Preliminary Investigation on the Deposition of Y-O and Si-O Films on V-4%Cr-4%Ti for the In-situ Forming of CaO Coatings *

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OBJECTIVE

According to our previous study we have demonstrated the in-situ CaO insulator coating forming, generating defects under the thermal cycling condition, and self-healing of defects on V-Cr-Ti alloys in liquid lithium system,[1] and sintered Y_2O_3 is compatible with liquid Li.[2] This encouraging results caused us to investigate O-charged V-4Cr-4Ti with a Y film deposited by means of PVD. We are now investigating the in-situ forming of a CaO layer on a surface V-4Cr-4Ti enriched with Y-O or Si-O. In the study of insulator coatings on the V/Li blanket, the electrical insulation behavior should be maximized to have a thinner film that high toughness and thermal conduction. What need to be eliminated or minimized is V incorporation into the insulator film and in-situ self-healing. The addition of Si was objected to minimize the V incorporation in the in-situ forming film.

SUMMARY

We have investigated two ways to modify the V-4Cr-4Ti surfaces (Y deposition and Cr-Si-O addition) in preparation for forming CaO coatings on V alloys in liquid Ca-Li. Our earlier experimental studies indicated that sintered Y_2O_3 is compatible with liquid Li. In continuing studies, we have deposited thin (0.2, 0.8, and 1.5 μm) yttrium films on V-4Cr-4Ti substrates by physical vapor deposition (PVD). Annealing the thin Y-metallic PVD film on O-charged V-4Cr-4Ti at 750°C for 17 h formed an oxide film by the solid-state reaction between O and Y. Both energy dispersive spectroscopy (EDS) and X-ray diffraction indicated that the 0.2 and 0.8 μm Y-metallic films converted to either YVO_3 or $Y_8V_2O_{17}$ after annealing, but the thicker (1.5 μm) Y-metallic film developed two phases as $Y_8V_2O_{17}$ and Y_2O_3. When these samples were exposed in 2.8 at.% Ca-Li at temperatures of 700°C for 99 h, a uniform-microstructure CaO layer was formed on the top of the Y-V oxides, but localized Y was not detected by cross-sectional EDS analysis. However, the thicker films were shown to have a localized spallation problem between V-4Cr-4Ti and the oxide after annealing, so we ceased the exposure tests. The Si-O addition was performed by $Cr+Cr_2O_3$ equilibrium inside a vacuum-sealed quartz (SiO_2) chamber at 950°C for 17 h followed by exposure to 2.8 at.% Ca-Li at temperatures of 700°C for 99 h. This yielded an adhesive, water insoluble, and highly resistive Ca-Si-O film.

INTRODUCTION

Also investigated was Cr-Si-O addition based on a thermodynamic evaluation. The addition of Si was objected to minimize the V incorporation in the in-situ forming film. Our previous investigations showed that the incorporation of V into the in-situ-formed CaO was normally 15 to 35 at.%. If V is highly incorporated, the film could be conductive due to the V having a wide range of ionic. Based on the thermodynamic evaluation, additions of Si could form as Ca-Si-O in the Ca-Li environment. Therefore, we performed surface modification by $Cr+Cr_2O_3$ equilibrium inside a vacuum-sealed quartz (SiO_2) chamber. When the oxygen partial pressure (pO_2) is low, such as the level corresponding to $Cr+Cr_2O_3$ equilibrium at high temperatures, the quartz becomes the source of Si, Si-O, and Cr that are incorporated into the V-4Cr-4Ti along with O in the chemical vapor.

Based on these concerns, we initiated study of the Y and Si additions to the in-situ CaO films, and we are reporting the results of short exposures and expect continuation of testing.

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EXPERIMENTAL PROCEDURE

PVD Y-film deposit: We O-charged a conventional argon-oxygen gas, and yttrium metal was evaporated by use of a tungsten-heating element within an ultra-high-vacuum chamber to deposit films with thicknesses of between 0.2 to 1.5 µm. Samples were annealed at 750°C for 13 h in the vacuum. The Y film reacted with the pre-charged O in the V-4Cr-4Ti to convert to Y-O. The films were analyzed by scanning electron microscopy, EDS, and investigated the microstructures by SEM and chemical analysis by EDS, and X-ray diffraction.

V-4Cr-4Ti annealing in the Cr+Cr_2O_3: We have performed the simultaneous additions of Si and O by means of Cr+Cr_2O_3 equilibrium inside the vacuum-sealed quartz (SiO_2) chamber at 950°C for 17 h. The above samples were exposed to 2.8 at.% Ca-Li at 600-700°C for between 99 and 747.5 h. Experimental details can be found in our previous reports.[3]

Y_2O_3 ceramic: For comparison, we exposed a rectangular sample of sintered Y_2O_3 ceramic in 2.8 at.% Ca-Li at 600°C for 623 h.

RESULTS AND DISCUSSIONS

Sintered Y_2O_3 ceramic: The sintered Y_2O_3 samples exposed to 2.8 at.% Ca-Li at 600°C for 623 h were intact except for surface darkening. The measured geometry remained the same before and after the exposure. This result was similar to our previous test in pure liquid Li at 425°C for 240 h.

Investigation on Y-coated V-4Cr-4Ti: Figure 1shows the stepwise X-ray diffraction studies for each process: Spectra are given for the Y-deposit, sample annealed at 750°C, and sample after exposure at 700°C in 2.8 at.% Ca-Li for 99 h. The x-ray spectrum for the exposure in the 2.8 at.% Ca-Li was identical with that for the samples exposed without Y deposit. Since the CaO film was formed and grew in-situ it was expected that those film structures might be identical. The CaO film in Y-O coated samples was thicker than without the coating. Table 1 presents film thickness for the in-situ coatings deposited on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure for 99 h at 700°C for the Y-coated (t = 0.5 µm) samples. The film chemical analysis done by EDS is shown in Fig. 2.

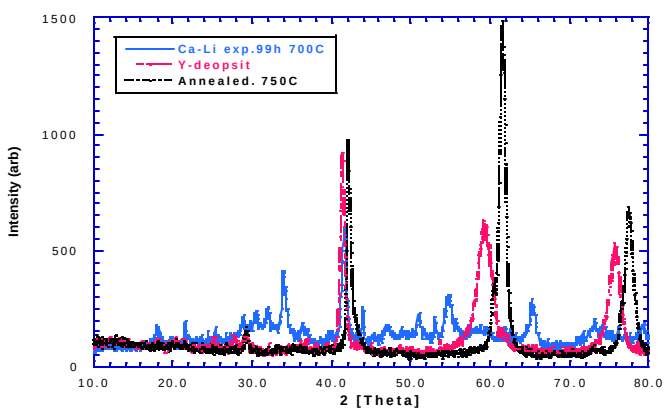

Fig. 1.

X-ray diffraction for sample #33 (Table 1). Pattern for Y-deposit, after annealing at 750°C, and after exposure at 700°C in 2.8 at. % Ca-Li for 99 h.

Table 1. Thickness of the in-situ coating deposited on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure for 99 h at 700°C for the Y-coated (t = 0.5 µm) samples.

Sample No.	O (wppm)	Y deposit (µm)	XRD, annealed @750°C 13 h	Film t (µm) SEM	Note
33	400	0.2	$Y_8V_2O_{17}$	11.8	Film thicker in Y-O coated samples.
47	7000	0.35	YVO_3	9.5	
48	6600	0.35	-	10.0	
79	400	none	-	4.3	

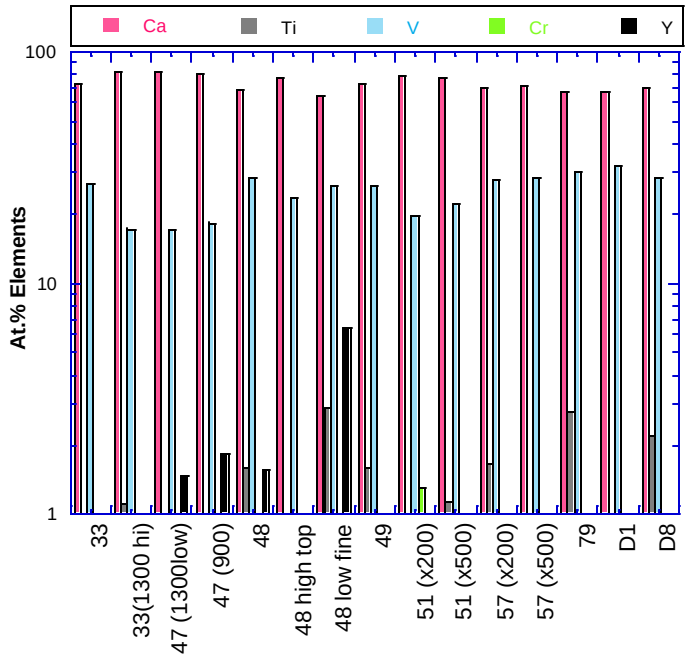

Fig. 2.

Elemental composition of the in-situ film formed on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure for 99 h at 700°C for the Y-coated samples. Parentheses indicate that the SEM magnification for the EDS analysis and hi = thicker area and low = thinner coating area (for the #79, D1, and D8 samples, not Y-coated samples)

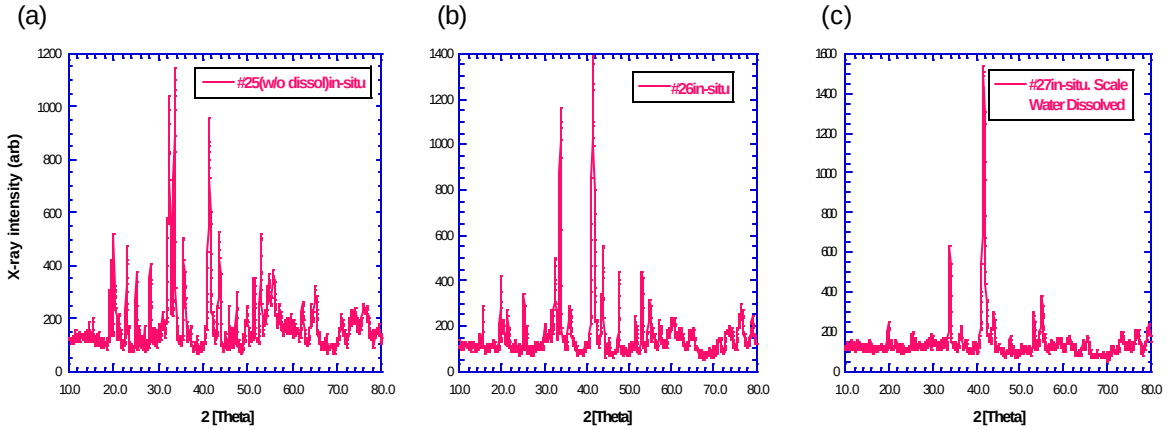

Fig. 3. X-ray diffraction for the in-situ formed scales on the V-4Cr-4Ti in the 2.8 at. % Ca-Li at 600°C for 747.5 h. O-charging done by $Cr+Cr_2O_3$ pack inside the vacuum-sealed quartz cell. (a) Without dissolution of the excessive Ca-Li residue on the sample surface (#25). The Ca-Li residue was minimized during removal of sample from the molten Ca-Li. (b) With dissolution in the ethanol (#26). (c) With dissolution in water, i.e. water insoluble layer (#27). (See Table 2.)

Si-Cr-O annealed V-4Cr-4Ti: Figure 3 shows the X-ray diffraction patterns for the in-situ formed films on the V-4Cr-4Ti in the 2.8 at. % Ca-Li at 600°C for 747.5 h. Shown are the patterns for the three distinct layers between the V-4Cr-4Ti and film: water insoluble layer, ethanol insoluble layer, and soluble layer. For the x-ray investigations the major spectrums are identical, but detailed analysis of the X-ray peaks still remains.

Table 2. Results of the EDS analysis for the sample surface from the in-situ coating performed on V-4Cr-4Ti in 2.8at.% Ca-Li exposure at 600C for 747.5 h for the samples annealed with $Cr+Cr_2O_3$ in a quartz cell. Beam energy (BE) = 10 keV otherwise noted otherwise.

No.	[a]O (Wppm)	Cal'd t (μm)	Meas'd t (μm)	Fraction of the element by EDS (at. fraction)					Note
				Ca	V	Ti	Cr	Si	
25	[4895]	-	-	0.513	0.462	0.0198	0.000	0.005	BE= 30 keV
26	[1838]	12.077	-	0.710	0.241	0.0018	0.000	0.047	
27	[12374]	11.154	-	0.476	0.163	0.0129	0.000	**0.348**	**[b]Water insoluble film**
28	[14691]	-	26.30	0.699	0.277	0.0000	0.000	0.024	
29				0.677	0.298	0.0000	0.000	0.025	
35	[1431]	5.5385	-	0.681	0.283	0.0155	0.000	0.020	
45				0.701	0.267	0.0017	0.000	0.031	
46				0.689	0.289	0.0067	0.000	0.015	BE = 40 keV

[a] Brackets indicate total wt. changed during the quartz sealing cell in test with the Cr/Cr_2O_3 atmosphere. Some Si and Cr may be affected. Real O-wppm should be lower than those in Brackets. This in-situ formed film was highly adhesive and high insulation based on our experience with in-situ formed films in Ca-Li environments. Currently, we do not have the electrical resistivity data required for the blanket design. Therefore, we plan to continue the study on the in-situ formed Ca-Si-O film on V-4Cr-4Ti.

Since we have found the adhesive with the V-4Cr-4Ti to be water insoluble and highly resistive (only checked at ambient temperature) for sample #27 (Table 2), we have calculated the free energy of formation for the Ca-Si-O shown in Fig. 4. As we see in Fig. 4, the Si incorporation in the in-situ formed Ca-Si-O film of #26 sample might effective as a buffer layer between CaO and V-4Cr-4Ti. In this film, V is 16 at.% (lowest) and Ca + Si = 83 at. % (highest) those are our targeted goal for the in-situ insulator coatings in Ca-Li environments.

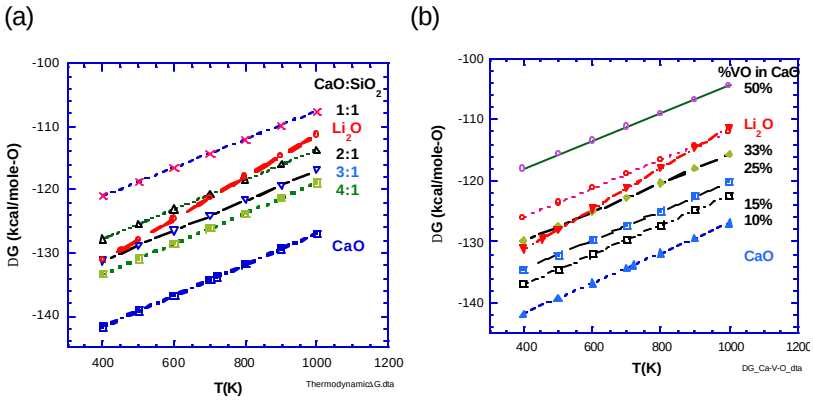

Fig. 4.

Gibbs free energy, ?G for the formation of ternary oxides per mole of O.
(a) Ca-Si-O with various ratios of CaO and SiO_2 and, (b) Ca-V-O. See water insoluble in-situ formed Ca-Si(V)-O (#27). (See Fig. 3 and Table 2.)

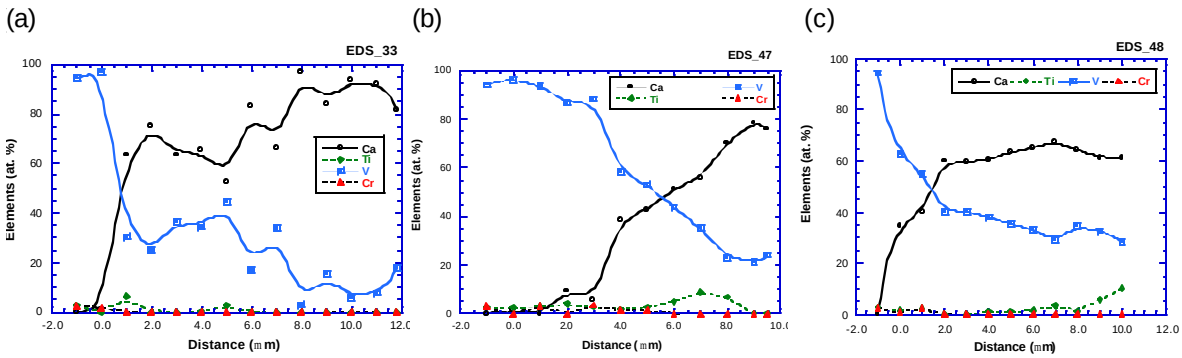

Fig. 5. Cross-section EDS analysis near the interface of V-4Cr-4Ti and film. Samples were exposed in 2.8 at.% Ca-Li at 700ºC for 99 h, and the excessive Ca-Li was dissolved in methanol for 20 h. Sample numbers are noted in the right top corner of the each figure. Sample description is given Table 1.

FUTURE SUGGESTED WORK

Our previous studies were limited to short (t = 100 h) exposures of Ca-Li at T = 700°C. Currently, the 700°C exposure for a longer time (t =1000 h) is the challenge. Y was intact based on our previous liquid metal-compatibility test, but Y collects hydrogen that penetrates through the metal wall from environmental moisture into the liquid metal to form the thermodynamically stable cubic yttrium hydride (YH_2) from the hexagonal cross-packed-Y. Therefore, for the deposition of Y-metallic film on the O-charged V-4Cr-4Ti, followed by exposure of the in-situ formed Y-Ca-O layer in the Ca-Li environment at 700°C, it is expected that the Y_2O_3 layer is intact. When a micro-crack is generated, however, the Ca and O will behave as self-healing defects. In this case, O in the micro-cracked zone reacts with Ca for the formation and dissolution; these processes will continue until the amount of O in the V-4Cr-4Ti is completely consumed. At 700°C rates for the forming and dissolution of film are high, so it is necessary to slow down or block the outward diffusion of (V and) O through the film layer after the film forms. This approach is similar to the reactive element effect in the high-temperature oxidation of metals obtained by the addition(s) of proper cations into the in-situ forming films beyond the yttrium oxide films. We expect that Si could be the best choice due to its stable thermodynamic nature in liquid-Li when it forms Ca-Si-O, as shown in Fig. 4.

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REFERENCES

1 J. -H. Park and T. F. Kassner, CaO Insulator Coatings and Self-healing of Defects on V-Cr-Ti Alloys in Liquid Lithium System, J. Nucl. Mater. 233-237, 476-481 (1996).

2 J. -H. Park, M. R. Fox, and G. Dragel, DOE/ER-0313/13, 260-275, and 290-294 (1992).

3 J. -H. Park, A. Sawada, K. Natesan, D. Rink, and R. F. Mattas, Progress of In-situ Coatings on the V-4Cr-4Ti in 2.8 at. % Ca-Li at 600 & 700ºC, Fusion Materials Semiannual Report Vol. #32 (2002).