

Progress on Development of In-situ Coatings for V-4Cr-4Ti^{*} J.-H. Park, A. Sawada, D. L. Rink, K. Natesan, and R. F. Mattas¹, Energy Technology Division and ¹Technology Development Division, Argonne National Laboratory, Argonne, IL 60439 USA

OBJECTIVE

Corrosion resistance of structural materials and magnetohydrodynamic (MHD) forces and their influence on thermal hydraulics and corrosion are major concerns in the design of liquid-metal blankets for magnetic fusion reactors (MFR).¹ The objective of this study is to develop in situ coatings at the liquid-metal/structural-material interface,² with emphasis on coatings that can be converted to an electrically insulating film to prevent adverse currents that are generated by MHD forces from passing through the structural walls.

SUMMARY

We are investigating the in-situ formation of CaO coatings on V-4Cr-4Ti structural material in liquid lithium under various conditions. Initially, the near surface of the V-4Cr-4Ti was oxygen-charged at 710°C and homogenized at 750°C for 17 h, then samples were exposed in 2.8 at.% Ca-Li at temperatures of 600 and 700°C for times between 50 and 747.5 h. The thickness of the in-situ-formed CaO was 4 to 26 μm under the experimental conditions. In the 50 h exposure, thicker CaO films were formed at higher oxygen contents and 700°C, while thinner CaO films were formed at lower oxygen contents and 600°C. For longer exposures at 600°C (623 and 747.5 h), the film thickness stayed the same, but for 700°C exposures (100-425 h) the CaO film chemistry changed, with the film becoming thinner as a result of the net effect from compensating for the film formation and dissolution. We measured the electrical resistivity in an inert-gas environment at between room temperature and 760°C for in-situ formed films at 600°C in 2.8 at.% Ca-Li for 623 and 747.5 h. The measured values for the electrical resistivity were shown to satisfy the design requirement for insulating coatings in the Li/V advanced blanket for the magnetic fusion reactor (MFR). We also performed a Ca-Li compatibility test for single-crystal CaO samples at 600°C for 623 h. The surface of the single-crystal CaO was dissolved 50 μm. These results indicate that the in-situ formed film could be a different phase from the pure CaO. As a result of our recent investigations, we may have met the important development issues for obtaining 700°C stable coatings in Li/V advanced MFR blankets.

INTRODUCTION

Current research on magnetic fusion reactors includes development of electrically insulating coatings for the V alloy in first wall/blanket applications. In this present study, we have focused on in-situ CaO film fabrication at 600 and 700°C in 2.8 at.% Ca-Li on the V-4Cr-4Ti of either US heat or National Institute of Fusion Science (NIFS) heats. Single-crystal CaO samples were also subjected to the compatibility test in the 2.8 at. % Ca-Li to compare with the in-situ formed CaO films.

EXPERIMENTAL DETAILS

Samples preparation is documented in our several previous reports.^{2,3} Samples of V-4Cr-4Ti were oxygen-charged at 700°C and homogenized in a vacuum-sealed (quartz) cell for 17 h at 750°C. Several samples were then arrayed together, and dipped into a Ca-Li pot at 600 and 700°C for 50-747.5 h. Each desired exposure times, the sample tree was raised above the liquid-Ca-Li level and then shaken to minimize residual Ca-Li around the samples. The excessive Ca-Li around the samples was dissolved in methanol to investigate the surface and cross section by scanning electron microscopy (SEM) and X-ray diffraction (XRD). Ex-situ electrical conductivity measurements were performed for the samples exposed

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in 2.8 at.% Ca-Li after the residual Ca-Li had been removed in ethanol. Details are found in our previous report.^{2,3} Two platinum discs were used as electrodes in the top and bottom positions. The electrical conductivity measurements were performed in 99.996% Ar at $25 = T = 760^{\circ}\text{C}$ using a high-input impedance Keithley Model 2001 multi-meter. To determine the CaO compatibility in 2.8 at.% Ca-Li, rectangular shapes of single-crystal CaO samples were also exposed at 600°C for 623 h.

RESULTS

In-situ formed films: Overall results for the coating performance at 600 and 700°C with different times of the in-situ coatings are summarized in Table 1.

Thickness of the film: The coating thicknesses on V-4Cr-4Ti in 2.8 at. % Ca-Li exposures at 600°C for 623 and 747.5 h are listed in Tables 2 and 3. Table 4 gives thicknesses for the 700°C exposure for 99 h. Thicknesses of the films were measured by the cross-section SEM view or calculated by the weight change, assuming that the film was CaO (density of 3.25 g/cm^3). Figure 1 shows the calculated thickness vs. O contents for the in-situ formed CaO film using the various weight. changes after exposure in the 2.8 at.% Ca-Li at 600°C for 623 h listed in Table 3. The CaO thickness was calculated from the amount of oxygen in the V-4Cr-4Ti being reacted with Ca in the 2.8 at.% Ca-Li, and was also determined from the weight change after the exposure at 600°C for 623 h. These values indicated that thinner films were formed than expected. This means that O is escaping from the process, or the in-situ formed CaO films are dissolved during the exposed period. From this trend, we can predict the dissolution rate, as given in Table 3.

Adhesion of the film: No physical data for the adhesion were obtained, but according to our experiences, longer exposures (compare with our previous exposures $t = 120\text{ h}$) should increase the film integrity.

Vickers hardness (VH) profiles: Figures 2 and 3 show the cross-sectional VH profiles for the V-4Cr-4Ti samples exposed to 2.8 at.% Ca-Li at 700°C for 99 h and 600°C for 747 h, respectively. These trends indicate that lower O in the V-4Cr-4Ti results in greater VH near the surface. This effect may be the result of the Ca incorporation into the alloy substrate at 700°C .

X-ray diffraction: For the stepwise dissolution in methanol and in water, three distinctive layers exist between the V-4Cr-4Ti and film: water insoluble layer, ethanol insoluble layer, and soluble layer. For the x-ray investigations, most major spectra are identical for the films formed in 2.8 at.% Ca-Li at 600°C , but detailed analysis on the X-ray spectra remains to be done.

Electrical resistance: Figures 4 and 5 show the measured electrical resistance times area of the in-situ formed CaO films in an inert gas atmosphere. Some measurements were also performed in air at temperatures between room temperature and 750°C . These measurements were made at a high input impedance of 10^{12} ohm with the Keithly 2001 multi-meter. In general, resistance times area (R^*A) values satisfied the MFR design requirement. but when it exposed in air, much lower R^*A values were measured (#45 sample) however, in the MFR design purposes, the air exposure may not be a consideration.

Chemical compositions for the CaO films: Surface and cross-sectional films were investigated by EDS analysis. The cross sectional EDS results are presented in Fig. 6.

Single-crystal CaO exposure: A CaO single crystal was dissolved $53\text{ }\mu\text{m}$ in 2.8 at. % Ca-Li for 623h at 600°C , and the dissolution rate was determined by the difference geometry before and after exposure. If we assume the dissolution to occur at a linear rate, it can be expressed as $R_d(\text{CaO single crystal}) = 8.51 \times 10^{-2}\text{ }\mu\text{m/h}$. This value is 10 to 15 times higher than that of in-situ formed films. However, the film dissolution rate increases with increasing O contents in the V-4Cr-4Ti (Table 3). For exposure times of 623 and 725 h at 600°C , the in-situ formed CaO layers and the CaO crystal are different from each other.

Table 1. Performance of the in-situ formed CaO coating on V-4Cr-4Ti in 0.0, 0.5, and 2.8 at.% Ca-Li at 600 and 700°C.

T (°C)	Time (h)	Films ^a	Remark	Note
600	120 ^b	Good insulator	Film thickness almost same for t =120 h. Film stop growing when O consumed in the V-4Cr-4Ti substrate.	2.8 at.% Ca-Li:
	623			
	747.5			
700	50	Good insulator	Rough surface microstructure.	Acceptable for 600°C, but not acceptable for 700°C time exposure 425 h.
	99	Good insulator	Smoother surface than 50 h exposure.	
	425	Conductive	Film showed lower Ca & higher Ti compare with the film formed at lower T and shorter time.	
	(1000)	(Conductive)	Did not pursue because the 425 h exposure became conductive with low surface Ca fraction.	
	100 (100 + 100)	Conductive	Film dissolved: 100 h exposed in 2.8at.%Ca-Li at 600°C for in-situ coating procedure, and then transferred to the pure Li pot for the 100 h exposure.	Pure Li: Not acceptable
	500 (100 + 500)	Conductive	Film dissolved: 100 h exposed in 2.8 at. % Ca-Li at 600°C for in-situ coating with the condition of all consumed O in the alloy substrate, then transferred to the 0.5 at. % Ca-Li pot for the 500 h exposure.	0.5 at.% Ca-Li:
	(1000)	(Conductive)	500 h exposure showed conductive with dissolved film so it is not desired to pursuit, but to learn the surface microstructure and chemistry, it is under running.	Not acceptable

^a "Good insulator" indicates satisfaction of the requirement resistance times area value in the MFR application.

^b For V-5Cr-5Ti.

Table 2. Thickness for the in-situ coating deposited on V-4Cr-4Ti in 2.8 at. % Ca-Li for 747.5 h at 600°C.

No.	O-charging method	^a O (Wppm)	Calcul'd film thickness (μm)	Meas'd film thickness (μm)
25	Cr/Cr ₂ O ₃	[4895]	-	-
26	Cr/Cr ₂ O ₃	[1838]	12.1	-
27	Cr/Cr ₂ O ₃	[12374]	11.1	-
28	Cr/Cr ₂ O ₃	[14691]	-	26.3
29	-	[400]	-	11.4
35	Cr/Cr ₂ O ₃	[1431]	5.5	-
45	Ar(O)	4858	4.9	-
46	Ar(O)	6400	-	25.0

Note: ^a Brackets indicate that O-Wppm, including total wt. changed during the quartz sealing cell in the Cr/Cr₂O₃ equilibrium. Some portion of the weights to be affected by the addition of Si and Cr; therefore, real O-wppm should be lower than those in brackets.

Table 3. Raw data for sample treatment for the exposure in 2.8 at.% Ca-Li at 600°C for 623 h (NIFS-II heat).

	Units	NIFS-II Heat Samples			
		2-D3	3-D3	7-D3	6-D5
As-received (AR) sample weight = W _i	(g)	1.1655	1.2482	1.122	1.1465
Surface area of sample	(cm ²)	4.745	5.039	4.590	4.677
Sample wt. after O-charged	(g)	1.1690	1.2522	1.1280	1.1533
Sample wt. O-homogenized, W _o	(g)	1.1691	1.2524	1.1278	1.1534
W(O) = [150 Wppm (AR) + W _o]	(Wppm)	3750	4350	5950	7050
	(mg/cm ²)	0.9211	1.0775	1.4544	1.7280
Thickness, film calculated by W(O), t(O)	(μm)	9.92	11.60	15.66	18.61
Post exposure in 2.8 at.% Ca-Li = W _f	(g)	1.1785	1.2615	1.1392	1.1663
W(I) = W _f - W _i = Wt. of CaO	(mg/cm ²)	2.7397	2.6393	3.7470	4.2331
Thickness calculated from W(I), t(CaO)	(μm)	8.43	8.12	11.53	13.03
W(II) = W _f - W _o = Wt. of Ca	(g)	1.9810	1.8059	2.4835	2.7580
Thickness calculated from W(II), t(Ca)	(μm)	8.53	7.78	10.70	11.88
Film dissolution rate, R _d = [t(O)-t(CaO)]/623 h	(μm/h)	[2.39 x 10⁻³]	5.56 x 10⁻³	6.62 x 10⁻³	8.96 x 10⁻³
Chemical composition EDS analysis (film surface)	at.% Ca	85.0	77.35	80.60	82.03
	at.% Ti	0.08	0.000	0.000	0.000
	at.% V	14.84	22.65	19.40	17.97
	at.% Cr	0.000	0.000	0.000	0.000

Table 4. Thickness for the in-situ coating on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure for 99 h at 700°C.

No.	O (Wppm)	Y-coated	Thickness Measured (µm)	Heat
79	as rec'd	no	4.3	US
D-1	2000	no	6.1	NISF
D-8	6000	no	8.5	NIFS

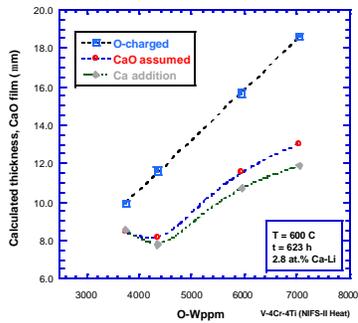


Fig. 1. Calculated thickness vs. O-content for the in-situ formed CaO film using the various weight change after exposure in 2.8 at. % Ca-Li at 600°C for 623 h. (See Table 3.)

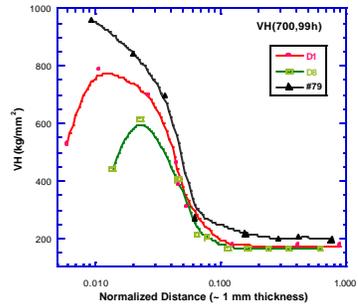


Fig. 2. Vickers hardness across the V-4Cr-4Ti exposed in 2.8 at.% Ca-Li at 700°C for 99 h with the D1, D8, and #79 samples.

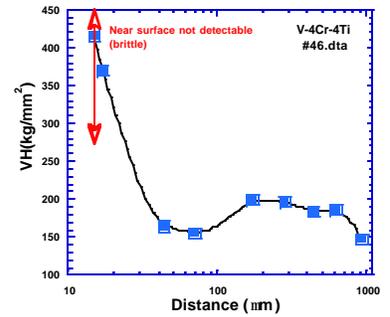


Fig. 3. Vickers hardness (VH) across the V-4Cr-4Ti (#46) exposed in 2.8 at. % Ca-Li at 600°C for 747.5 h. Near surface was very brittle.

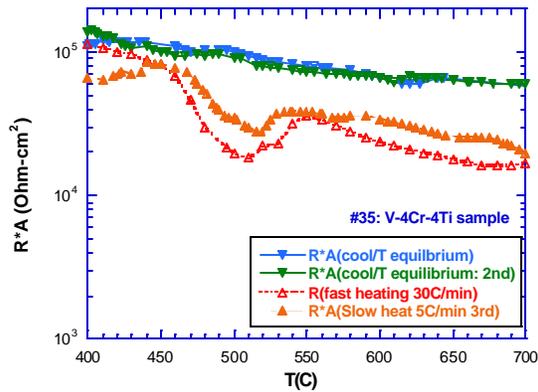


Fig. 4. Electrical resistance times area vs. temperature in an inert atmosphere for the film formed on the V-4Cr-4Ti (#35) after exposure in the 2.8 at. % Ca-Li at 600°C for 747.5 h.

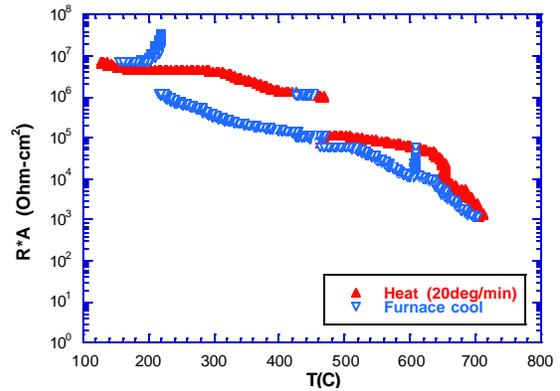


Fig. 5. Electrical resistance times area for the in-situ coated V-4Cr-4Ti in 2.8 at. % Ca-Li for 623 h (#7D3) (NIFS-II heat). For the heat cycled performance from heating and then cooling.

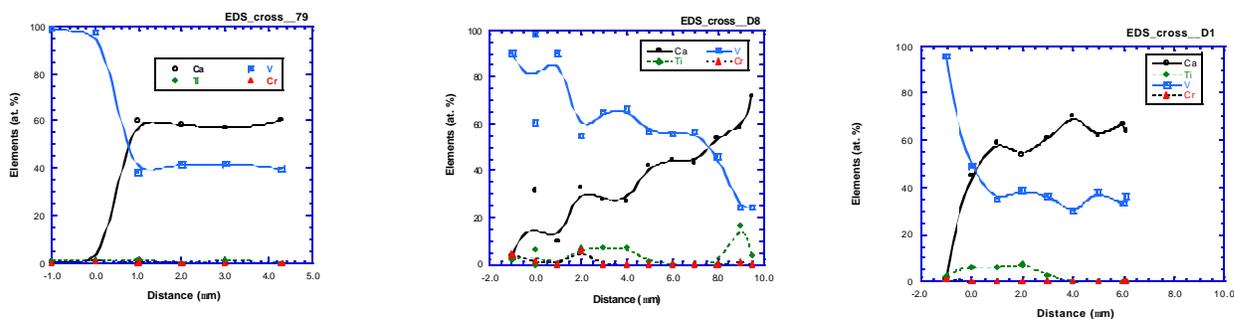


Fig. 6.

Cross-section EDS analysis near the interface of V-4Cr-4Ti/film. Samples were exposed in 2.8 at.% Ca-Li at 700°C for 99 h, and the excessive Ca-Li dissolved in methanol for 20 h. Sample numbers are noted in the right top corner of each figure. Sample description is in Table 4.

Table 4. Thickness for the in-situ coating on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure for 99 h at 700°C.

No.	O (Wppm)	Y-coated	Thickness Measured (μm)	Heat
79	as rec'd	no	4.3	US
D-1	2000	no	6.1	NISF
D-8	6000	no	8.5	NIFS

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