The in situ growth of Er_2O_3 coatings on V–4Cr–4Ti in liquid lithium

Zhenyu Yao [a,*], Akihiro Suzuki [b], Takeo Muroga [c],
Olga Yeliseyeva [d], Takuya Nagasaka [c]

[a] *Department of Fusion Science, School of Physical Sciences, The Graduate University for Advanced Studies,*
322-6 Oroshi, Toki, Gifu 509-5292, Japan
[b] *Nuclear Engineering Research Laboratory, School of Engineering, University of Tokyo,*
2-22 Shirakata-Shirane, Tokai, Naka, Ibaraki 319-1188, Japan
[c] *Fusion Engineering Research Center, National Institute for Fusion Science,*
322-6 Oroshi, Toki, Gifu 509-5292, Japan
[d] *Karpenko Physico-Mechanical Institute, National Academy Sciences of Ukraine,*
5 Naukova Street, L'viv 79601, Ukraine

Abstract

The in situ Er_2O_3 insulating coating is under development for self-cooled Li/V-alloy type fusion blankets. A previous study showed formation and long-term stability of the coating by exposing V–4Cr–4Ti substrate to liquid Li doped with Er. In this study, the mechanisms for nucleation and growth of the coating are investigated. By oxidation and annealing, oxygen was charged into the substrate to form a Ti–O net phase as oxygen source to the coating. The surface layer formed on V–4Cr–4Ti consists of two sub-layers, an insulating Er_2O_3 coating and an intermediate layer of mixed ErN and Er–V–O. The measured growth rate shows logarithmic kinetics with high exponent ($n \approx 3$ or 4) at 873 and 923 K, suggesting that the rate of growth to Er_2O_3 coating should be very low. The growth was accelerated suddenly at 973 K resulting in a low exponent ($n \approx 2$) that almost obeys a parabolic law. A phenomenological model was proposed to describe the mechanism of coating, which showed the growth of the Er_2O_3 coating is controlled by the diffusion of oxygen and delivery of erbium to interface between V-alloys substrate and liquid Li.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Erbium oxide; Coating; Vanadium alloy; Liquid lithium; Blanket

1. Introduction

Self-cooled Li/V-alloy blanket are thought to be a very attractive blanket concepts for fusion. One of

* Corresponding author. Tel.: +81 572 58 2314;
fax: +81 572 58 2676.
E-mail address: yao@nifs.ac.jp (Z. Yao).

the critical issues of this class of blanket concepts is large magneto-hydrodynamic (MHD) pressure drop when liquid Li flows in metallic duct under magnetic field. A promising solution is to apply an electrically insulating coating on the inner wall of the metallic ducts.

Some materials including AlN, CaO and Y_2O_3 had been studied as candidates for the insulating coating [1,2]. Recently, the research is being focused on Er_2O_3, which is regarded as a promising candidate material for an insulating coating because it shows high thermodynamic stability at high temperature, good compatibility with liquid Li, high electrical resistivity and high stability in air [3,4].

Among various coating methods for producing Er_2O_3 coating, the in situ formation in liquid Li is particularly attractive because of the possibility to produce the coating on complex surfaces after fabrication of the components, and the potential to heal cracks of the coating without disassembling the component.

In previous studies, the authors showed the feasibility of in situ formation of Er_2O_3 coating by exposing V–4Cr–4Ti to liquid Li doped with Er [3], followed by the characterization and demonstration of long-term stability of Er_2O_3 coating [5]. In this study, the mechanisms of nucleation and growth of the coating were investigated.

2. Experimental procedure

The size of the V–4Cr–4Ti sample is about 7 mm × 7 mm × 0.5 mm. The samples were pre-charged with oxygen at 973 K for 6 h by exposure in flowing argon of nominal purity of 99.9999% with flow rate of 400 ml/min in a thermo-gravimetric (TG) apparatus. Subsequently the sample was annealed in vacuum ($\sim 10^{-5}$ Pa) at 973 K for 16 h to diffuse oxygen into bulk. The oxidized plus annealed samples were finally exposed in static liquid lithium (nominal purity of 99.9%) doped with erbium powder (99.9% purity) at 873 K for 20–750 h, at 923 K for 20–300 h and at 973 K for 20–300 h under the cover of high purity argon. After exposure, the samples were cleaned by water and ethanol. The cross-section of the samples was observed by scanning electron microscopy (SEM). The Vickers hardness profile of the cross-section was mea-

sured with a load of 10 gf. The microstructure of near surface region was analyzed by transmission electron microscopy (TEM) and electron diffraction (ED). The thickness of the coating was measured by combined use of SEM and X-ray photoelectron spectroscopy (XPS).

3. Results and discussion

Fig. 1 shows the thickness (T) of Er_2O_3 coating formed on the V–4Cr–4Ti substrate (oxidized for 6 h at 973 K, annealed for 16 h at 973 K and finally exposed in liquid Li doped with Er) at 873, 923 and 973 K as a function of the exposure time (t). $T^n = k \cdot t + a$, here $a = 0$ was assumed, corresponding to a negligible nucleation duration. The figure shows the growth kinetics of Er_2O_3 coating obey a logarithmic law with high exponent ($n \approx 3$ or 4) at 873 and 923 K, suggesting that the rate of growth to Er_2O_3 coating should be significantly low. As was shown by the authors in the previous work, the solubility of erbium is very low (0.15 wt.%) in liquid lithium at 873 K [3]. It is thus reasonable to assume that both the diffusion of oxygen in vanadium alloy and the delivery of erbium in liquid lithium were so slow that the growth of Er_2O_3 coating was slow. The growth process was expedited suddenly at 973 K exhibiting a low exponent ($n \approx 2$) that almost obeys a parabolic law resulting in the quick growth of the coating.
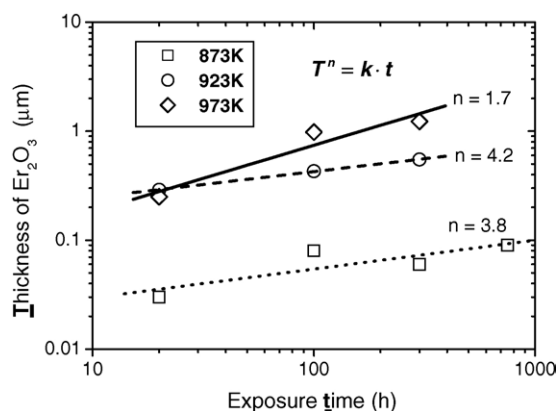

Fig. 1. The thickness of Er_2O_3 coating on V–4Cr–4Ti substrate as a function of the time of exposure to liquid Li doped with Er. Here T is thickness of Er_2O_3 coating, t is exposure time in Li (Er), n is exponent and k is constant.