

Effect of Lithium Purity on In-Situ Formation of Er_2O_3 Oxide Layer on V-4Ti-4Cr Alloy^{*})

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Effect of Li purity with respect to N on the features of in-situ formation of Er_2O_3 oxide coating on the surface of V-4Ti-4Cr alloy was investigated. Samples of V-4Ti-4Cr alloy (NIFS HEAT 2) were pre-charged by oxygen in Ar-7% O_2 at 700°C. The hardened zone with needle shaped Ti–O net structure was formed in the near-surface layers of V-alloy after oxidation. Oxygen pre-charged samples were exposed to N-containing Li ($C_{\text{N}[\text{Li}]} \leq 0.2$ wt%) at 700°C and Li pre-cleaned by getter (Zr) at 650°C for 100 h. Both melts were doped with active Er impurity. It was shown that *in-situ* formation of Er_2O_3 oxide coating on the surface of V-alloys depends strongly on the purity level of Li with regard to the N. In N-containing Li the coating was not formed on the surface of V-alloy, while whole oxygen pre-stored in V-matrix was dissolved by Li. On the contrary, in Li pre-cleaned with respect to N by Zr getter, the insulating oxide film was formed.

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1. Introduction

For self cooled V/Li blanket concept, with liquid metal circulating in the direction perpendicular to the strong magnetic field, the effect of magnetohydrodynamic pressure drop (MHD effect) can be a potential problem [1]. To mitigate the MHD effect the surface of V-alloy should be electrically separated from the liquid Li by means of insulator coating. Limited number of oxides and nitrides possessed the required insulating properties and thermodynamic stability in the liquid Li at the same time. Er_2O_3 and Y_2O_3 oxides and AlN nitride are considered as main candidates [1]. The *in-situ* formation of Er_2O_3 layer on the surface of V-alloy is a promising technology to form the multi-functional coating (insulator, corrosion and tritium-permeation barrier) on the inner surfaces of channels with complex shape directly in the liquid Li. This technique requires pre-charging of V-alloy with oxygen in gaseous medium before immersion in Li while liquid metal should be doped by active impurity (Er) [1]. Insulator Er_2O_3 coating was successfully formed *in-situ* on the surface of V-4Ti-4Cr alloy (NIFS HEAT 2) and the phenomenological model of oxide layer growth and evolution was developed [2–5]. Most of the works were carried out under the “ideal” conditions when all the ingredients used were of high purity. However in the real system the contamination of the liquid lithium by non-metallic impurities is unavoidable. The effect of the lithium purity with regard to the non-metallic impurities (N, O, C) on the formation and vi-

ability of Er_2O_3 oxide layer, however, has not been elucidated yet in a full measure. Recently, Nagura et al. demonstrated the effect of O concentration in Li on the corrosion of Er_2O_3 ceramic [6]. Nitrogen, is known to be the most influencing admixture which is able to change the mass-transfer in the “liquid Li – solid metal” system [7]. This work, therefore, is aimed to determine the influence of purity of liquid Li with respect to N on the features of *in-situ* formation of Er_2O_3 oxide coating on the surface of V-4Ti-4Cr alloy.

2. Experimental Procedure

Specimens ($15 \times 10 \times 0.5$ mm) of V-4Ti-4Cr alloy (NIFS-HEAT-2) were thermally treated in vacuum (5×10^{-6} Pa) at 1050°C for 1 h after machining. Then samples were oxidized in Ar-7% O_2 gas mixture at 700°C for 3 h followed by the vacuum annealing at 800°C for 34 h. Ar-7% O_2 it was experimentally determined is an optimal mixture to avoid severe oxidation of V-alloy and at the same time to provide formation of Ti–O net structure in the near-surface zone of V-alloy which is optimal for supplying O from the side of the solid metal towards the liquid Li doped with active Er admixture to form Er_2O_3 film at the “solid metal – liquid metal” interface. After pre-charging by O, samples were exposed to N-contaminated liquid Li ($C_{\text{N}[\text{Li}]} \leq 0.2$ wt%) at 700°C and Li pre-cleaned with regard to N by Zr getter at 650°C for 100 h. Both melts were doped with active Er impurity (~ 1.84 wt%) to promote *in-situ* formation of Er_2O_3 oxide coating on the “V[O]-Li[Er]” interface by means of mass exchange be-

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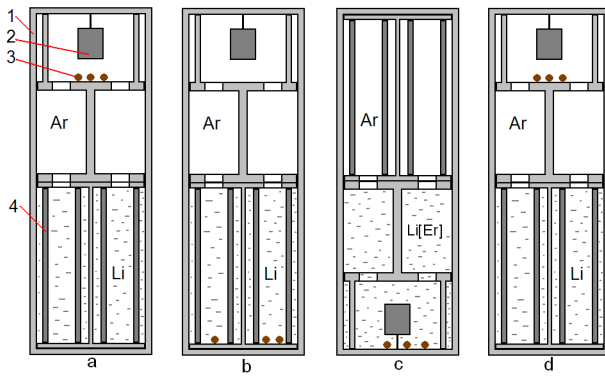


Fig. 1 Schematic representation of test in Li including cleaning procedure. (1) - reaction ampoule (Nb); (2) - V-4Ti-4Cr sample; (3) - Samples of Er; (4) - Zr getter.

tween solid and liquid metals. The details of the both tests are described in detail hereafter.

Test in N-contaminated liquid Li: the reaction ampoule (Nb) filled with Li contaminated with N and doped with Er samples (~ 1.84 wt%) was initially heated to 700°C under the Ar gas atmosphere and exposed for 48 h to dissolve erbium. Er samples (Ø1-2 mm) were mechanically polished before the test to remove natural oxide film, which can suppress mass-exchange. Then oxygen pre-charged V-alloy samples were immersed into Li[Er,N] melt and exposed for 100 h.

Test in Li pre-cleaned with regard to N by Zr getter: Fig. 1 shows the scheme of test including prior cleaning of Li by means of Zr getter. The experimental procedure consists of several steps:

1. Cleaning of Li with respect to N by Zr getter at 700°C for 24 h to (Fig. 1 a);
2. Dissolution of Er in Li at 700°C for 48 h (Fig. 1 b);
3. Turnover (180°) of capsule followed by the reaction of Li[Er] and V-4Ti-4Cr[O] to form Er_2O_3 at 650°C for 100 h (Fig. 1 c);
4. Turnover (180°) of capsule to remove Li from the reaction zone (20 min) followed by the cooling (Fig. 1 d).

After the tests, the samples were cleaned in water to remove adhered Li residuals followed by the cleaning in acetone and ethanol. The scanning (SEM) and transmission (TEM) electron microscopy and X-ray diffraction analysis (XRD, $\text{CuK}\alpha$ radiation, $2\text{-theta} = 0.05^\circ$) were used to determine morphological, compositional and phase-structural changes in the near-surface layers of the samples. The Vickers hardness was measured under the loading of 50 gf for 30 sec.

3. Results and Discussion

3.1 Initial state

Figure 2 shows bright-field (BF) image of the V-4Ti-4Cr alloy microstructure after thermal treatment. The typ-

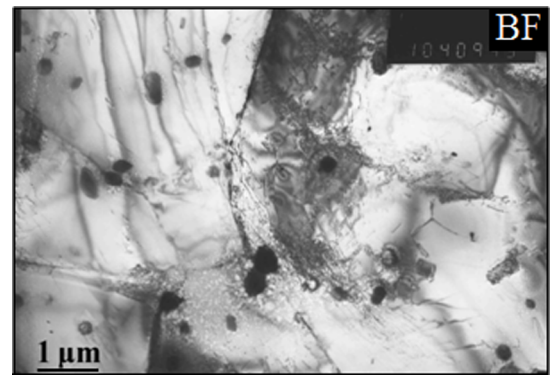


Fig. 2 TEM micrograph of V-4Ti-4Cr alloy after vacuum annealing at 1050°C for 1 h.

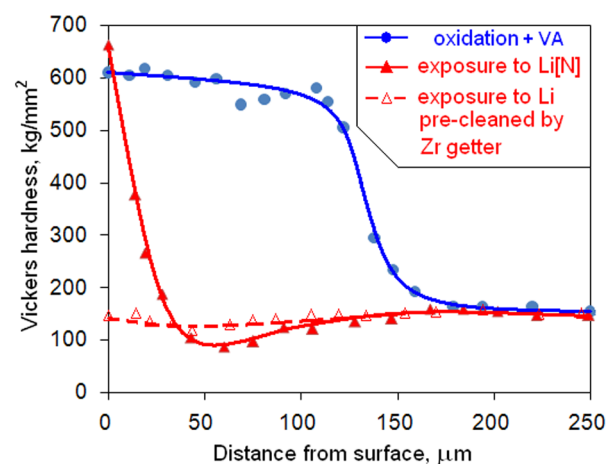


Fig. 3 Hardness profiles of V-4Ti-4Cr alloy samples after: oxidation followed by the vacuum annealing and exposure tests in Li[N] and Li pre-cleaned by Zr getter.

ical rod-shaped Ti-CON precipitates were detected in the grains and along low-angle grain boundaries [8].

3.2 Oxidation

The hardened zone (130 µm) was formed in the near-surface layer of V-alloy after oxidation and subsequent vacuum annealing (Fig. 3). Hardness gradually decreased from 600 kg/mm², starting from the surface, to 500 kg/mm² towards the matrix. At the depth of 125 µm it sharply dropped to 300 kg/mm² and then gradually decreased to the value typical for the initial state.

Samples sowed weight gain averaged 1.0 mg/cm². The calculated concentration of oxygen in the hardened zone reached 4.95 at% while O/Ti ratio is 1.17 which means that quantity of oxygen is not enough to bond all Ti into TiO₂ oxide.

Figure 4 shows the Bright Field (BF) and Dark Field (DF) TEM images obtained from the oxidized (hardened) zone (Fig. 3). The thin plate-like precipitates were detected in this zone. The Selected Area Diffraction pattern (SAD), obtained from the plate-like precipitates, indicates that it

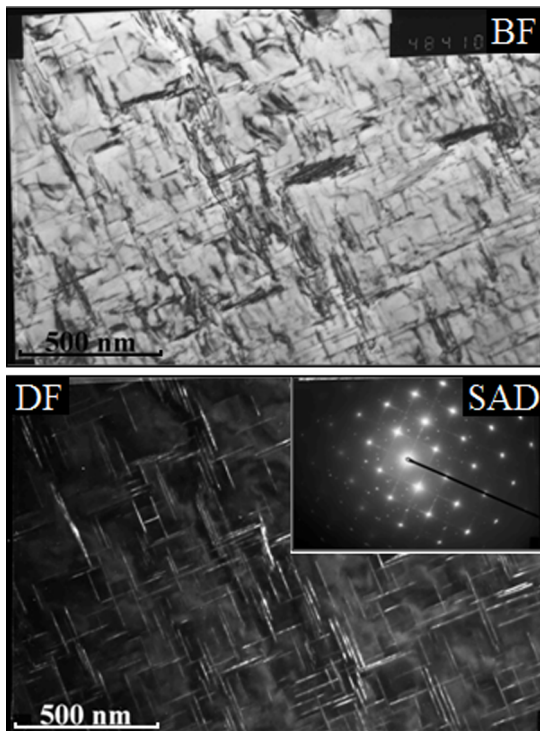


Fig. 4 Bright Field (BF) and Dark Field (DF) images accompanied with Selected Area Diffraction Pattern (SAD) of hardened zone of V-4Ti-4Cr alloy after oxidation (Ar-7%O₂, 700°C, 3 h) and vacuum annealing (800°C, 34 h).

is the network of {200}-oriented titanium oxides (Fig. 4). This is in a good agreement with the results of the previous works in which the formation of Ti-O-net structure, was shown, to be an indispensable condition of oxygen flow towards the surface to form Er₂O₃ oxide layer during immersion in Li[Er] [2].

3.3 Liquid Li immersion test

3.3.1 N-containing Li

As tested, disassembled and cleaned off solidified Li, both the V-alloy and Er samples did not show any changes in weight. However, the cross section examinations of the V-alloy revealed substantial changes in the near-surface composition and structure. Thus, the hardness measurements showed that pre-stored oxygen was completely dissolved by Li (Fig. 3, Li[N]). As a result the etched-like weakened zone A (Fig. 5), possessed by clear grain structure, was formed. It is an indirect illustration of the prevalence of oxygen flow towards the surface along the fast diffusion paths, i.e. grain boundaries. Hardness, in this grain-zone, decreased to the level even lower than that for the initial state (Fig. 3). However, in the vicinity of the interface (25 μm), hardness gradually increased to ~650 kg/mm². This layer B contrary to the weakened zone A, did not reveal any visible grain structure. EDX analyses demonstrated that surface composition of tested samples corresponds to that of initial composition of alloy. However, TiN and VN_{0.2} nitride phases were detected in XRD pat-

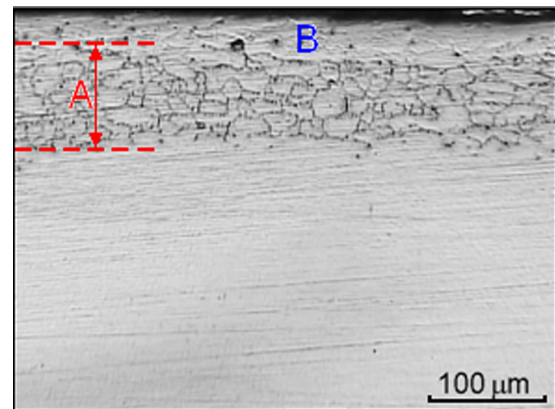


Fig. 5 Optical micrograph of cross section of V-4Ti-4Cr alloy sample exposed to Li[N] at 700°C for 100 h. A – weakened zone; B – nitride zone.

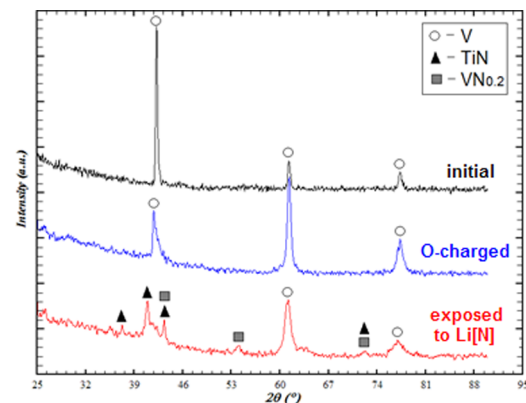
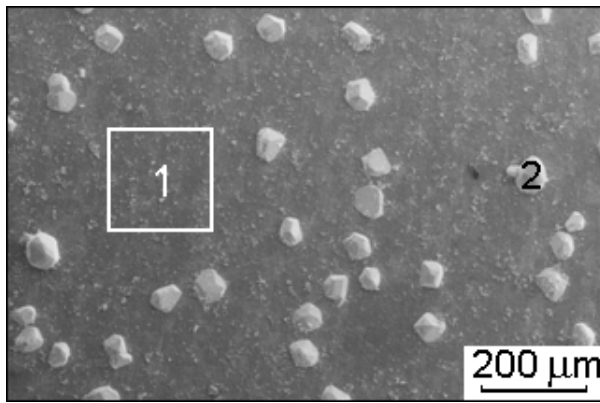


Fig. 6 XRD patterns obtained from the surface of V-4Ti-4Cr alloy samples in initial, oxidized and exposed to Li[N] conditions.

tern (Fig. 6).

Thus, at least two processes, i.e. dissolution of O and nitriding take place in the near-surface layer of V-alloy during immersion in Li[N] melt. The redistribution of non-metallic impurities is in a good accordance with the stated regularities of mass exchange in the complex “structural material – alkali metal – non-metallic elements” system [7]. The expected formation of Er₂O₃ oxide layer on the surface of V-alloy does not occur in the N-containing Li, while whole oxygen pre-stored in V-matrix was dissolved by Li. There are two possible explanation of this behavior: misbalanced flow of reactive components (Er from Li and O from V-alloy), i.e. for instance more rapid dissolution of O from V-alloy than Er in Li; and/or influence of N on the mass transfer. Because the samples were immersed into the Li after the certain period dedicated to dissolution of Er the second assumption can be a main reason. Actually, the thermodynamic evaluation indicates that affinity of Er to N is higher in comparison with Li and as a result Er samples, similar to the V-alloy, did not dissolve but was nitrified. In the previous works [2, 3] it was shown that be-



wt% (at%)	V	Ti	Cr	Er	O
whole surface	50.24 (28.41)	2.85 (1.72)	3.08 (1.71)	6.60 (1.14)	37.22 (67.03)
area 1	69.07 (60.44)	6.75 (6.29)	3.27 (2.81)	11.01 (2.93)	9.88 (27.54)
spot 2	-	-	-	53.30 (9.84)	46.70 (90.16)

Fig. 7 SE image of V-4Ti-4Cr surface covered with insulating Er-oxide layer obtained using VPSE detector accompanied by the results of EDX (table) analyses versus different areas marked on the figure.

neath outer Er_2O_3 oxide layer, the intermediate ErN film is formed. However, in those experiments, N concentration in Li did not exceed 65 wppm which is much less than that in the present test (≤ 0.2 wt%).

3.3.2 Li pre-cleaned with respect to N by Zr getter

After disassembling, it was detected visually, that V-alloy sample is almost completely free from Li probably due to decrease in wetting conditions of the surface.

Figure 7 shows SE image of surface of V-alloy sample exposed to $\text{Li}[\text{Er}]$ obtained using variable pressure secondary electron detector (VPSE) which allows the surface with insulating properties to be observed clearly. It can be seen that surface of sample covered with continuous layer which, in turn, populated by spherical crystals.

According to the results of EDX analyses continuous surface film (area 1 in Fig. 7) is erbium oxide. Oxide film is very thin since EDX spectrum contains intensive peaks of V, Ti and Cr and probably does not exceed $0.2 \mu\text{m}$. Spherical crystals are composed of Er and O. It is reasonable to suppose that, during cooling of Er-saturated Li, Er precipi-

tates on the surface of V-alloy samples in the view of crystals due to temperature dependence of the solubility. During cleaning Er crystals react with water followed by the formation of $\text{Er}(\text{OH})_3$. Hardness of the near-surface layer of V-alloy decreased to the initial level before oxidation (Fig. 3). This indicates that in spite of formation of oxide film the V-alloy completely lost the oxygen which was partially spent on the formation of oxide and mainly dissolved by Li. However, the nitriding of V-alloy was successfully suppressed by pre-cleaning procedure. Surface of Zr foil (getter) became golden-like colored that is peculiar to nitriding and increased their weigh. V-alloy samples also demonstrated the weight gain. However, based on surface observations (Fig. 7) and hardness measurement (Fig. 3), the weigh change includes both decrease in value because of oxygen dissolution and increase due to precipitation of Er crystals. Er samples demonstrated weight loss which is equivalent to the solubility value of Er in Li ~ 0.12 wt% at 700°C .

Electrical resistivity measurements at room temperature in air by means of the two-electrode method indicated good insulating properties of formed thin film.

Thus, cleaning of liquid Li with regard to N impurity promotes the successful mass transfer in $\text{Li}[\text{Er}]-\text{V}, \text{Ti}[\text{O}]$ system resulted in the formation of E_2O_3 insulator coating.

4. Conclusions

Based on the obtained results it was concluded that:

- *In-situ* formation of E_2O_3 coating on the surface of V-alloys depends strongly on the purity level of Li with regard to the N;
- The cleaning of Li by means of getters is a sine qua non of successful mass transfer in $\text{Li}[\text{Er}]-\text{V}, \text{Ti}[\text{O}]$ system and successful formation and operation of Er_2O_3 insulator coating.

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