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Chemical formation of erbium oxide layer on V–4Cr–4Ti during exposure to liquid lithium doped with erbium

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Abstract

The promising way to mitigate magneto-hydrodynamic (MHD) pressure drop in self-cooled Li/V-alloy blanket is to use electrical insulating coating. The chemical formation of Er_2O_3 layer on V–4Cr–4Ti during exposure in liquid Li doped with Er was explored. V–4Cr–4Ti specimens were oxidized at 973 K for 0.5–8 h, annealed at 973 K for 16 h, and finally exposed for 20–300 h at 873 K. The Er_2O_3 layer formed on V–4Cr–4Ti specimens that were oxidized plus annealed, but did not form on either as-received or oxidized only specimens. The resistivity of V–4Cr–4Ti coated with Er_2O_3 is $\sim 10^{13}$ Ωcm at room temperature which is much larger than the minimum requirement. The Er_2O_3 layer is stable in liquid Li after 300 h at 873 K. The results indicate that the oxygen source to form Er_2O_3 layer is the pre-charged oxygen in V–4Cr–4Ti, and that annealing after oxidation to homogenize the oxygen distribution in specimen is necessary.

1. Introduction

A self-cooled lithium/vanadium alloy blanket is an attractive concept, because of its high operation temperature, high tritium-breeding ratio without use of neutron multiplier beryllium. One of the critical issues for this concept is the magneto-hydrodynamic (MHD) pressure drop, which occurs when liquid Li flows in the magnetic field. The promising way to mitigate it is to use an electrical insulating coating on the inner wall of the lithium ducts.

The in situ formation of the coating in liquid Li is a quite attractive technology, because it will form the coating on complex surfaces after fabrication of components and has the potential to heal coating cracks without disassembling the component. For development of the in situ method to form an insulating coating, significant work has been performed on CaO [1–4].

However the stability of CaO in liquid lithium at high temperature was shown to be a serious issue. It was reported that bulk polycrystalline CaO reacts with lithium resulting in significant mass loss above 773 K [5]. High mass loss for single-crystal CaO bulk also was reported after exposure at 873 and 973 K [6]. The use of a CaO coating may be limited to exposure temperatures below 873 K. Another problem is that CaO reacts easily with any moisture and carbon dioxide in the environment to form calcium hydroxide or calcium carbonate, resulting in disintegration [4,7].

Among the materials recently investigated, Er_2O_3 ceramics showed good compatibility with liquid Li up to 1073 K, a high electrical resistivity, and a high stability in air with moisture, and thus is regarded as a promising candidate material for an insulating coating [6]. Er_2O_3 has similar thermodynamic stability as CaO based on the database of Gibbs free energy of formation at high temperature, and has low solubility in liquid Li. Er_2O_3

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does not disintegrate in ambient air and thus various fabrication techniques are expected to be applicable.

In this study, the chemical formation capability of an Er_2O_3 layer was investigated by exposing V–4Cr–4Ti (NIFS-HEAT-2) [8] to liquid lithium doped with erbium at high temperature.

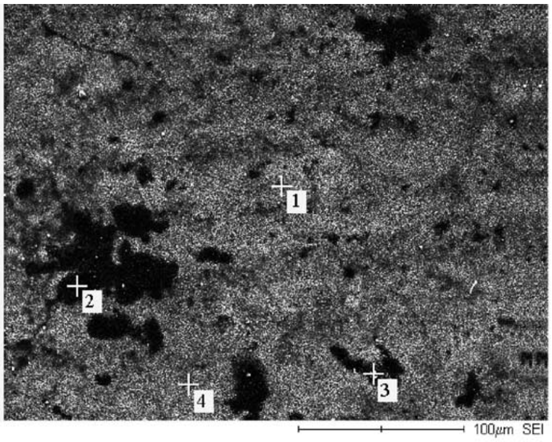
2. Experimental procedure

V–4Cr–4Ti (NIFS-HEAT-2, O-48 ppm, N-122 ppm) sheet with thickness of 0.5 mm was cut to ~6×6 mm (~105 mg). Specimens were pre-charged with oxygen at 973 K for 0.5, 1, 2, 4, 6 and 8 h by exposing to flowing argon of nominal purity of 99.9999% (O_2<0.1 ppm, N_2<1 ppm, H_2O<0.5 ppm) and flow rate of 400 ml/min, using a thermogravimetric (TG) apparatus. After the oxidation, the oxygen concentrations in sample calculated from weight gain were about 1800, 2500, 3800, 5600, 7600 and 8700 ppm correspondingly. Subsequently, half of each sample was annealed in vacuum (about 10^{-5} Pa) at 973 K for 16 h to diffuse oxygen from the surface into bulk without weight change. The as-received, oxidized only and oxidized plus annealed samples were then exposed in static liquid lithium (nominal purity of 99.9%) doped with erbium powder (99.9% purity) to a concentration of 0.15 wt% for 20, 100, 300 h at 873 K, under the cover of high purity argon (99.9999%). The erbium concentration in lithium was estimated by sampling the lithium after exposure and analysis with atomic absorption spectrometry. After exposure, the samples were cleaned by water and ethanol. The weight change was measured with an analytical balance with accuracy of 10^{-5} g. The surface and cross section of the samples were observed and analyzed by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), and the surface and depth profile were analyzed with X-ray photoelectron spectroscopy (XPS) under sputtering with Ar ions at a rate of ~13 nm/min. The resistivity of as-received, oxidized, and Li exposed samples were measured in air at room temperature by means of the two-electrode method.

3. Results and discussion

3.1. The formation of Er_2O_3 layer on V–4Cr–4Ti

Fig. 1 shows a SEM image and EDS element analysis of the surface of a specimen oxidized for 6 h, annealed for 16 h at 973 K and exposed in liquid lithium doped with erbium for 300 h at 873 K. The analysis shows clearly that the surface of V–4Cr–4Ti is enriched with erbium and oxygen. The EDS analysis also showed 30–40 wt% in total of V, Cr and Ti that are considered to be from the vanadium alloy substrate.



	1	2	3	4
O (wt%)	11.26	12.47	2.56	10.14
Er (wt%)	47.31	54.12	54.84	50.96

Fig. 1. SEM image and EDS element analysis of surface of V–4Cr–4Ti oxidized for 6 h and annealed for 16 h at 973 K, exposed in Li doped with Er for 300 h at 873 K.

Fig. 2 shows a SEM image of the polished cross section of V–4Cr–4Ti specimen that was oxidized for 6 h, annealed for 16 h at 973 K and exposed in liquid lithium doped with erbium for 300 h at 873 K. It is obvious that a layer with fairly uniform thickness of about 1.5 μm formed on the surface of V–4Cr–4Ti. Fig. 2 also shows the EDS element line scans through the cross-section, showing enrichment of erbium near the surface.

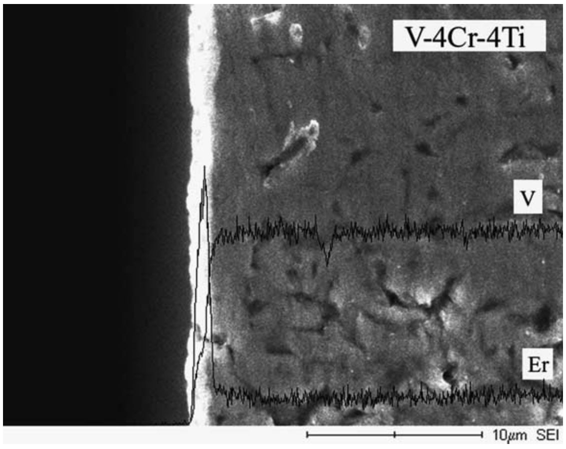


Fig. 2. SEM image and EDS line element scan of cross-section of specimen shown in Fig. 1.

Fig. 3 shows the Er4d spectrum of XPS on the surface of various test specimens. The peak (a) corresponds to the layer containing Er and O made by exposing V–4Cr–4Ti in liquid lithium doped with erbium in the present experiment. The peak (b) is from a coating fabricated by radio frequency (RF) sputtering which was identified to be Er_2O_3 by X-ray diffraction (XRD) [9]. The figure shows that the peak position of Er4d for the two specimens is almost the same. For further confirmation, a specimen of as-received unalloyed Er was examined and shown in (c). The (d) spectra is from the same Er specimen after sputtering with Ar ions for 20 min. The as-received Er specimen has a native Er_2O_3 film on the surface but the film is deleted after sputtering. The Er4d peak positions of (a)–(c) were similar confirming Er_2O_3 in the formed layer. The peak in (d) shows metallic Er.

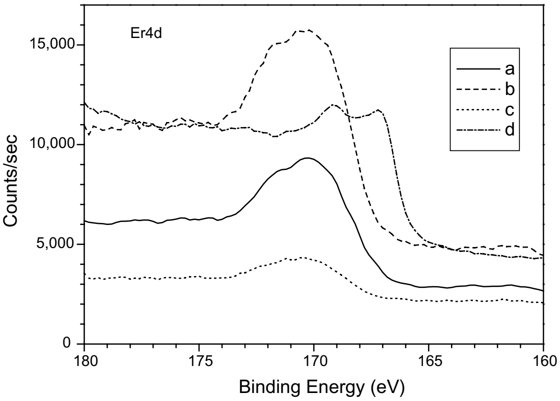


Fig. 3. The Er4d spectrum of XPS on the surface. (a) Layer containing Er and O by exposing in Li (specimen shown in Figs. 1 and 2). (b) Er_2O_3 coating by RF sputtering. (c) As-received Er plate (native oxide film). (d) Er plate after sputtering for 20 min (metallic).

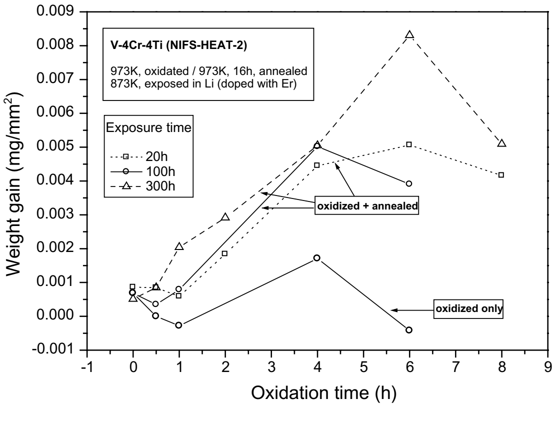


Fig. 4. The weight gain of V–4Cr–4Ti after exposure in liquid Li doped with Er.

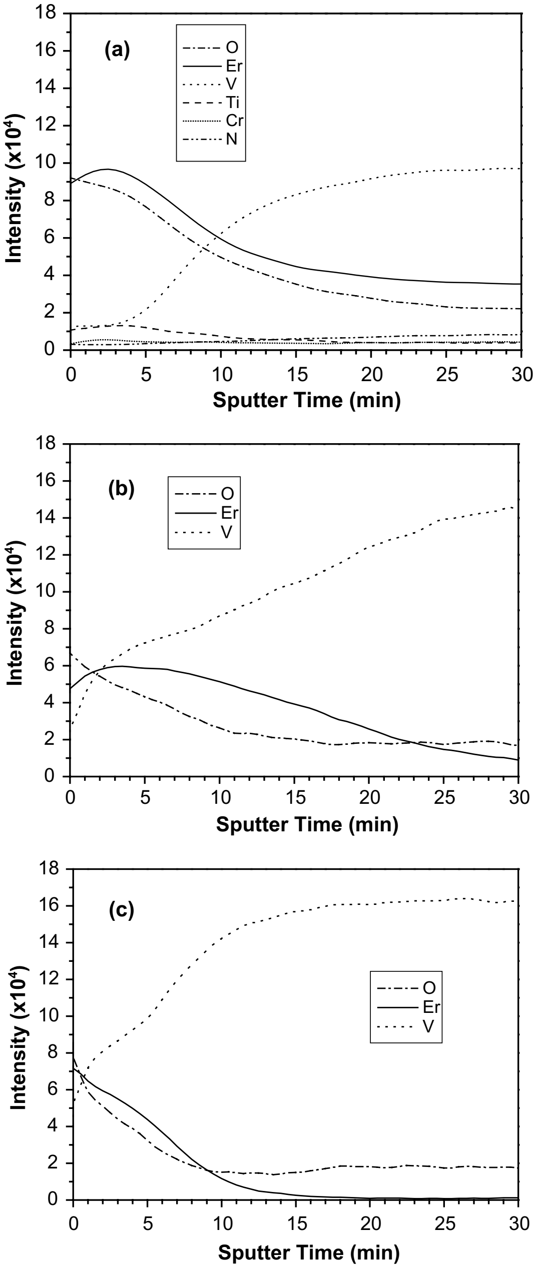


Fig. 5. The XPS depth profile of element in V–4Cr–4Ti specimens exposed in Li doped with Er for 100 h at 873 K, under Ar ion sputtering at rate of ~13 nm/min. (a) Oxidized for 6 h at 973 K, annealed for 16 h at 973 K. (b) Oxidized only for 6 h at 973 K. (c) As-received.

3.2. The fabrication procedure of Er_2O_3 layer on V–4Cr–4Ti

Fig. 4 shows the effect of pre-treatment on the weight gain after exposure in liquid lithium doped with erbium. It indicates that the pre-oxidation is necessary for weight gain during exposure. The weight gain increased with pre-oxidation time suggesting that the main oxygen source to form the layer is not impurity oxygen in the lithium but oxygen from pre-charging. Fig. 4 also shows that annealing after oxidation strongly increases the weight gain.

Fig. 5 shows the depth profile of elements by XPS using Ar ion sputtering. Fig. 5(a)–(c) correspond to V–4Cr–4Ti oxidized for 6 h plus annealed for 16 h, only oxidized for 6 h at 973 K and as-received, respectively, after exposure in liquid lithium doped erbium for 100 h at 873 K. In the case of oxidation followed by annealing, the area in the vicinity of the surface is composed mainly of Er and O but the subsequent area is a mixture of Er, V, Ti, Cr, N and O, perhaps including such phases as Er_2O_3, ErN, V_xO_y, and TiO_2. In the cases of as-received and oxidation without subsequent annealing, only a mixed layer was formed without the thin Er_2O_3 layer. Comparison of Figs. 4 and 5 clearly shows that the weight gain corresponds to the formation of the Er_2O_3 layer.

When the V–4Cr–4Ti specimen was only oxidized, a layer containing oxygen formed on the sample surface. During exposure, the oxygen at the surface dissolved into lithium, quickly exhausting the oxygen source and limiting the formation of an erbium oxide layer. Annealing after oxidation allowed the surface oxygen to diffuse into bulk, lowering the oxygen concentration at the surface and slowing down the reaction with erbium in liquid lithium.

3.3. The resistivity of coated V–4Cr–4Ti

Fig. 6 shows the resistivity of various samples measured by the two-electrode method at room temperature. For comparison, the data for unalloyed Er plate as-received and mechanically polished are also shown. Fig. 6 indicates that the as-received, oxidized only, oxidized plus annealed V–4Cr–4Ti and polished Er plate are all highly conductive. The resistivity of V–4Cr–4Ti appears only after exposure in liquid lithium doped with erbium. The resistivity of V–4Cr–4Ti after exposure in liquid lithium doped with erbium is higher than the native oxide formed or unalloyed Er. The resistivity of 10^{13} Ω cm of coated V–4Cr–4Ti is several orders of magnitude larger than the minimum requirement of 10^4 Ω cm for the MHD insulating layer [10]. The result for oxidized vanadium alloys indicates that the oxygen enrichment does not form an insulating layer by oxidation only. Further characterization of the resistivity is necessary such as in Li and at high temperature.

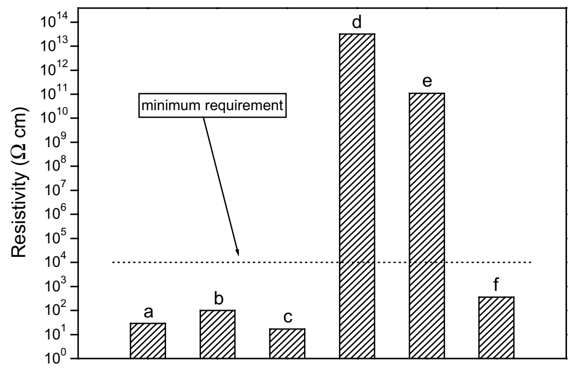


Fig. 6. The resistivity of various materials at room temperature. (a) V–4Cr–4Ti as received. (b) V–4Cr–4Ti, oxidized only. (c) V–4Cr–4Ti, oxidized + annealed. (d) V–4Cr–4Ti, oxidized + annealed + exposed in Li doped with Er. (e) Er plate exposed in air. (f) Er plate polished with sand paper. The dotted line shows the minimum requirement for MHD insulator [10].

4. Summary

The chemical formation of Er_2O_3 layer on V–4Cr–4Ti (NIFS-HEAT-2) during exposure in liquid lithium doped with erbium was characterized. An Er_2O_3 layer was formed on V–4Cr–4Ti after it was oxidized, annealed and exposed in the liquid lithium doped with erbium. Weight gain of the specimen after exposure increased with pre-oxidation time. The resistivity of V–4Cr–4Ti coated with Er_2O_3 layer is about 10^{13} Ω cm which is much larger than the 10^4 Ω cm of minimum requirement for MHD insulation. The Er_2O_3 layer is stable in liquid lithium to 300 h at 873 K. An Er_2O_3 layer was not formed on V–4Cr–4Ti either as-received or oxidized only, after exposed in liquid lithium doped with erbium. These results indicate that the oxygen source to form Er_2O_3 layer is from the pre-charging oxygen in the V–4Cr–4Ti and the annealing after oxidation is a necessary process.

The present study demonstrated that the chemical formation of an Er_2O_3 insulating layer on V–4Cr–4Ti during exposure in liquid lithium doped with erbium is a possible coating deposition method. Further effort is necessary to characterize the layer and optimize the processing conditions for the formation of the layer.

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