

Microstructures of Y-O, Si-O, and In-Situ Formed CaO Coatings on V-4%Cr-4%Ti in Liquid 2.8 at.% Ca-Li^{*} J.-H. Park and K. Natesan, Energy Technology Division, Argonne National Laboratory, Argonne, IL 60439 USA

OBJECTIVE

The object of this work is development of electrically insulating coatings for vanadium alloys, one of the leading candidate materials for the first-wall/blanket structures in fusion reactors.

INTRODUCTION

In a previous study, we demonstrated the in-situ formation of a CaO insulator coating, generating defects under thermal cycling conditions, and self-healing of defects on V-Cr-Ti alloys in the liquid lithium system.¹ We also found that sintered Y₂O₃ is compatible with liquid Li.² These encouraging results caused us to investigate O-charged V-4Cr-4Ti with a Y film deposited by means of physical vapor deposition (PVD). We are now investigating the in-situ formation of a CaO layer on a V-4Cr-4Ti surface enriched with Y-O or Si-O. In the study of coatings on the V/Li blanket, the electrical insulation behavior should be maximized to have a thin film with high toughness and thermal conduction. What needs to be eliminated or minimized is V incorporation into the insulator film and in-situ self-healing. In this report we present microstructures for the electrical insulator coating reported previously.³

Also investigated was Si-O addition based on a thermodynamic evaluation. The addition of Si was tested to minimize the V incorporation in the in-situ CaO 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 valence states. Based on the thermodynamic evaluation, we determined that additions of Si could form as Ca-Si-O in the Ca-Li environment. Therefore, we performed surface modification by Cr+Cr₂O₃ equilibrium inside a vacuum-sealed quartz (SiO₂) chamber. When the oxygen partial pressure (pO₂) is low, such as the level corresponding to Cr+Cr₂O₃ equilibrium at high temperatures, the quartz becomes the source of the 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.

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 and 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 and we investigated the microstructures by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray diffraction.

Si-O enrichment on the surface of V-4Cr-4Ti by annealing in Cr+Cr₂O₃ pack sealed quartz cell: We have performed the simultaneous addition of Si and O by means of Cr+Cr₂O₃ equilibrium inside a vacuum-sealed quartz (SiO₂) 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

RESULTS AND DISCUSSIONS

Investigation of Y-coated V-4Cr-4Ti: Figure 1 shows a typical PVD film deposit on V-4Cr-4Ti and post-annealed specimen #33. Figure 2 shows the X-ray diffraction patterns for each step of the process:

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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 the 2.8 at. % Ca-Li exposure for 99 h at 700°C for the Y-coated ($t \leq 0.5 \mu\text{m}$) samples. Figure 3 shows the typical microstructure for the Y-O film prepared by conventional gas-phase oxidation after PVD Y-deposition on the V-4Cr-4Ti substrate at 500°C in a flowing argon gas, with a trace amount of oxygen being used for the oxidation process. However, PVD film deposition started showed limitation when it desire thickness, $t \geq 1\text{-}\mu\text{m}$ film. Figure 4 shows the typical local buckling initiation during the Y-deposition, when we tried to fabricate $t \geq 2\text{-}3\mu\text{m}$ films, buckling became enlarged as we expected from the mechanical stress dissipation by the film failure. Figure 5 shows the SEM surface microstructure for YVO_3 film prepared from a thin ($t = 0.35 \mu\text{m}$) Y-metallic PVD film deposited on V-4Cr-4Ti and then annealed at 750°C for 13 h in vacuum for the specimen #47 (see Table 1).

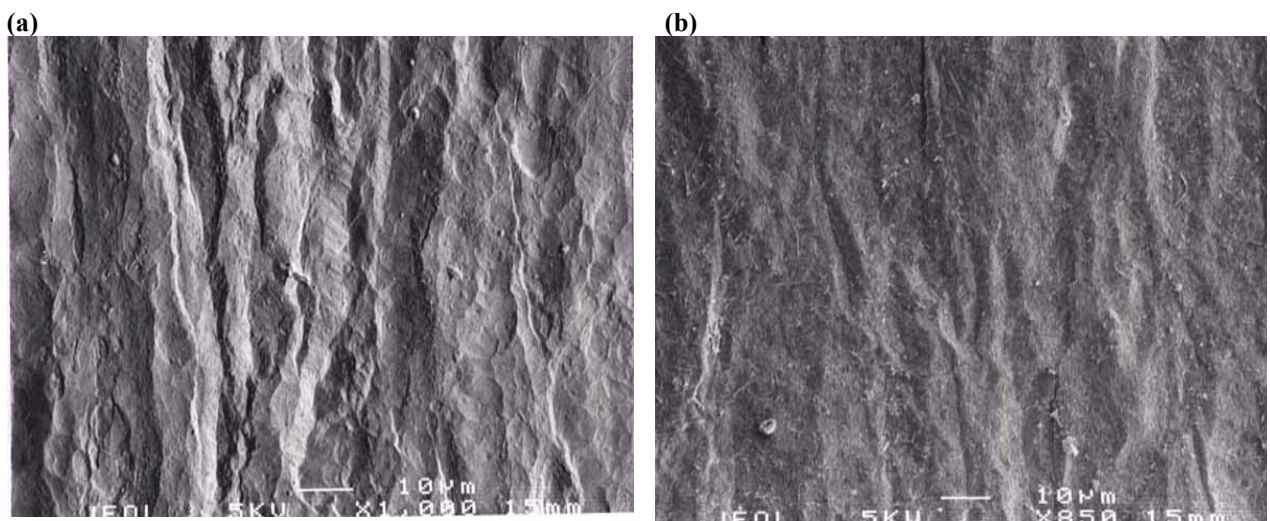


Fig. 1. SEM surface microstructure for (a) thin ($t = 0.2 \mu\text{m}$) Y-metallic PVD film deposit on V-4Cr-4Ti, and (b) sample #33 annealed at 750°C for 13 h in vacuum to convert $\text{Y}_8\text{V}_2\text{O}_{17}$ film.

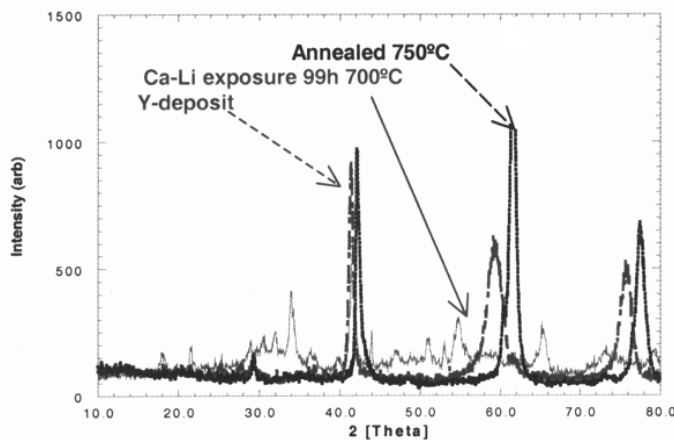


Fig. 2.

X-ray diffraction for sample #33 (see 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.

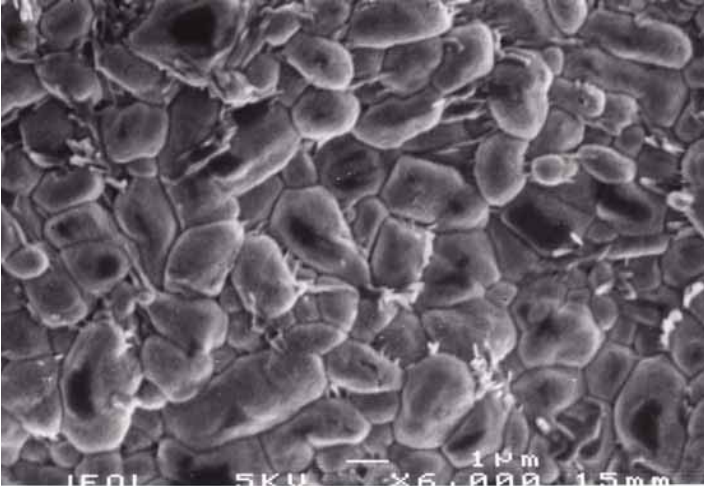


Fig. 3.

Typical microstructure for the Y-O film prepared by the conventional gas phase oxidation after Y-deposition on V-4Cr-4Ti substrate at 500°C in flowing Ar gas.

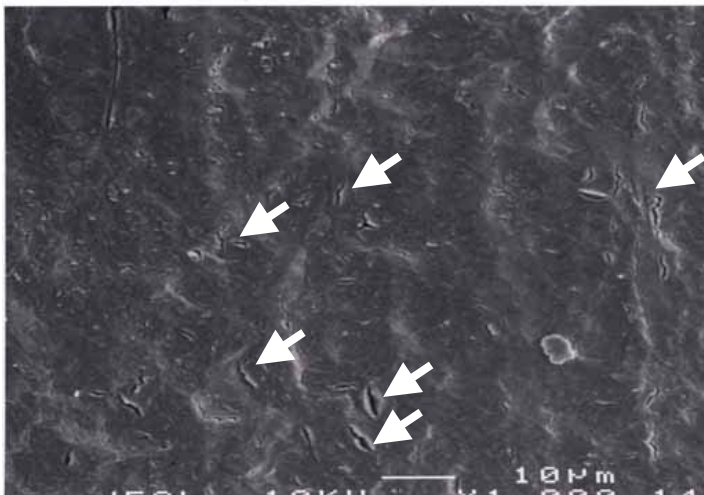


Fig. 4.

Typical microstructure for the thicker ($t \geq 1.0 \mu\text{m}$) Y-metallic film deposit on V-4Cr-4Ti by PVD. Spots or area shown by arrows started buckling.

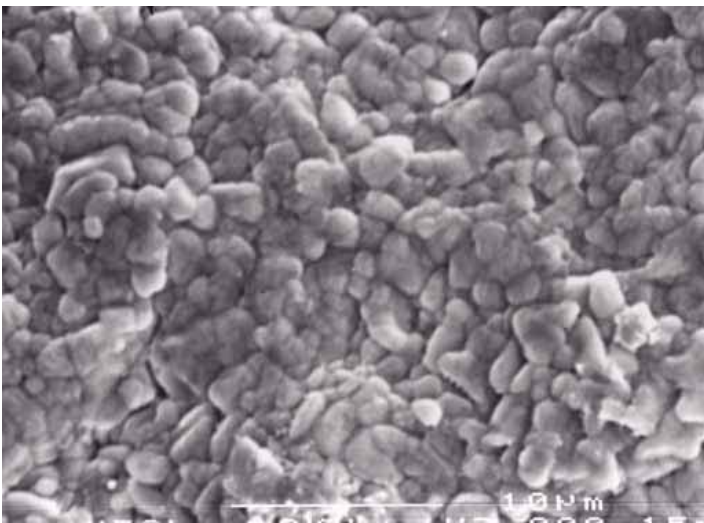


Fig. 5.

SEM surface microstructure for YVO_3 film prepared from a thin ($t = 0.35 \mu\text{m}$) Y-metallic PVD film deposited on V-4Cr-4Ti and then annealed at 750°C for 13 h in vacuum for the specimen #47 (see Table 1).

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 ($t \leq 0.5 \mu\text{m}$) samples.

Sample No.	O (wppm)	Y deposit (μm)	XRD annealed @750°C 13 h	Film t (μm) by SEM
33	400	0.2	$\text{Y}_8\text{V}_2\text{O}_{17}$	11.8
47	7000	0.35	YVO_3	9.5

Si-Cr-O annealed V-4Cr-4Ti: Figure 6 shows the X-ray diffraction pattern and SEM micrographs for the in-situ formed films on the V-4Cr-4Ti in 2.8 at. % Ca-Li at 600°C for 747.5 h. Shown are the patterns for the layer between the V-4Cr-4Ti and water insoluble layer in Fig. 6 (a), and for the cross-section SEM view near the V-4Cr-4Ti/CaO film in Fig.6 (b), which shows a very adherent film to the V-4Cr-4Ti substrate. Initially, O-charging was done by a Cr+Cr₂O₃ pack inside the vacuum-sealed quartz (SiO₂) cell.

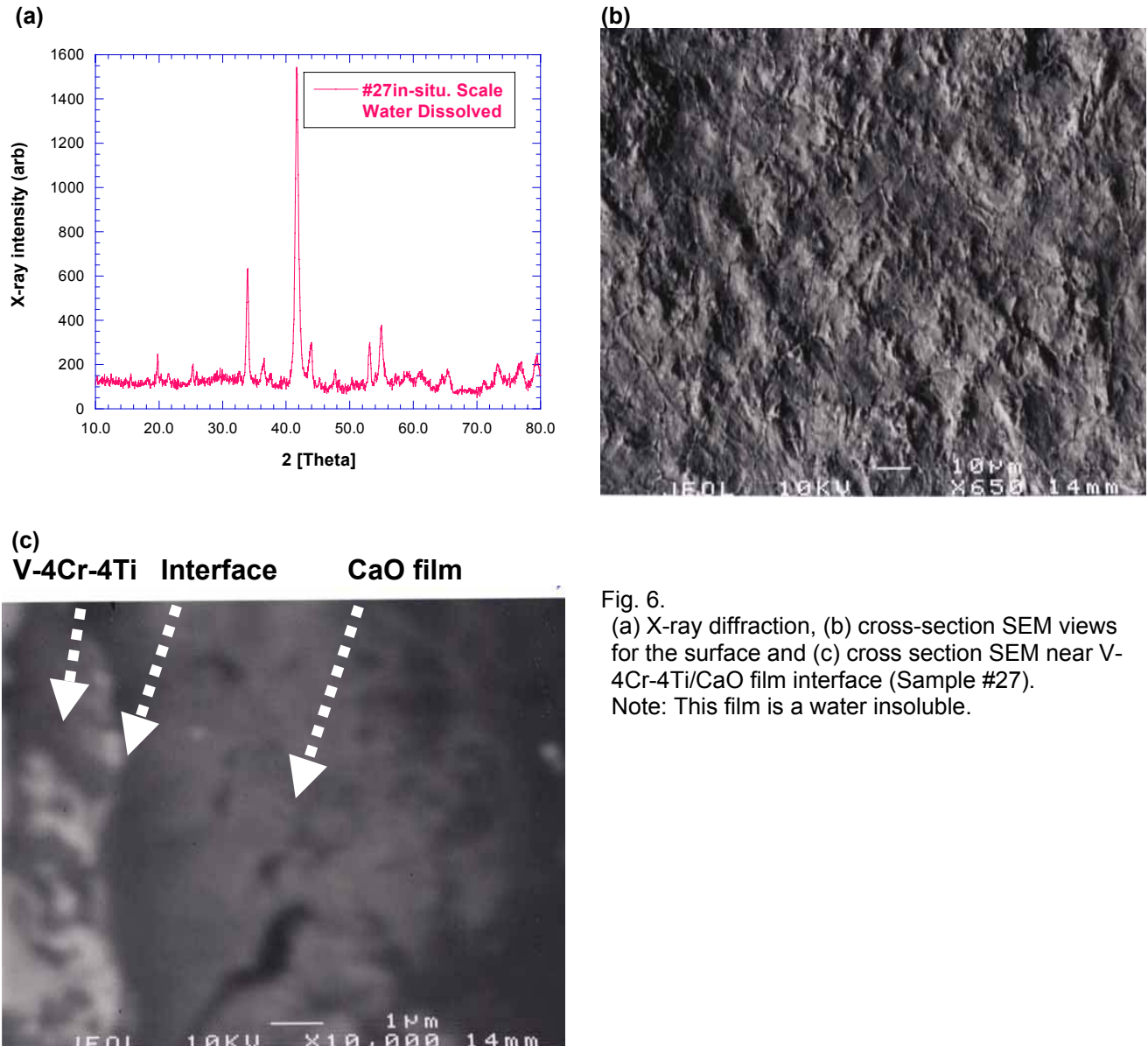


Fig. 6.
 (a) X-ray diffraction, (b) cross-section SEM views for the surface and (c) cross section SEM near V-4Cr-4Ti/CaO film interface (Sample #27).
 Note: This film is a water insoluble.

Table 2. Results of EDS analysis for sample surface from in-situ coating performed on V-4Cr-4Ti in 2.8 at. % Ca-Li exposure at 600°C for 747.5 h for the samples annealed with Cr+Cr₂O₃ in a quartz cell.

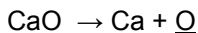
No.	^a O (Wppm)	Cal'd t (μm)	Meas'd t (μm)	Fraction of the element by EDS (at. fraction)					Note
				Ca	V	Ti	Cr	Si	
27	[12374]	11.154	-	0.476	0.163	0.0129	0.000	0.348	^b Water insoluble film

^a Brackets indicate total wt. changed during the quartz sealing cell in test with the Cr/Cr₂O₃ 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 insulating 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. ^bsee Fig. 6.

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

FUTURE SUGGESTED WORK

We expect that Si additive could be the best choice due to its stable thermodynamic nature in liquid Li where it forms Ca-Si-O, as shown in Fig. 4 in the previous semiannual report.³ So far we have focused on the formation of an in-situ film on the O-charged V-4Cr-4Ti. As we expected that the charged O will be consumed for the CaO-coatings or O-dissolution into the liquid metal, we expect that that adding of O into the lithium-(calcium) by CaO or Li₂O (i.e., similar idea to adding CaO) into the liquid metal might be an alternative approach to achieve thermodynamic stability of the in-situ formed films for longer time services. With both O and Ca in the lithium, the CaO layer will be much more stable. CaO does not dissolve in the lithium, but Ca does. Therefore, for CaO to be moved by the lithium, the following reaction has to occur:



The stability of CaO depends on the activity product of $a_{\text{Ca}}a_{\text{O}}$. Therefore, we will need to keep Ca concentration in the lithium, as well as O concentration in the lithium. With only Ca concentration, the product of $a_{\text{Ca}}a_{\text{O}}$ is near zero. The reaction above will go to the right, and Ca will dissolve in the lithium. Therefore, addition of O to the lithium improve the performance of the CaO coating ought to be pursued.

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