



## Conception of operation of in situ oxide coating as applied to V/Li blanket

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### A B S T R A C T

Development of in situ insulating coating onto inner wall of ducts is a promising way to mitigate the MHD pressure drop concerning V/Li blanket. The interdependence between structure of oxygen-containing V–4Ti–4Cr alloy and durability of Er<sub>2</sub>O<sub>3</sub> insulator coating during contact with Li[Er] melt were studied and summarized. It was revealed that the inner oxidizing zone containing TiO<sub>2</sub> precipitations and non-equilibrium defects formed in the V–4Ti–4Cr during pre-charging procedure provided the most efficient oxygen consumption for Er<sub>2</sub>O<sub>3</sub> formation during contact of V-alloy with Li[Er]. The kinetic model of interaction of components in the V, Ti[O]–Li[Er] system is proposed.

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### 1. Introduction

Development of effective and reliable insulating coating to mitigate the MHD pressure drop is a key to the viability of V/Li blanket concept [1]. The permanent operation of oxide layer at the interface should be sustained by diffusion of oxygen from the vanadium alloy and soluble admixture (Er, Ca or Y) from liquid lithium. Regardless of the fact that feasibility of erbium oxide coating was verified previously [2–6] the mechanism of oxide layer growth has not been elucidated yet.

In previous paper [7] much attention was paid to the phenomenon of inner oxidation of V–4Cr–4Ti in the restricted temperature range 650–750 °C where specific TiO<sub>2</sub> net-structure was formed. The aim of present work is to establish the relationship between structure of pre-oxidized V-alloy and durability of Er<sub>2</sub>O<sub>3</sub> coating during contact with Li[Er].

### 2. Experimental

The samples (7 × 7 × 0.5 mm) of V–4Ti–4Cr (NIFS-HEAT-2, Ti – 3.98, Cr – 4.02 wt.%, O – 148, N – 122, C – 69 wppm, grain size 20 μm) were pre-charged by oxygen using two-stage procedure [2]. After oxidizing in Ar–O<sub>2</sub> mixture (700 °C, 1 h) the vanadium oxide layer was formed on the surface of alloy. After vacuum annealing (700 °C, 16 h) the stored oxygen (8000 wppm) was homogeneously diffused into depth of 150 μm and specific ordered TiO<sub>2</sub> net-structure with high hardness (HV = 800) was formed in the inner oxidation zone. Then samples were exposed to static Li doped with Er at 500, 550, 600, 650 and 700 °C for 20, 100, 300 and 750 h. After

exposures the microstructure of V-alloy was investigated by scanning electron microscopy (SEM). Vickers hardness (HV) was measured under 10 gf load.

### 3. Results

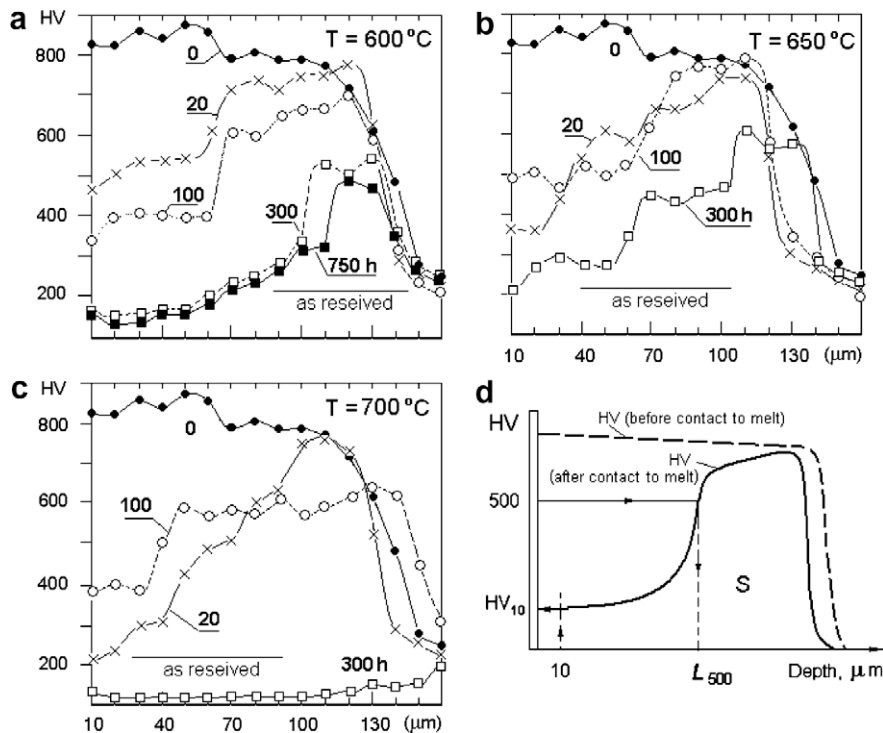
The micro hardness profiles were used to estimate deoxidizing of V-alloy after long-term contact with Li[Er] (Fig. 1(a)–(c)). In order to evaluate the kinetics of deoxidation the following values were determined from the HV profiles (Fig. 1(d)): S – square under HV-curves reflects oxygen storage in the alloy; HV<sub>10</sub> – hardness of matrix on the depth 10 μm reflects oxygen concentration near the interface; L<sub>500</sub> – zone with HV < 500 characterizes the depth of disintegration of TiO<sub>2</sub> net-structure.

Fig. 2 shows the determined values (HV<sub>10</sub>, S, L<sub>500</sub>) together with coating thickness versus time at 600, 650 and 700 °C. With respect to lower temperatures, it should be noted that Er<sub>2</sub>O<sub>3</sub> coating was not detected after exposure at 500 °C. The thin oxide layer (~0.1 μm) appeared after 100 h exposure at 550 °C, while the V-matrix lost nearly half of oxygen content stored during pre-charging procedure.

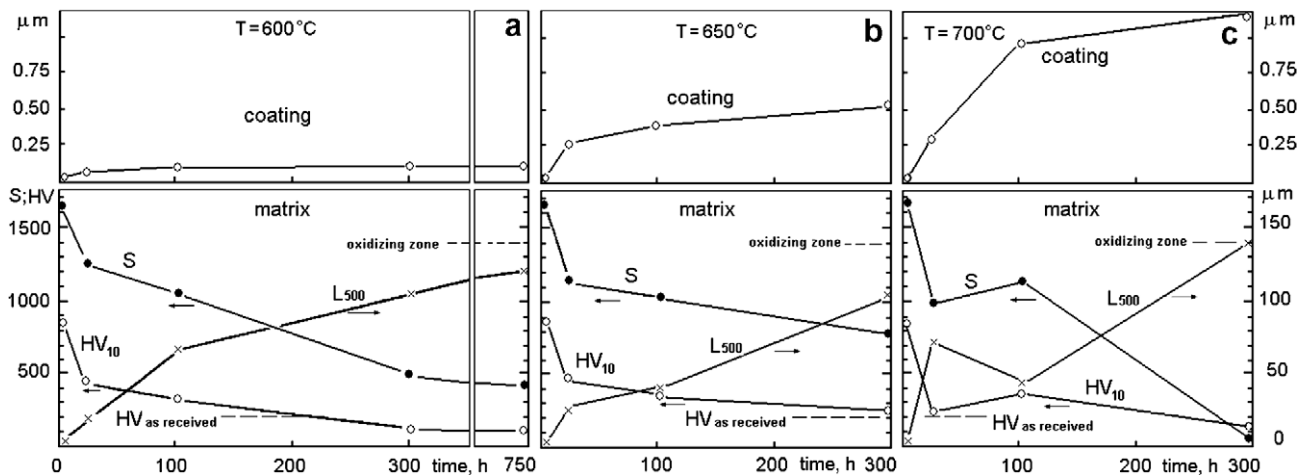
Judging from the H<sub>10</sub> and S curves (Fig. 2(a)) only a limited amount of oxygen was used after 20 h exposure in order to form the thin coating at 600 °C. With time, the deoxidizing rate of alloy diminishes. After 750 h exposure, the oxygen storage (S) and TiO<sub>2</sub> net-structure (L<sub>500</sub>) remain closely to that after 300 h exposure (Fig. 2(a)).

At 650 °C the coating becomes thicker (0.5 μm) and the values (H<sub>10</sub>, S and L<sub>500</sub>) defined at 300 h testify about large oxygen storage in the vanadium matrix (Fig. 2(b)). It means more effective oxygen consumption and implies better durability of Er<sub>2</sub>O<sub>3</sub> coating at 650 in comparison with 600 °C.

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**Fig. 1.** Vickers hardness depth profiles in V-4Cr-4Ti[O] alloy after exposure to Li[Er] at (a) 600, (b) 650 and (c) 700 °C for 0, 20, 100, 300 and 750 h (d) method of evaluation of S, HV<sub>10</sub> and L<sub>500</sub> characteristics on the hardness profile.



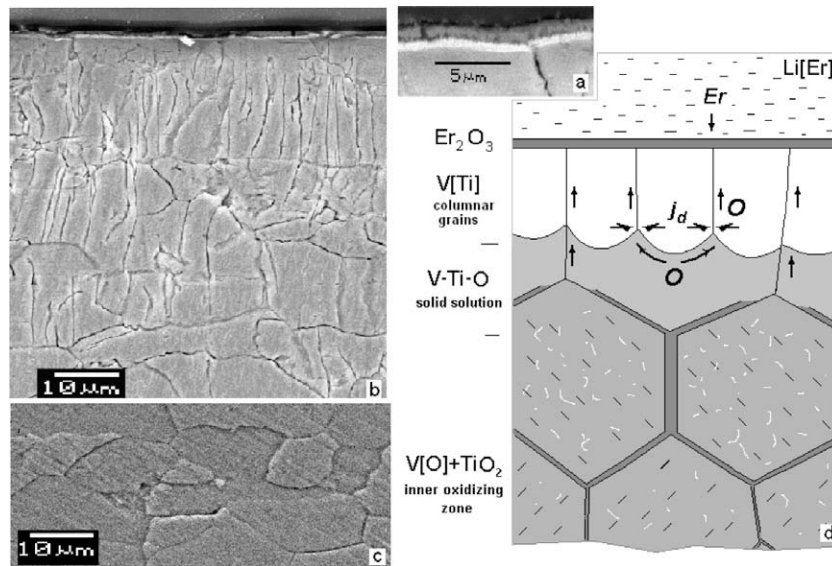
**Fig. 2.** Kinetics of Er<sub>2</sub>O<sub>3</sub> coating growth and deoxidation of V-Cr-Ti[O] during the contact with Li[Er] at (a) 600, (b) 650 and (c) 700 °C according to determined of S, HV<sub>10</sub> and L<sub>500</sub> characteristics.

The temperature 700 °C provides the most intensive growth of Er<sub>2</sub>O<sub>3</sub> at the interface (Fig. 2(c)). This process is accompanied by depletion of matrix by oxygen. In the beginning (0–100 h) the intensity of matrix deoxidizing is comparable to that at lower temperatures (600 and 650 °C). At the same time, a little oxygen diffuses deeper into matrix (see curve 100 h in Fig. 1(c)). With time the growth rate of coating slows down and, vice versa, the deoxidizing of matrix accelerates drastically. The surface oxygen concentration (H<sub>10</sub>) drops to the as-received level. Judging from rising L<sub>500</sub> curve the TiO<sub>2</sub> net-structure has been vanished completely after 300 h exposure (Fig. 2(c)). TEM investigation of undersurface region of alloy confirmed this fact [5].

After exposure to Li[Er] the compact layer (Fig. 3(a)) with a high electrical resistance (10 E13 ohm cm) identified as Er<sub>2</sub>O<sub>3</sub> was

formed on the surface of V-alloy [2]. The undersurface zone (40–50 μm) with columnar grains (Fig. 3(b)) corresponds to the region with reduced hardness (380–400 HV) without TiO<sub>2</sub> net-structure (see curve 100 on Fig. 2(c)). The deeper zone with the equiaxial grains is thought to be a region with the intact net-structure. The hardness of this region is lower than that in the pre-charged samples (600 and 800 HV correspondently). It indicates that density of TiO<sub>2</sub> decreased with time. Thus, after lithium tests the structure of undersurface zone (Fig. 3(b)) differed completely from the inner oxidizing zone of alloy formed after charging procedure (Fig. 3(c)).

Taking into account the obtained results the following mechanism of interaction could be realized during contact of V-4Cr-4Ti[O] with Li[Er] (Fig. 3(d)). V-alloy donates oxygen to lithium. The deoxidizing starts near the ‘solid metal–liquid metal’ interface.



**Fig. 3.** SEM image of (a)  $\text{Er}_2\text{O}_3$  coating, (b) near surface zone after contact with  $\text{Li}[\text{Er}]$  at 973 K for 100 h and (c) structure of alloy charged by oxygen. (d) Mechanism of deoxidation of V-4Ti-4Cr[O] alloy at contact with  $\text{Li}[\text{Er}]$ .

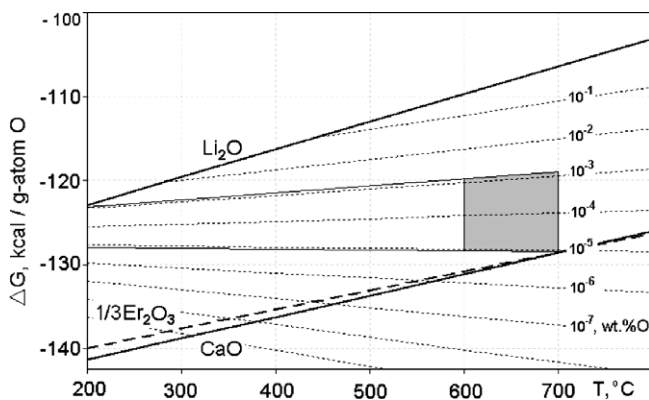
The oxygen drop in solid solution causes the dissipation of ordered  $\text{TiO}_2$  net-structure and appearance of non-equilibrium defects (dislocations, vacancies) in the V-Ti-O solid solution. The released defects (flow  $J_d$ ) produce new diffusion paths for oxygen. New columnar grains, free from oxygen, originate near the interface and grow toward the matrix where the oxygen outflow causes dissipation of  $\text{TiO}_2$  net-structure in the initial grains (Fig. 3(d)). In fact, it is the reverse phase-structure transformation relatively to that during pre-oxidation of alloy explained previously [7].

#### 4. Discussion

Both thermodynamic and kinetic factors of oxide coating formation and deoxidizing of V-alloy oxygen during contact with  $\text{Li}[\text{Er}]$  are considered below.

##### 4.1. Thermodynamic estimation

The possibility of oxides formation at the interface in the temperature range 200–700 °C can be assessed tentatively by means of comparison of Gibbs free energy of oxides ( $\text{Li}_2\text{O}$ ,  $\text{Er}_2\text{O}_3$ ,  $\text{CaO}$ ) with that for oxygen solutions in liquid lithium (Fig. 4).



**Fig. 4.** Gibbs free energy of selected oxides formation and lithium–oxygen solutions. The shaded area corresponds to the temperature–concentration region of erbium oxide coating formation.

If the oxygen content in liquid lithium  $C_{\text{O}[\text{Li}]}$  is near saturation ( $10^{-1}$ – $10^{-3}$  wt.% O) Li would be expected to react with oxygen resulting in formation of surface oxide layer without insulator properties.

$\text{Er}_2\text{O}_3$  and  $\text{CaO}$  are stable at 200–700 °C in the interval  $10^{-5} < C_{\text{O}[\text{Li}]} < 10^{-3}$  (marked by thin solid line in Fig. 4). Taking into account low Er solubility in Li (~0.15 wt.% or 0.006 at.% at 600 °C) the region of  $\text{Er}_2\text{O}_3$  formation should be restricted by isotherm 600 °C. Thus,  $\text{Er}_2\text{O}_3$  coating can be produced within shaded area (Fig. 4).

At low oxygen concentration ( $C_{\text{O}[\text{Li}]} < 10^{-5}$  wt.%) oxides of added metal became unstable, especially in high temperature region. Hence, at this condition the transfer of oxygen from V-alloy to liquid lithium prevails.

The outlined thermodynamic considerations are confirmed by experimental facts. For example, after exposure to  $\text{Li}[\text{Er}]$  at 700 °C the samples of V-alloy with the highest oxygen gradient (pre-oxidized in  $\text{Ar-O}_2$  at 700 °C, 1 h) were covered by lithium oxide. The resistance measuring demonstrated the lack of insulator property of the surface layer. Certainly, such kind of treatment provides  $C_{\text{O}[\text{Li}]} > 10^{-3}$  wt.% near the surface of sample immersed into  $\text{Li}[\text{Er}]$ .

When the surface concentration of oxygen was reduced by vacuum annealing (700 °C, 16 h) the  $\text{Er}_2\text{O}_3$  coating was formed on the surface of oxidized sample [2].

Needless to say, no coating was revealed on the oxygen-free V-alloy. Moreover, pure vanadium pre-oxidized together with V-alloy did not produce the coating, although the content of oxygen in it was even higher than that in V-alloy (10.000 and 8.000 wppm, respectively) [4]. This phenomenon arises due to high solubility of oxygen in pure vanadium resulting in low oxygen gradient after vacuum treatment. Obviously, this treatment of pure vanadium provides  $C_{\text{O}[\text{Li}]} < 10^{-5}$  wt.% during contact with  $\text{Li}[\text{Er}]$ .

##### 4.2. Kinetics

The rate of coating growth depends on both O and Er diffusion towards the ‘liquid metal–solid metal’ interface. It is reasonably to suppose that at lower temperature, when Er solubility is low, the growth of oxide layer is mostly controlled by the erbium delivering from the liquid lithium to the interface than by oxygen diffusion

from the V-alloy. Extremely likely, that oxygen diffusion from the solid metal to lithium started during heating, below the temperature of  $\text{Er}_2\text{O}_3$  formation. Lack or very weak formation of erbium oxide at 500–550 °C at the simultaneous oxygen losses argue for this assumption. In general, the coating thickness ( $x$ ) versus time ( $\tau$ ) could be described as

$$x^n = k \cdot \tau \quad (1)$$

here:  $n$  – exponent,  $k$  – const.

Logarithmical representation of relationship (1) showed that at 700 °C it approaches to parabola ( $n \approx 1.7$ ), i.e., to the diffusion control of oxide growth. At 600 and 650 °C the oxidation kinetics obeys logarithmic law ( $n \approx 4$ ) which is typical for thin surface layers, when the process is controlled by the delivering of component (in our case Er) from environment to the surface of solid metal.

The obtained kinetic results demonstrate the intensification of  $2\text{Er} + 3\text{O} \rightarrow \text{Er}_2\text{O}_3$  reaction with temperature from 500 to 700 °C, that could be explained by increase of Er solubility in the melt. However, with temperature the recovery process in solid metal intensifies as well. As a result the destabilization of TiO net-structure dissipates while oxygen diffuses partially into the non-oxidized V-alloy matrix (see Fig. 1(c), curve 100 h). This oxygen leakage may be an addition contribution to the coating failure at long-term lithium tests.

Nevertheless, the formed coating is thought to be stable enough. It can be seen from Fig. 2(c) once formed the coating exists on the surface of alloy after 300 h exposure at 700 °C in spite of total depletion of matrix by oxygen. Moreover, it was shown that the coating previously formed in Li[Er] kept its integrity in pure lithium at 700 °C for 400 h [6]. The addition investigation [6] showed that small cracks in the coating were initiated by cleaning procedure of samples and therefore could be avoided in real cooling system. The cracks were recovered after re-exposure in Li[Er] by a thin layer with high content of erbium and oxygen. This argues for self-healing capability of  $\text{Er}_2\text{O}_3$  coating [6].

As it follows from the deoxidizing mechanism of alloy during contact with Li[Er] (Fig. 3(d)), the non-equilibrium defects (dislocations, vacancies, etc.) accumulated in the oxidized zone during charging procedure play a significant role for  $\text{Er}_2\text{O}_3$  coating viability at the interface. As the grain boundary diffusion of oxygen dominates at 500–700 °C [7] the new diffusion paths supplying the

oxygen from the bulk to the interface are of primary importance for keeping  $\text{Er}_2\text{O}_3$  coating.

It is evident from Fig. 2 that the most intensive consumption of oxygen occurs during first 20 h. In order to short this dangerous stage the pre-formation of  $\text{Er}_2\text{O}_3$  coating (by different methods) on the surface of oxygen containing V-alloy can be recommended; or alternatively an additional doping of melt by element with a larger solubility in lithium (especially Ca). Smith et al. [8] shown that CaO coating was quite viable just at lower temperature range. This simple technique is expected to be useful in order to avoid the waste of oxygen during heating since calcium can react with oxygen at lower temperature.

## 5. Summary

The relation between structure of oxygen containing V–4Ti–4Cr alloy and durability of in situ  $\text{Er}_2\text{O}_3$  coating at the interface during contact with Li[Er] melt has been determined.

During pre-charging procedure of V–4Ti–4Cr alloy by oxygen the inner oxidation zone ( $\sim 150 \mu\text{m}$ ) containing  $\text{TiO}_2$  precipitates and non-equilibrium defects was formed. This structure provides the most efficient oxygen consumption for  $\text{Er}_2\text{O}_3$  formation during contact of V-alloy with Li[Er]. The required oxygen concentration is maintained owing to high density of  $\text{TiO}_2$  precipitates (additional sources of oxygen) and non-equilibrium defects (additional diffusion paths for oxygen). Consequently, as applied for in situ oxide coatings, the essence of the pre-charging of alloy by oxygen should be aimed at the creation of structure contained both oxygen and non-equilibrium defects.

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