

A conception of formation and operation of CaO coating in regime of self-healing

O.I. Yeliseyeva ^{a,*}, V.M. Chernov ^b, M.M. Potapenko ^b, T.V. Tsaran ^a

^a G.V. Karpenko Physico-Mechanical Institute National Academy Sciences of Ukraine, 5, Naukova Street, L'viv 79601, Ukraine

^b A.A. Bochvar Institute of Inorganic Materials, 123060, P.O. Box 369, Moscow, Russia

Abstract

Based on analysis of test results and literature data, a phenomenological model of components interaction in Li[Ca]–V[O] system is proposed. The model demonstrates a cyclic process. Each cycle consists of: I – oxygen transfer from vanadium into lithium; II – CaO layer grows and simultaneously titanium oxides dissolve and oxygen and titanium spreading into solid solution; III – liquid metal penetration into solid metal according to the mechanism of reactionary diffusion accompanied by triple oxide formation; IV – decay of a meta-stable triple oxide and recovering of CaO layer. Within the framework of the proposed model the possible behavior of a CaO coating under isothermal condition is considered.

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1. Introduction

Creation of a protective insulating coating on the structural material – heat transfer interface currently is a critical issue in the development of a liquid metal cooled system. Despite intensive development in this area, in particular, the techniques of continuous control of impurity activity in the melt, the mechanism of components interaction on the interface in the solid metal – impurity – liquid metal system is still unclear. This, in turn, does not allow a generalized model of protective layer operation, and, thus, to predict the system's behavior during operation. Earlier, by means of Auger-spectroscopy, an interaction between calcium-containing lithium and vanadium–titanium alloys was examined [1]. The kinetics of liquid metal penetration into the substrate was determined and a structural irregularity in the advancement of the corrosion front was revealed. There is a latency period, during which the lithium does not penetrate into V–20Ti alloy. During this period a thin CaO layer appeared on the solid metal, and Ti_xO_y

particles dissolved in the adjacent substrate. After the latency period, the lithium penetrates into the alloy and the protective layer decays possibly of calcium depletion in the melt.

2. Main aspects of the physical and chemical processes in V[Ti]–O–Li[Ca] system

Observations on the Me[O]–Li[Ca] system allow us to suggest a concept of CaO formation and operation in a self-healing mode (Fig. 1) based on the following physical–chemical qualities of this system:

- Li and Ca are not solved in and make no compounds with pure V [2];
- V does not dissolve in Li [3];
- O dissolves in V and makes various oxide phases with it including α' -phase (the lowest oxide or ordered solid solution in V) [4];
- O migrates from V into Li when vanadium is in contact with lithium [5];
- If an α' -phase is formed in a solid metal Me (V, Nb, Ta), a liquid metal L (Li or Ca) can penetrate into the Me under the mechanism of reactionary diffusion forming a complex oxide $L_xMe_yO_z$ [6];

* Corresponding author. Tel.: +380-65 4343; fax: +380-322 6494-27.

E-mail address: olgayeliseyeva@ipm.lviv.ua (O.I. Yeliseyeva).

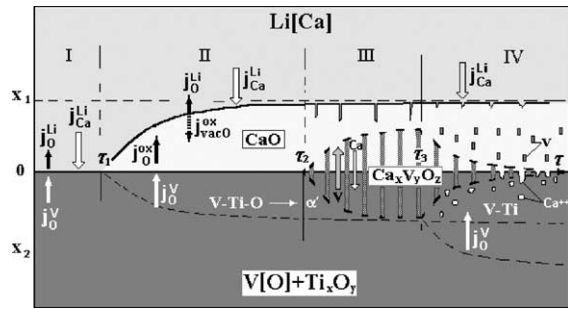


Fig. 1. The model of CaO oxide development on the surface of the oxygen containing vanadium alloy ($V[O] + Ti_xO_y$) exposed to the calcium containing lithium ($Li[Ca]$): I – oxygen migration from vanadium into lithium and calcium deposition (J_O^V , and J_O^{Li} – oxygen flows in the solid and liquid phases; J_{Ca}^{Li} – calcium flow in the liquid phase); II – growth of oxide layer (J_{vacO}^{ox} – flow of anion vacancies in oxide), formation of V–Ti–O solid solution zone and α' -phase appearing; III – solid phase reaction $Ca^{++} + \alpha' \rightarrow Ca_xV_yO_z$; IV – change of $Ca_xV_yO_z$ triple oxide and restore of CaO layer.

- Alloying of Me with Ti stabilizes the α' -phase [7];
- O dissolves in Li (up to 0.8–1.0%) [3]; Ca-additions to liquid Li reduce oxygen solubility in Li and helps to form CaO (since Ca has higher affinity with O) [3,8–10];
- Oxygen equilibrium concentration, at which CaO oxide is stable in liquid Li, is 0.029% and 0.23% at 400° and 700°, respectively; thus, in higher Li purity, CaO is unstable [3].

3. Kinetic model of CaO in situ formation

In the solid metal/liquid metal system, where $V[O] + Ti_xO_y$ is vanadium containing oxygen in the solid solution $V[O]$ and in Ti_xO_y -particles; ($Li[Ca]$) is lithium melt containing calcium (Fig. 1). It is possible to note stages of interaction of the components in this system (Fig. 1) [11].

3.1. Stage I ($0 \div \tau_1$)

Oxygen migrates from V into Li (J_O^{Me} is the flux in the solid phase and J_O^{Li} in the liquid). Calcium comes from the liquid phase (J_{Ca}^{Li}) and deposits on the surface ($x = 0$). If the oxygen concentration on the interface diminishes faster than calcium accumulates, then, in spite of favorable thermodynamic conditions, the CaO will not form at the interface.

3.2. Stage II ($\tau_1 \div \tau_2$)

When both calcium and oxygen reach the concentration required for CaO formation, the oxide appears at

the interface. The oxide growth is of particular interest. First of all, the typical mechanism of calcium oxidation (via prevalent cation diffusion through the CaO) is impracticable here, because the solid metal hampers the oxide growth. Oxygen delivery is limited by diffusion in the solid phases (J_O^V and J_O^{ox}), while calcium is supplied from the liquid phase (J_{Ca}^{Li}), and most likely, therefore, the oxidation proceeds at an oxygen deficit. The anion vacancies' appearing at the 'oxide–melt' interface (J_{vacO}^{ox}) stipulates oxygen diffusion through the CaO and the growth of the CaO towards the liquid phase.

While the oxide layer grows, certain structural changes occur in the substrate. Oxygen outflow causes an imbalance between Ti_xO_y and solid solution $V[O]$. It is likely that Ti_xO_y particles will lose their oxygen and either turn into sub-oxides or completely dissolve. O goes to the interface and Ti, because of its low diffusion mobility, segregates in the V matrix.

As the CaO coating becomes thicker, the diffusion of vacancies to the interface slows and the oxygen flux decreases. Therefore, α' -phase may appear in the substrate. Titanium also contributes to this modification as it stabilizes the α' -phase in vanadium [7]. As a result, in turn, the oxygen concentration diminishes at the $x = 0$ interface and CaO-layer donates more oxygen to the melt then it receives from the matrix, anion defects increase, and CaO becomes unstable.

3.3. Stage III ($\tau_2 \div \tau_3$)

A solid-state reaction takes place at the $x = 0$ interface and complex oxide is produced: $Ca^{++} + \alpha' = Ca_xMe_yO_z$ [11]. Due to this reaction, calcium appears in the matrix and vanadium in the oxide.

3.4. Stage IV ($\tau > \tau_3$)

Because of $Ca_xV_yO_z$ formation the concentrations of the elements at the interface change as do their fluxes. Consequently, the oxide composition, structure, and morphology change. An important factor here is the greater volume of the triple oxide compared to that of the vanadium matrix [3,6]. Thus, the new phase provokes significant tensile stresses. In the oxide layer, such stresses can cause cracks; in the metal they may induce clusters of dislocations that facilitate oxygen diffusion. In any case, the inflows of both diffusion components (oxygen from the matrix and calcium from the melt) may increase which could be beneficial to the external oxide layer. $Ca_xMe_yO_z$ formed in previous stage changes its composition.

In general, the physical and chemical processes at the fourth stage are similar to those at the second stage. However, both the oxide and the structural material degrade with time. Calcium penetrates in the vanadium,

and vanadium enriches the CaO layer. The lengths of each stage is determined by the contact conditions between liquid and solid metals (temperature; calcium concentration in the melt; oxygen storage in the solid metal, etc.).

This model adequately reflects the physical–chemical effects within the metal, and oxide their interface. The model includes all known interaction mechanisms in V[O]–Li[Ca] system and explains their alternation. However, in situ creation of good protective oxide coating seems to be impracticable. First of all, it is difficult to establish required concentrations of the components at the $x = 0$ interface (Stage I). Then, CaO constantly loses oxygen and, thus, cannot quickly gain a protective thickness (Stage II, the beginning). Finally, the limited supply of oxygen is largely consumed during oxide creation. And so, it is technically easier to create the CaO coating a priori using different methods and more favorable conditions, and then to maintain its integrity in situ [8–10]. One method is to cover the vanadium surface with pure calcium, and later oxidize it in an O-containing atmosphere. During such a procedure, the oxide layer grows in accordance with the typical cation-vacancy mechanism, i.e., due to the prevalent Ca-diffusion towards gas–oxide interface. As a result, Ca_{1-n}O layer appears with a concentration gradient along the cross-section.

4. Physical and chemical processes in Me[O]–CaO–Li[Ca] system

For the interaction between Li[Ca] and vanadium alloy, with a CaO non-stoichiometric layer (X_1 in thickness), it was assumed that two phases ($[\text{Me}-\text{O}] + \text{Ti}_x\text{O}_y$) were present in the vanadium. At $\tau = 0$ CaO comes into contact with Li[Ca] under isothermal conditions (Fig. 2).

In the first stage, the coating reacts to Li[Ca]. Oxygen from the coating migrates to the liquid phase (J_{O}^{Li}), its concentration in the oxide (C_{O}^{ox}) decreases relative to that of calcium ($C_{\text{Ca}}^{\text{ox}}$). The anion vacancies ($J_{\text{vacO}}^{\text{ox}}$) generated on the $x = X_1$ level annihilate at the $x = 0$ interface because of the flux of oxygen coming from the matrix (J_{O}^{V}).

In the second stage, the oxide's composition becomes quasi-stoichiometric ($C_{\text{O}} \approx C_{\text{Ca}}$) and the coating becomes protective. Its inner diffusion slows down; oxygen outflow from the matrix decreases and the conditions for the appearance of α' -phase in matrix are created.

In the third stage, the α' -phase forms. As a result, the oxygen concentration at the $x = 0$ interface decreases, and oxygen vacancies increase in the CaO coating. The CaO composition becomes more non-stoichiometric, and at some critical oxygen concentration ($C = C_{\text{Ocr}}$) the oxide becomes unstable.

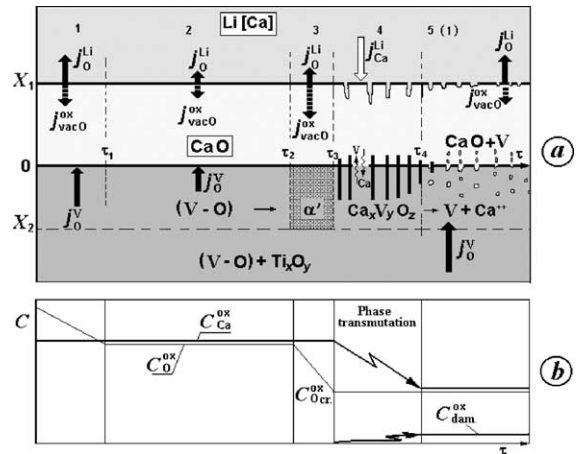


Fig. 2. Kinetic scheme of the CaO-coating operation in a self-healing mode (a) and change of the oxygen (C_{O}^{ox}), calcium ($C_{\text{Ca}}^{\text{ox}}$) and defects ($C_{\text{dam}}^{\text{ox}}$) concentrations in it (b): J_{O}^{V} and J_{O}^{Li} – oxygen flows in vanadium and lithium, respectively; $J_{\text{vacO}}^{\text{ox}}$ – flow of anion vacancies in the oxide; $J_{\text{Ca}}^{\text{Li}}$ – calcium flow in lithium (explanations of Stages 1–5 according to the text).

In the fourth stage, a solid state reaction $\text{Ca}^{++} + \alpha' \rightarrow \text{Ca}_x\text{Me}_y\text{O}_z$ begins at the $x = 0$ interface. Calcium migrates from the oxide to the matrix and the structure and composition of the oxide coating are changed (cracks, porous, V inclusions and other damages are present). Thus, damage ($C_{\text{dam}}^{\text{ox}}$) accumulates in the coating. Because of this damage, the Ca- and O- fluxes increase.

As in previous concept (Fig. 1), when the triple oxide forms calcium penetrates into the matrix and vanadium into the coating. The adhesion between the artificially created coating and the matrix improves. Insulating properties of the coating also improve. When the coated samples are exposed to Li–Ca melts (at 500 °C, up to 100 h) their electrical resistance improves. In addition, CaV_2O_5 [12], CaVO_3 , and $\text{Ca}_5\text{V}_2\text{O}_{10}$ [10] were detected in the oxide coating. Measurement of elements near the interface reveals interpenetration. Thus, after exposure of a CaO-coated vanadium alloy to Li–0.5%Ca (at 400 °C for 120 h) calcium was found (1–2%) in the matrix to a depth of 2 μm [8]. Vanadium was found (up to 10%) in the oxide coating after exposure at 700 °C [13]. With time, the processes of interaction described above lead to inevitable deterioration of properties of both the coating and structural material because of accumulation of vanadium in the coating and calcium penetration into vanadium.

According to the proposed concept the behavior of the coating can be assessed when the Ca- and O-concentrations are varied in the melt and metal.

Anion vacancies appear in the coating (Stages I–III at Fig. 2) when oxygen migrates to the lithium. If the O flux from the V-matrix (J_{O}^{V}) does not provide annihila-

tion of the vacancies at the interface $x = 0$, the oxide will decay at a critical vacancy concentration from CaO_{1-n} to $\text{CaO} + \text{Ca}$. As a result of this reaction, liquid calcium segregates to the structural defects of the coating and the coating loses its insulating properties and dissolves in the melt.

Experimental data confirms the impracticability of the oxide coating without oxygen supply from the matrix [8]. So, a very thin and damaged CaO layer was tracked on the surface of V–4Cr–4Ti sample with low oxygen content (250 wt ppm) after its exposure to Li–23 wt%Ca for 150 h at 700 °C. The same effect occurred to a sample with a high oxygen content though tested at low temperature, which does not provide a sufficient flux of oxygen from the matrix. For example, the initial high resistance ($10^9 \Omega \text{cm}^2$) of the CaO coated sample decreased ($10^1 \Omega \text{m}^2$) after exposure to the Li–Ca melt at 250 °C [10].

According to model, cracks appear in the external oxide layer because of triple oxide formation (Fig. 2, stage 4). If calcium content in the lithium is not high enough, the cracks will not heal. With a lack of calcium, the CaO binary oxide may react with lithium and produce $\text{Ca}_x\text{Li}_y\text{O}_z$. Such a mechanism takes place during high-temperature contact between Li and Y_2O_3 coating, where a LiYO_2 phase forms [14].

CaO coating exposed to Li–10 at.%Ca (600 °C, 100 h) had a satisfactory adhesion and thickness (13–20 μm). X-ray analyses detected CaO and CaV_2O_5 oxides on the surface. Calcium content in the oxide layer was 40–45%. After the exposure (700 °C, 106 h) in lithium, the thickness of the coating did not exceed 2–5 μm . Peaks from the vanadium matrix appeared in the X-ray spectra. Calcium concentration in the near-surface oxide layer decreased to 1–5% [12].

Thus, when calcium migrates from the oxide into the matrix and there is no appropriate maintenance of its concentration on the $x = X_1$ level, total degradation of the coating and Li penetration into the matrix become inevitable. This will give rise to a zone with calcium oxides in the matrix (directly under $x = 0$ interface), and the lithium will appear in deeper layers [1].

5. Conclusions

1. A phenomenological model of interaction between the components in $\text{Li}[\text{Ca}]\text{–V}[\text{O}]$ system is proposed. The basic idea of the model is the alternation of the interaction mechanisms and the recurrence of the whole process: (I) oxygen migration from V into Li; (II) the external CaO growth while the dispersed titanium oxides dissolve in the vanadium matrix; (III) liquid metal penetration into the solid metal forming a meta-stable triple oxide $\text{Ca}_x\text{V}_y\text{O}_z$; (IV) irregular oxy-

gen and calcium fluxes and the external oxide layer recovers.

2. Within the framework of the proposed model, a concept of CaO coating operation is considered:
- Under an isothermal regime at continuous inexhaustible supply of oxygen and calcium in vanadium and lithium, respectively, different defects develop in turn on the opposite boundaries of the coating. At the ‘oxide–melt’ interface, anion vacancies are generated. Accumulation of these vacancies up to a certain limit causes the development of a new phase $\text{Ca}_x\text{V}_y\text{O}_z$ on the ‘oxide–metal’ boundary. As a result, micro defects develop and the mechanism of coating re-healing changes. Annihilation of anion defects on the ‘oxide–metal’ interface at the expense of matrix oxygen is changed now by re-healing recovery of micro defects on ‘oxide–melt’ interface with calcium.
 - Under non-stationary conditions due to a decrease of component concentration at the interface, two types of CaO coating degradation take place. The decrease of oxygen concentration causes the calcium segregates in the coating. The decrease of calcium concentration reduces the effective section of the coating.

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