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In situ formation of CaO insulator coatings on vanadium alloys

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Abstract

A key issue for the self-cooled lithium blanket concept with a vanadium alloy structure is the development of an electrically insulating coating on the coolant channel walls to mitigate the magneto-hydrodynamic pressure drop in a high magnetic field. A systematic investigation of the thermodynamics and kinetics of oxygen and calcium interactions in the vanadium alloy/lithium system is being conducted to define the system parameters required for in situ formation of a CaO coating on vanadium alloys. This paper presents results of theory and modeling as well as experimental results on the formation of CaO coatings on vanadium alloys after exposure at temperatures of 600–700 °C to lithium with a small fraction of Ca added. Coatings of 10–30 μm with high electrical resistivity ($>10^8\ \Omega$cm) have been formed on V-alloys.

1. Introduction

The self-cooled lithium blanket with a vanadium alloy structure offers a potential for high performance with attractive safety and environmental features [1–4]. Features include high heat load capability, high operating temperature, potential for long lifetime, design simplicity, low-operating pressure and use of low-activation materials. Key remaining issues for the lithium/vanadium blanket concept include effects of fusion-relevant helium transmutation rates on the properties of neutron irradiated vanadium alloys and development of electrically insulating coolant channels to mitigate the magneto-hydrodynamic (MHD) pressure drop in the lithium coolant. Formation of electrically insulating coatings on channel walls is the proposed approach to mitigate the MHD effects. In situ formation of the coatings after fabrication of the blanket appears necessary and self-healing of any defects in the coatings that might occur during operation is considered essential to provide acceptable reliability. The temperature range of primary interest for the lithium blanket with the reference V–4Cr–4Ti alloy structure is 400–750 °C.

Design analyses have been conducted previously to define the performance requirements for insulator coatings under projected fusion system conditions [5,6]. These analyses indicate that only modest electrical resistivities or very thin coatings are adequate to suppress the MHD pressure drop. A value of 100 Ωcm for the product of the electrical resistivity and the thickness will reduce the MHD pressure drop to negligible levels. This corresponds to a coating thickness of 1 μm for an electrical resistivity of $10^6\ \Omega$cm. A coating thickness of 10 μm is considered desirable.

Oxide, nitride and carbide coatings have all been considered; however, only a few oxides are stable in lithium and many nitrides, carbides and silicides do not exhibit adequate electrical resistivities [7,8]. CaO has been selected as the leading candidate coating material for the lithium/vanadium system on the basis of its properties and the requirements for the coating. This paper presents a status of in situ formed CaO coatings on V-alloy substrates by exposure of V-alloy specimens to lithium containing small amounts of Ca. Related investigations are also being conducted on CaO coatings

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produced by thermal–physical vapor deposition and chemical vapor deposition techniques [9].

2. Coating requirements – CaO assessment

The requirements for the coating material are quite complex. CaO has been selected as the leading candidate for the coating material because it appears to best meet the stringent requirements for the insulator coating for the Li/V system application. Key considerations for the selection of candidate coating materials include the following:

1. reasonably high electrical resistivity,
2. chemical stability/compatibility with Li at elevated temperatures,
3. potential for coating complex channel configurations,
4. potential for in situ self-healing of any defects that might occur,
5. mechanical integrity/thermal expansion match with V-alloy,
6. safety/environmental characteristics, e.g., low activation,
7. materials availability/cost,
8. favorable neutronic properties,
9. resistance to irradiation damage.

The reported electrical resistivity of monolithic CaO is among the highest of the potential candidate coating materials, varying from $\simeq 10^{16}$ Ω cm at 300 °C to $\simeq 10^{9}$ Ω cm at 750 °C compared to a minimum requirement of $\simeq 10^{6}$ Ω cm [5,6]. Based on fundamental thermodynamic data, CaO is one of the most stable oxides and is predicted to be stable in low-oxygen lithium as indicated in Fig. 1. The thermal expansion mismatch for the CaO/V-alloy interface is fairly low since the coefficient of linear thermal expansion for CaO ($\simeq 12 \times 10^{-6}$/°C) is fairly close to that for vanadium ($\simeq 11 \times 10^{-6}$/°C). As discussed in detail later, the CaO system with vanadium exhibits favorable properties with respect to in situ coating and self-healing. The neutronic, environmental and safety-related characteristics of calcium are generally favorable, the resources are ample and the cost is low. The radiation response has not been determined, but the margin for electrical resistivity is quite large and self-healing should also mitigate some of the radiation effects. Overall, CaO exhibits characteristics that are favorable to the proposed coating application.

3. In situ coating procedure

The approach for in situ coating under investigation involves a reaction of calcium dissolved in the lithium with oxygen dissolved in the vanadium alloy to form CaO at the solid/liquid interface as indicated schematically in Fig. 2.

$$\underline{O}_V + Ca_{Li} = CaO.$$

The vanadium alloys under investigation for the structure typically contain about 300 wppm oxygen; however, the solubility of oxygen in vanadium is over 1 wt% at the temperatures of interest. Oxygen is also relatively mobile in vanadium with a diffusivity of about 10^{-9} cm^2/s at 600 °C. Therefore, at temperatures of primary interest, 500–700 °C, oxygen is sufficiently mobile to diffuse to the surface of the V-alloy. Additional oxygen is precharged into the surface of the alloy to provide sufficient oxygen to form the desired CaO coating thickness. The amount of oxygen precharge can be varied to obtain the desired coating thickness, e.g., the oxygen required for a 10 μm CaO coating corresponds to about 0.94 mg/cm^2 of oxygen in the V-alloy.

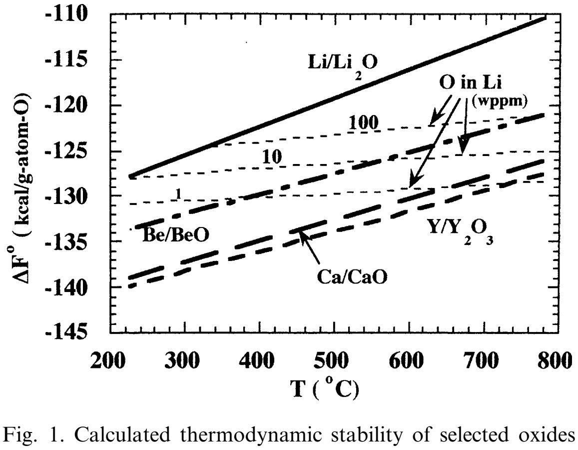


Fig. 1. Calculated thermodynamic stability of selected oxides relative to lithium with various oxygen concentrations.

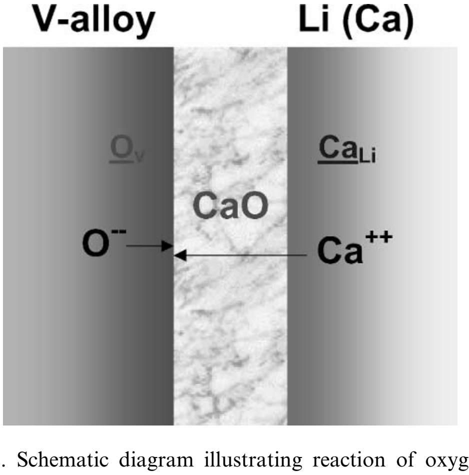


Fig. 2. Schematic diagram illustrating reaction of oxygen in vanadium alloy with calcium in lithium to form CaO coating.

The oxygen precharge involves exposure of the V-alloy to a low-pressure oxygen environment at ≃700 °C for time sufficient to pickup the desired amount of oxygen, typically 10–20 h. The V-alloy is then conditioned, e.g., 750 °C for 17 h, to diffuse the oxygen into the subsurface region and to reduce any vanadium oxide on the surface. Reduction of any V-oxide is necessary to avoid the formation of a Ca–V–O complex oxide, since the calcium vanadates typically do not exhibit high electrical resistivity. For the case of the reference V–4Cr–4Ti alloy, internal oxidation of the Ti in the alloy occurs, which maintains the oxygen in the near-surface regions as indicated in Fig. 3. The calculated oxygen profile based on an internal oxidation model is in good agreement with the hardness profile, which is related to the oxygen content. Similar calculations and experimental results for vanadium and V-alloys with lower Ti concentrations show deeper penetration of the oxygen into the metal. Retention of the oxygen in the near-surface regions facilitates the subsequent coating formation.

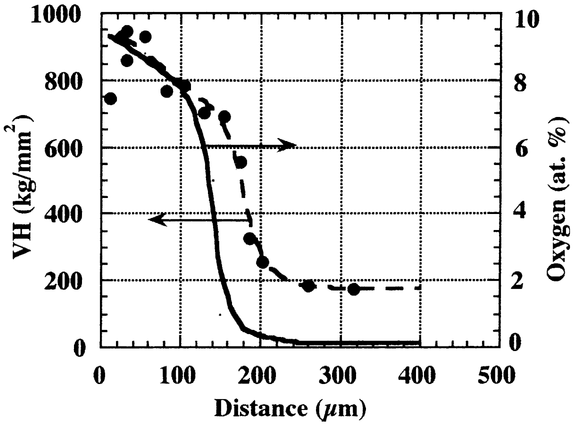


Fig. 3. Calculated oxygen profile and hardness profile in V–4Cr–4Ti alloy after precharging in low-pressure oxygen and homogenizing at 750 °C for 17 h.

The oxygen precharged V-alloy specimens are then exposed to lithium containing small amounts of calcium to form the CaO coating. Calcium is highly soluble in lithium with a eutectic at ≃8 at.% Ca with a melting temperature ≃40 °C below the melting point of lithium. Any oxygen in lithium preferentially reacts with the Ca to form CaO, which reduces the oxygen activity in the Li–Ca alloy as indicated by the calculated distribution of oxygen between Li and Ca indicated in Fig. 4. Nitrogen reacts with calcium in a similar manner such that the nitrogen activity in the Li–Ca alloy is also very low. In past studies on lithium corrosion, Ca additions to Li have been shown to decrease the nitrogen content of the lithium to very low levels by cold trapping the calcium nitride [10,11]. Earlier investigations on in situ formation of CaO coatings were conducted at temperatures of

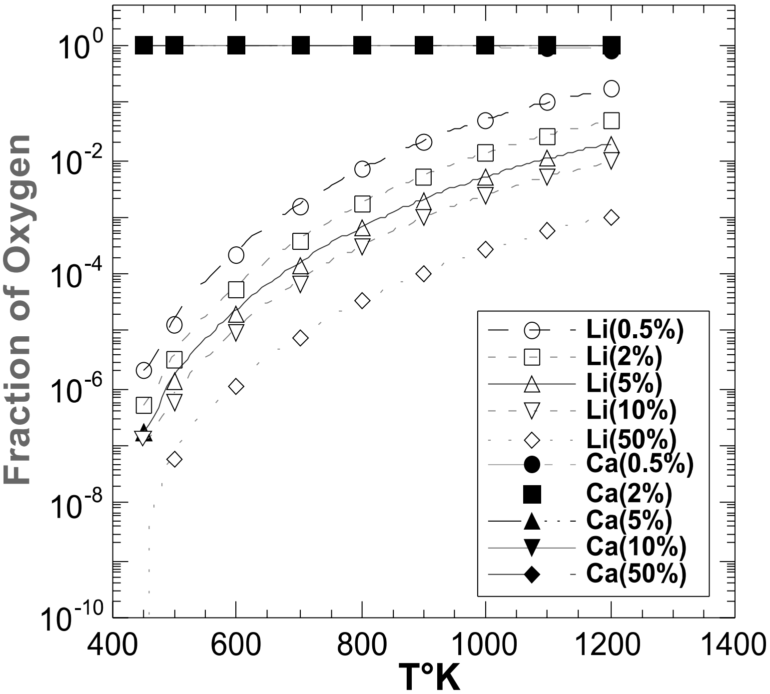


Fig. 4. Calculated distribution of oxygen between Ca and Li in LiCa alloy as a function of composition and temperature.

350–500 °C in Li–Ca alloys with a wide range of Li–Ca compositions [12–14]. Recent investigations have been focused on higher temperature exposures of V-alloys, typically 600–700 °C, in Li with 2.8 at.% Ca.

4. Results of in situ formed coatings

Fig. 5 shows the EDS analysis of coatings formed on vanadium and a V–5Cr–5Ti alloy exposed to Li–2.8 at.% Ca at 600 °C for 120 h. The transition from the base metal to the calcium-rich surface coating is evident. Similar results are shown in Fig. 6 for V–4Cr–4Ti alloys that were precharged to different oxygen concentrations and then exposed to Li–2.8 at.% Ca at 700 °C for 50 h. Fig. 7 is a plot of the hardness profile for the two V–4Cr–4Ti alloys with oxygen precharged to levels similar to those for specimens indicated in Fig. 6. The solid symbols indicate the hardness profiles after oxygen charging and the open symbols indicate the hardness profiles after exposure to the Li–Ca alloy. The reduction in the surface hardness of the V-alloy represents the oxygen that has diffused out to form the coating. The coating thicknesses indicated by the EDS profiles in Fig. 6 correlate well with the predicted CaO coating thickness corresponding to the amount of oxygen precharge. Fig. 8 shows micrographs of the coating formed on the V–5Cr–5Ti alloy exposed at 600 °C.The coating thickness indicated in the micrograph in Fig. 8(a) correlates well with the EDS profile in Fig. 5. The backscattered electron image in Fig. 8(b) shows the uniformity of the coating in a lower magnification. Additional analyses are in progress to further characterize these coatings. Electrical resistance measurements have also been performed on the coatings at temperatures up to 500 °C. Liquid gallium has been used for the electrical contact on the coating surface. Previous experiments on resistance measurements performed by exposure of the coatings to

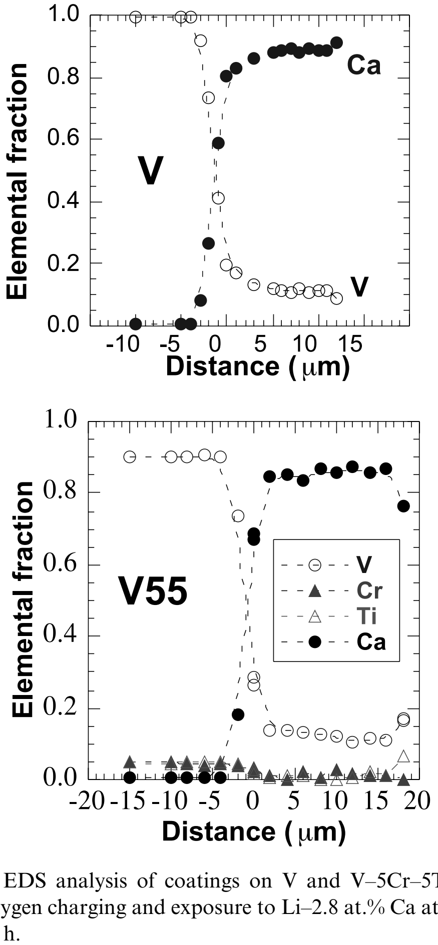


Fig. 5. EDS analysis of coatings on V and V–5Cr–5Ti alloy after oxygen charging and exposure to Li–2.8 at.% Ca at 600 °C for 120 h.

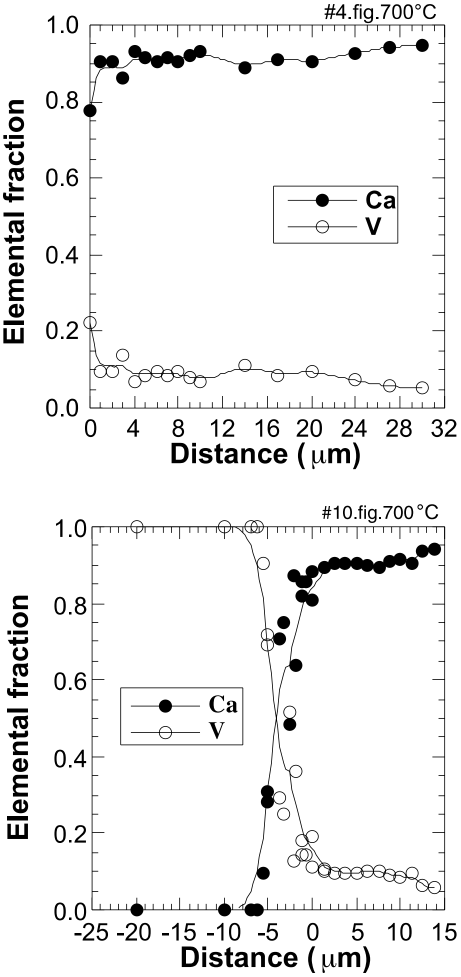


Fig. 6. EDS analysis of coating formed on V–4Cr–4Ti alloy after oxygen precharge to (a) 2.7 mg O/cm^2 and (b) 1.5 mg O/cm^2 and exposure to Li–2.8 at.% Ca at 700 °C for 50 h.

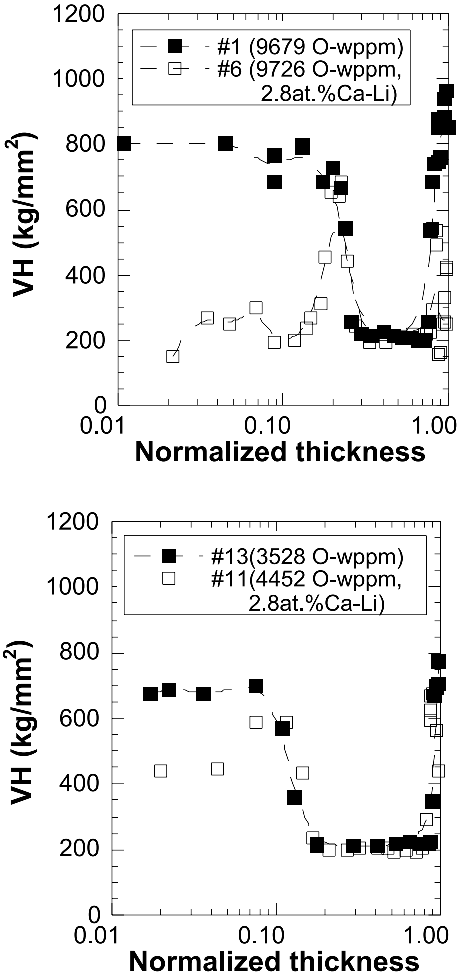
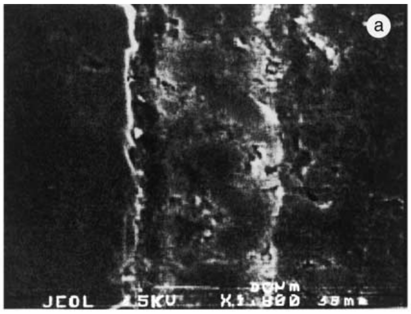


Fig. 7. Hardness profile of V–4Cr–4Ti alloys (a) after oxygen precharging to ~2.7 mg$\underline{O}$/cm^2 before (solid symbols) and after exposure to Li–2.8 at.% Ca at 700 °C for 50 h (open symbols), and (b) similar plot for specimens after oxygen precharge to ~1.5 mg$\underline{O}$/cm^2.

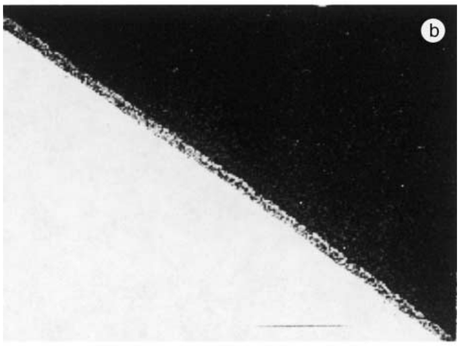
liquid gallium indicated that micron-sized defects in the coatings could be readily detected [12]. Electrical resistivity values in excess of 10^8 Ω cm were obtained at temperatures to 500 °C for the coatings formed on the V–4Cr–4Ti alloy at 700 °C.

5. Summary and conclusions

CaO has been identified as a leading candidate for an electrically insulating coating to mitigate the MHD pressure drop in a self-cooled Li system with a V-alloy structure. Key features include favorable electrical and physical properties, chemical stability in lithium, and potential for in situ coating and self-healing.



V-55 CaO mount



BEI V55/CaO

Fig. 8. (a) SEM of in situ formed coating of CaO on V–5Cr–5Ti after exposure to Li–2.8 at.% Ca at 600 °C for 120 h and (b) low-magnification backscattered electron image of same coating.

The approach for in situ coating involves an interfacial reaction of calcium dissolved in lithium with oxygen dissolved in the V-alloy to form a CaO coating on the V-alloy substrate. Factors that aid the coating formation include a high solubility of Ca in Li relatively high solubility and mobility of oxygen in V-alloys, and the stability of CaO in Li with low-oxygen concentration.

Calcium oxide coatings have been successfully formed on V-alloy substrates by exposure of oxygen-charged V-alloys to Li with small additions of Ca for a range of conditions. Oxygen charging of V-alloys was varied from 0 to ≃2.5 mg$\underline{O}$/cm^2. The V-alloys were conditioned at ≃750 °C to dissolve surface oxide into metal to avoid formation of complex Ca–V–O compounds that exhibit low-electrical resistivity. V-alloy specimens were exposed to Li–2.8 at.% Ca at 600 °C for 120 h and at 700 °C for 50 h. Coating thicknesses up to ≃30 µm were obtainable with a thickness of ≃10 µm desired. The coating thickness correlated with oxygen precharge and varied with exposure time and temperature. The coatings appear to be adherent and relatively uniform, and they exhibit high electrical resistivity (≃10^8 Ω cm at 500 °C).

Results obtained to date indicate that CaO coatings that meet the design requirements can be formed in situ on vanadium alloys over a relatively wide parameter range that is acceptable for practical applications. Further investigations in forced-circulation lithium systems are now required to demonstrate that the lithium chemistry can be adequately controlled in a practical system.

Acknowledgements

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