffraction phase analysis of the surfaces of the specimens has shown that vanadium oxides VO and V_2O_3 are present on these surfaces [3]. Therefore, the present study focuses on the influence of thermodynamic parameters of liquid Na – K alloy to other aspects of the corrosion behavior of vanadium alloy that are not related to the formation of hardened surface layers.

2. Thermodynamic properties of oxygen in dilute liquid solutions of Na–K–O system

The thermodynamic driving force for liquid metal corrosion is the chemical potential equalization for components present in the liquid metal coolant and on all surfaces in contact with it. When vanadium or vanadium alloy is exposed to sodium-potassium alloy, the kinetics and the thermodynamics of the corrosion processes essentially depend on thermodynamic parameters of Na–K–V–O system. Among these characteristics, the coefficient of thermodynamic activity of oxygen in liquid phase is decisive.

Knowledge of activity coefficients of oxygen in ternary Na–K–O system is useful for predicting the corrosion behavior of vanadium-based alloys, even if we don't have the thermodynamic data for quaternary Na–K–V–O system. Based on analysis conducted by Zhang [2] and Krishnamurthy [6], we assumed that only one oxide Na_2O, exists in Na–K–O system at the equilibrium. Among all the oxides, Na_2O has the lowest Gibbs free energy for the formation and is the most stable. Then, the activity coefficient is determined based on the oxygen solubility data using the following expression

$$\ln \gamma_{O(Na-K)} = \Delta G_f^\circ (Na_2O)/RT - \ln x_{O,\ sat}, \qquad (1)$$

where $\gamma_{O(Na)}$ is the activity coefficient of oxygen in ternary Na–K–O system; $x_{O,sat}$ is the saturation solubility of oxygen in Na–K alloy (all concentrations are in mole fractions); $\Delta G_f^\circ (Na_2O)$ is the free energy of formation of Na_2O.

Krishnamurthy et al. [6] determined the solubility of oxygen in liquid sodium-potassium alloy as a function of temperature and alloy composition. Also, based on the equations of coordination-cluster model (CCM) [7], the authors of [6] calculated thermodynamic activity coefficient of oxygen over full composition range at 473 K. As shown in Fig. 1 the use of only one adjustable parameter, allows one to achieve a satisfactory agreement between calculated and experimental data. If we consider the concentration range $0 < x_K < 0.9$, then the oxygen activity coefficient takes on values lower than those obtained for oxygen in pure sodium solvent (x_K is concentration of potassium). As will be shown this aspect of oxygen behavior is important for the understanding of the mechanisms of corrosion processes in of Na–K alloy.

It should be noted that if the graph of $\gamma_{O(Na\text{-}K)}$ as a function of potassium content can be approximated by a straight line connecting the two end points, and then it would mean closeness of oxygen solutions of Na–K–O system to ideality. In fact, the negative deviations from ideal solution (Fig. 1) indicate the existence of a stronger metal – oxygen bond in the ternary Na–K–O system, as compared with the one which exists in binary Na–O and K–O systems.

Such behavior of oxygen in the system substantially determines features of corrosion processes in the Na–K alloy in comparison with similar processes in sodium coolant. For the system of Na–K–V–O, these differences can be seen in the process of formation of the ternary vanadium oxide on surface of vanadium-based alloy exposed to Na–K alloy. This is reflected in the difference between the threshold concentrations for the formation of $NaVO_2$ on the surface of solid vanadium in two coolants: liquid sodium and Na–K. In addition, the negative deviations from the ideality for Na–K–O system is one reason that explains the

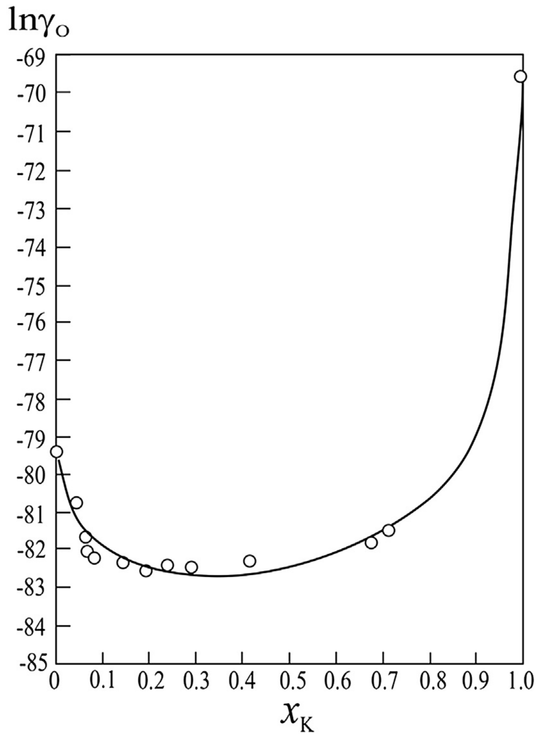

Fig. 1. The activity coefficient of oxygen at high dilution in liquid Na–K alloys at 473 K (x_K – potassium concentration, in mole fractions): ○ – experiment [6]; solid line – curve is calculated according to the CCM equation.

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[1] is the *designation* for the Na–K alloy eutectic composition (32 mol.% Na and 68 mol.% K).