

DEVELOPMENT AND CHARACTERIZATION OF ELECTRICALLY INSULATING CaO COATINGS

K. Natesan, M. Uz, D. L. Rink, and D. L. Smith (Argonne National Laboratory)

OBJECTIVE

The objectives of this task are to (a) develop electrically insulating coatings, with emphasis on understanding the basic thermodynamic conditions and kinetic processes needed to develop stable coatings of CaO that are compatible in an Li/Li-Ca environment; (b) perform detailed postexposure analysis of the surface layers by several electron/optical techniques to characterize the elemental and phase compositions, quantify stratification in the layers, and establish the role of compositional changes in the coating and microstructure; (c) measure the electrical resistance of the coatings, before and after exposure to Li; and (d) establish optimal procedures from the standpoint of sample preparation, exposure time and temperature, and sequence of operations to obtain reliable and reproducible coatings with adequate electrical resistance for use in a Li environment.

SUMMARY

As part of the Department of Energy's Fusion Reactor Program, studies have been in progress at Argonne National Laboratory (ANL) to develop electrically insulating coatings on V-Cr-Ti alloys, in particular, on V-4Cr-4Ti which is the primary candidate for use in various structural applications, including in the first wall structure/blanket of a fusion reactor. The first wall will be in contact with liquid Li coolant and electrical conductivity across the wall will lead to magnetohydrodynamic, pressure losses during flow in the magnetic field. Hence, among the critical requirements of the rather stringent design criteria for the first wall material are that the coating on it be non-porous, tenacious, electrically insulating, and capable of maintaining its structural integrity while in use in a liquid Li environment at temperatures of 400-700°C. More information on the material requirements of fusion reactors is reported in an earlier publication.¹

This report addresses the development and characterization of a CaO coating that was applied on V-4Cr-4Ti alloy by a vapor transport (or thermal/chemical vapor deposition) process. Several coupon and rod specimens were coated with CaO by a double Ca-deposition/oxidation process that was developed at ANL.² The specimens were analyzed and the coating was characterized after each step of the process as well as before and after exposure to a liquid Li environment. The analysis and characterization involved the use of one or more of scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and X-ray diffraction (XRD) techniques. Results are presented, with emphasis on microstructural analysis of the samples and on the details of the developed experimental procedure.

EXPERIMENTAL PROGRAM

The pertinent parts of the experimental setups used for depositing CaO coating on V-4Cr-4Ti alloy specimens by the He-flow and vacuum processes are shown in Figs. 1 and 2, respectively. The materials, system details, and experimental procedures used in this study are described below.

MATERIALS AND SYSTEM DETAILS

The nominal composition of the alloy used in this study was V-4 wt.%Cr-4 wt.%Ti. The samples were either 1-mm-thick coupons or 5-mm-diameter rods. All of the specimens were annealed for 1 h at 1000°C in 10^{-7} torr vacuum before use. The Ca metal was redistilled -6-mesh granules with a purity of 99.5% on the metals basis. Stainless steel wire screen with 1-mm square openings was used to fabricate the \approx 20-mm-diameter cylindrical inner specimen chamber. The outer chamber, \approx 35-mm in diameter, was a quartz tube for the vacuum process, and a stainless steel tube for the He-flow process. Stainless steel wire and bolts/nuts were used to hold the

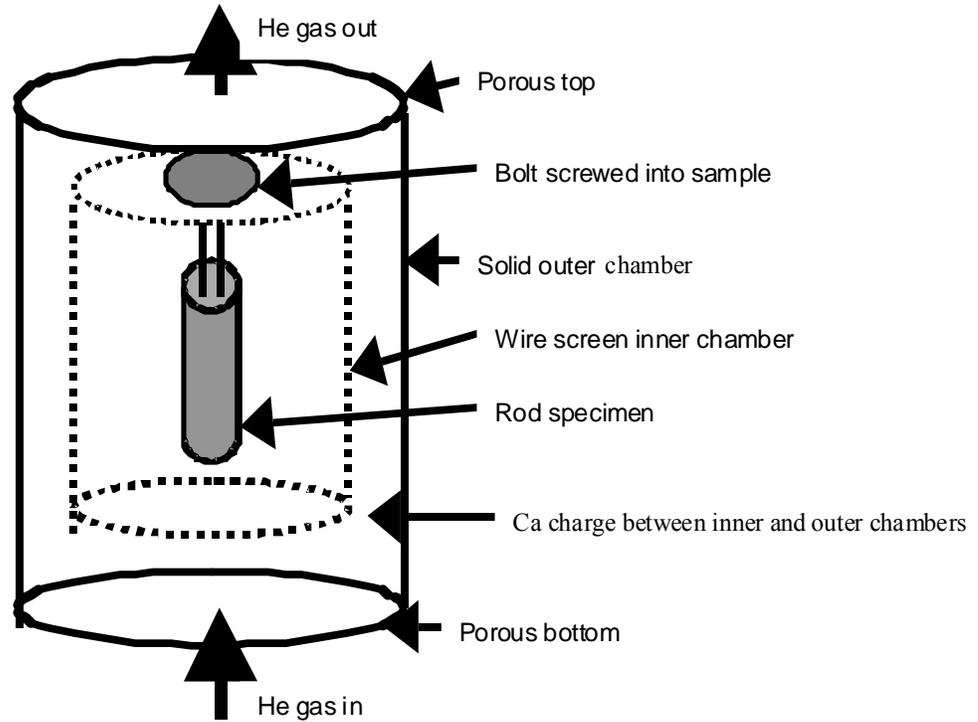


Fig. 1. Schematic illustration of experimental setup used during Ca-deposition steps of double Ca-deposition/oxidation process in He flow. All parts of setup were stainless steel.

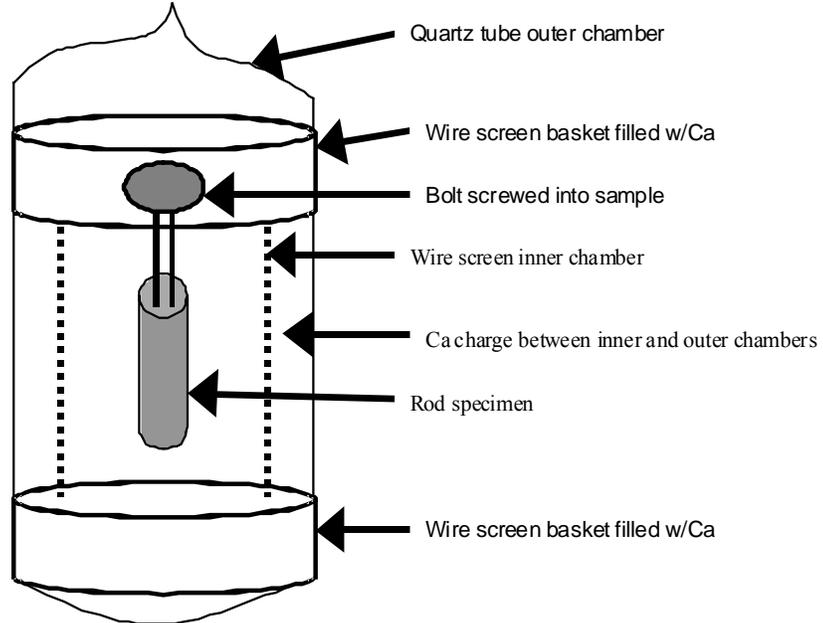


Fig. 2. Schematic illustration of experimental setup used during Ca-deposition steps of double Ca-deposition/oxidation process in vacuum. All parts of setup inside the quartz tube were stainless steel.

coupon samples and threaded rod samples, respectively, during the heating steps. A vertical high-temperature tube furnace, equipped with gas inlets/outlets, was used for Ca deposition by the He-flow process and for the oxidation step. A high-temperature muffle furnace was used to heat the sealed quartz tubes for Ca deposition by the vacuum process. The experimental environment consisted of flowing He or vacuum of 10^{-4} torr during the Ca-deposition steps and flowing Ar during the oxidation steps of the processes. Both He and Ar gases were 99.999% pure.

PROCEDURE

Calcium deposition by vapor transport relied on the relatively high vapor pressure of Ca metal at temperatures $>700^{\circ}\text{C}$. As can be seen from Fig. 3, the vapor pressure of Ca metal is >0.1 torr at 700°C , and approaches 1 torr at 800°C . Also, Ca metal readily oxidizes in any of the environments used in this study. Evaluation, testing, and analysis of specimens coated by a single Ca deposition/oxidation process showed that CaO produced this way did not exhibit the desired insulating characteristics or stability in liquid Li. Therefore, two processes that involve double Ca deposition/oxidation steps were developed to successfully coat V-4Cr-4Ti alloy samples with stable CaO.

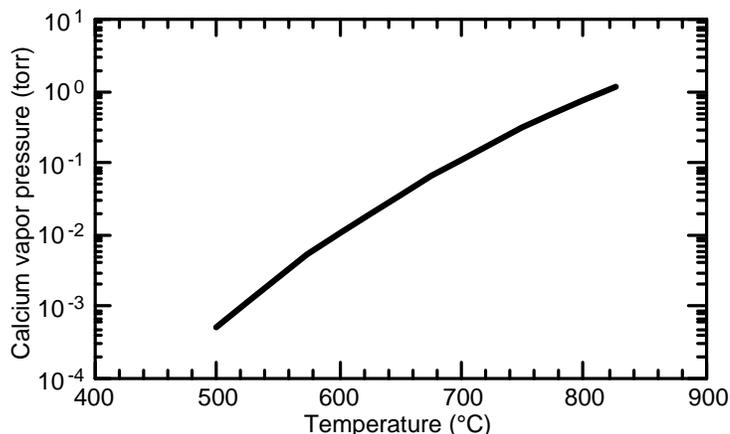


Fig. 3. Plot of Ca vapor pressure versus temperature.

He-flow process: The experimental setup used for Ca deposition in a flowing He environment is schematically illustrated in Fig. 1 with a rod specimen in place. The samples (coupons and/or rods) were hung vertically from the top of the wire screen inner chamber, which was placed inside the steel outer chamber that had a porous bottom and top. Granular Ca charge was placed between the inner and outer chambers. The first deposition of Ca was performed by heating the entire assembly in a flowing He environment at $775\text{-}800^{\circ}\text{C}$ for 100-150 h. Photographs of the inner chamber with the sample in place and parts of the experimental assembly after the Ca-deposition step are shown in Figs. 4a and 4b, respectively. Calcium-deposited specimens were subsequently oxidized in flowing Ar at $\approx 700^{\circ}\text{C}$ for 130-200 h in a quartz chamber inserted into a vertical resistance-wound furnace. The sequence of Ca deposition followed by oxidation was repeated to complete the double Ca deposition/oxidation process in He flow to obtain samples that were fully coated with stable CaO.

Vacuum process: A schematic representation of the experimental setup for depositing Ca during the vacuum process is shown in Fig. 2. The setup consists of a wire screen sample chamber that was sealed in a quartz tube with a vacuum of 10^{-4} torr. Granular Ca charge was placed around the inner chamber and in a cylindrical wire basket at the bottom, as shown in the figure A. A wire basket filled with Ca granules was also placed above the.

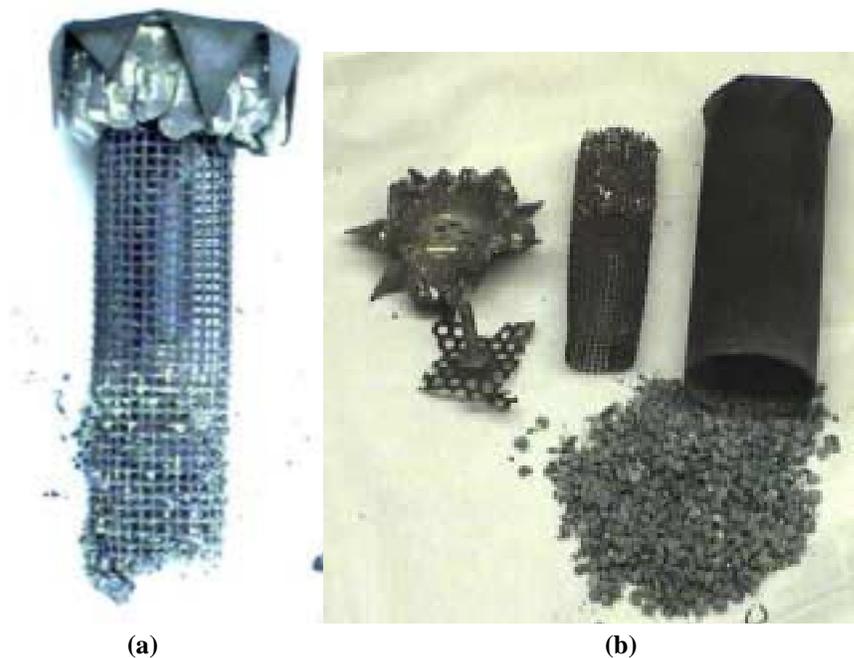


Fig. 4. Photographs of experimental set up after Ca-deposition step of of double Ca-deposition/oxidation in He-flow process. (a) Inner chamber with lid and rod specimen in place. (b) All experimental parts, including granular Ca charge, after use. All parts shown were stainless steel.

inner chamber to serve as a heat sink and to prevent the Ca charge from premature oxidation during the sealing of the quartz tube. The first Ca deposition step in this process involved a heat treatment of 100-150 h at 775-800°C in a muffle furnace. Figures 5a, b and c, respectively, show the inside of the quartz tube, the sample with its assembly, and a close-up of the coated sample following the Ca deposition step in vacuum. Ca-deposited samples were oxidized as described in the He flow process. Development of stable CaO on sample surfaces via double Ca deposition/oxidation in vacuum was again accomplished by repeating the Ca deposition and oxidation steps.

Following each step (Ca1, Ox1, Ca2, Ox2), sample surfaces were examined by SEM to characterize their microstructure. Chemical composition of the surface was determined by EDX and XRD analysis. After exposure to Li at 500, 600, and 700°C, both surfaces and cross-sections of several specimens were analyzed and characterized by the techniques described above

RESULTS AND DISCUSSION

Preliminary work on the development of the He-flow process, and the results from the testing and characterization of several V-4Cr-4Ti coupons coated with CaO were presented in earlier reports.²⁻⁵ It was reported that CaO coatings on V-4Cr-4Ti coupon samples remained intact after exposure to Li for 68 h at 500°C.^{1,5} The structural integrity of the CaO coating on each sample before and after exposure to Li was confirmed by examination and characterization of its surface and cross-sectional area by SEM for microstructure and SEM/EDX for elemental analysis of the surface and depth profile of the cross-sectional area. It was also reported that the electrical resistance, measured external to Li, of these coated samples was high and was in excess of the design requirements for a fusion device.



Fig. 5. Photographs of experimental setup after Ca-deposition step in double Ca-deposition/oxidation in vacuum. (a) quartz outer chamber. (Dark layer inside is Ca deposit.); (b) inner chamber with portion of quartz tube that contains some used Ca charge, and rod specimen with a bolt/nut assembly that held it in place inside inner chamber; (c) close-up of Ca-coated rod specimen. Except for quartz tube, all parts were stainless steel.

.During the present reporting period, several V-4Cr-4Ti specimens in the form of 1-mm-thick coupons and 5-mm-diameter rods were coated with CaO by the He-flow process, and exposed to Li for ≈ 100 h at 600 and 700°C. Li used for the 600°C exposure contained ≈ 10 at.% Ca, and Li used for the 700°C exposure was pure, i.e. contained no added Ca. Specimen surfaces and cross sections were analyzed by SEM/EDX after each step of the process and after exposure to Li. The coating on each sample exposed to Li was also identified by XRD; the results are presented in Table 1. SEM photomicrographs of the tip, middle, and top portions of the rod sample after exposure to Li (w/10 at.%Ca) at 600°C are shown in Fig. 6. Cross-sectional area of the coupon sample exposed to Li at 600°C and that for the rod sample exposed to pure Li at 700°C are shown in Fig. 7. X-ray diffraction analysis results are presented in Fig. 8 for the surfaces of rod and tab samples exposed for ≈ 100 h to Li that contained 10 at.% Ca. Figure 9 shows XRD patterns obtained from various locations along the length of a 70-mm-long rod specimen after exposure to pure Li for ≈ 106 h at 700°C, along with those from the rod specimen given in Fig. 8.

The results show that CaO coating on both the rod and coupon specimens was intact after exposure to Li-10 at.% Ca for ≈ 100 -h at 600°C. This was confirmed by SEM/XRD elemental analysis of each sample surface before and after Li exposure (see Table 1), and by XRD analysis after exposure to Li, which indicated the presence of CaV_2O_5 in the coating on these samples (see Fig. 8). Both samples were electrically insulating at room temperature before and after the exposure to Li. The 70-mm-long rod specimen that was exposed to pure Li at 700°C exhibited similar surface coating and electrically insulating characteristics at room temperature before exposure to Li. This sample was exposed to pure Li (i.e., Li with no Ca), for ≈ 100 h at 700°C. After the exposure, the sample exhibited no measurable electrical conductivity at room temperature. However, elemental

	Process Step ^a	T (°C)	Time (h)	Ca-Range ^b (Area) (at.%)	Ca _{min} (Spot) ^b (at.%)	O ₂ -Range ^b (Area) (at.%)	V-Range (Area) ^b (at.%)	CaO Thickness ^c (μm)	Phases identified by XRD ^d
4S14 coupon	Ca	737	125	30 - 50	25	30 - 60	1 - 25	13 - 20	CaO, CaV ₂ O ₅
	Ox	700	135	20 - 30	1	15 - 55	25 - 65		
	Ca	735	125	65 - 78	50	22 - 48	0 - 1		
	Ox	700	164	50 - 55	45	40 - 50	0 - 5		
	Li(w/Ca)	600	100	40 - 45	37	50 - 59	0 - 5		
44Rod2 rod	Ca	790	141	30 - 70	1	20 - 50	1 - 72	2 - 5	CaO, CaV ₂ O ₅ , V
	Ox	600	48						
		700	165	10 - 30	3	42 - 50	30 - 51		
	Ca	775	125	60 - 69	50	30 - 36	0 - 2		
	Ox	700	200						
44Rod3 rod	Ca	795	130	20 - 80	9	26 - 41	0 - 30	10 - 15	CaO, CaV ₂ O ₅
	Ox	700	174	20 - 50	1	13 - 50	0 - 80		
	Ca	780	125	25 - 60	25	28 - 58	0 - 30		
	Ox	700	200						
	Li(w/Ca)	600	100	30 - 52	30	39 - 60	0 - 18		

Table 1. Experimental conditions and results of coupon and rod samples coated with CaO by the process of double Ca-deposition/oxidation in He-flow

^aSteps in development of CaO coating by double Ca-deposition/oxidation process and subsequent exposure to Li; Ca and Ox indicate Ca-deposition and oxidation steps, respectively; Li (w/Ca) and Li indicate exposure of specimens to Li-10 at.% Ca and to pure Li, respectively.

^bObtained from EDX analysis of areas or spots on specimen surfaces.

^cObtained from measurement of scale thickness in SEM photomicrographs of specimen cross sections.

^dDetermined from the patterns obtained from XRD analysis of sample surfaces.

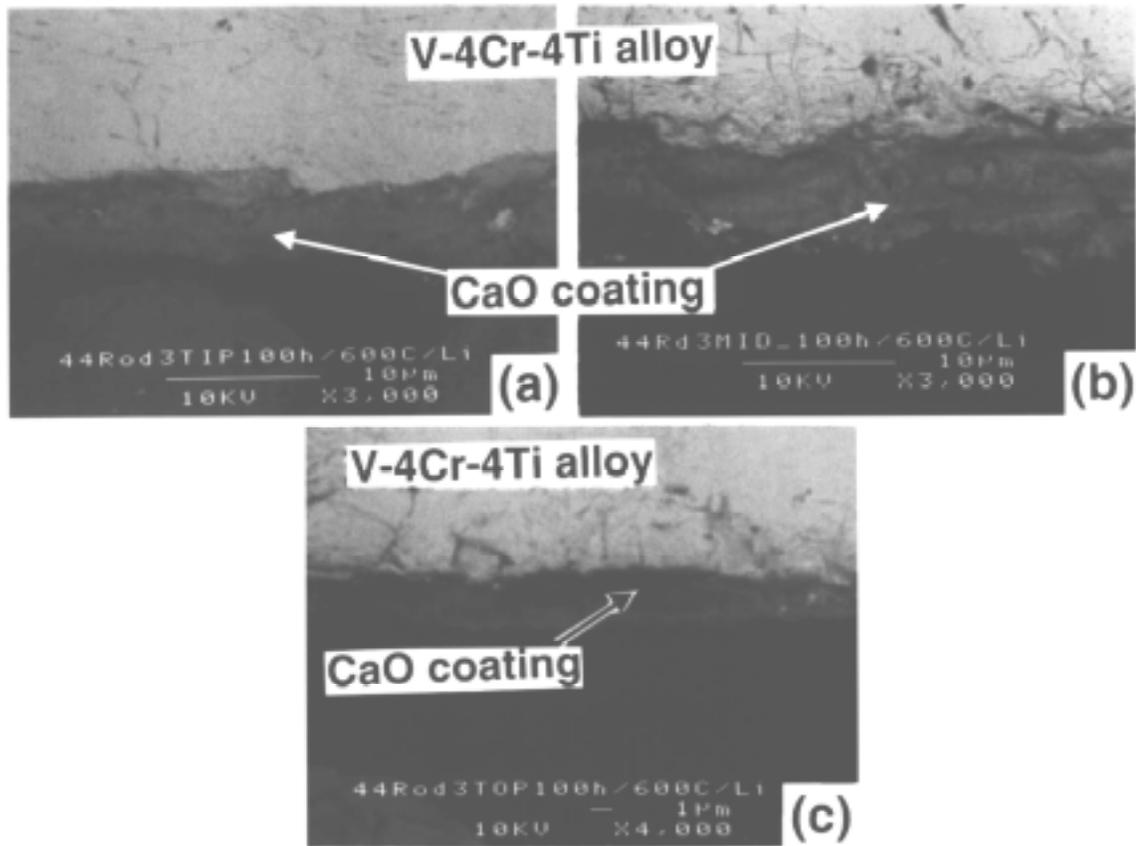


Fig. 6. SEM photomicrographs showing cross sections of (a) tip, (b) middle, and (c) top portions of 70-mm-long V-4Cr-4Ti rod specimen after exposure to Li-10 at.% Ca at 600°C for \approx 100 h. Specimen was coated with CaO by process of double Ca-deposition/oxidation in He flow.

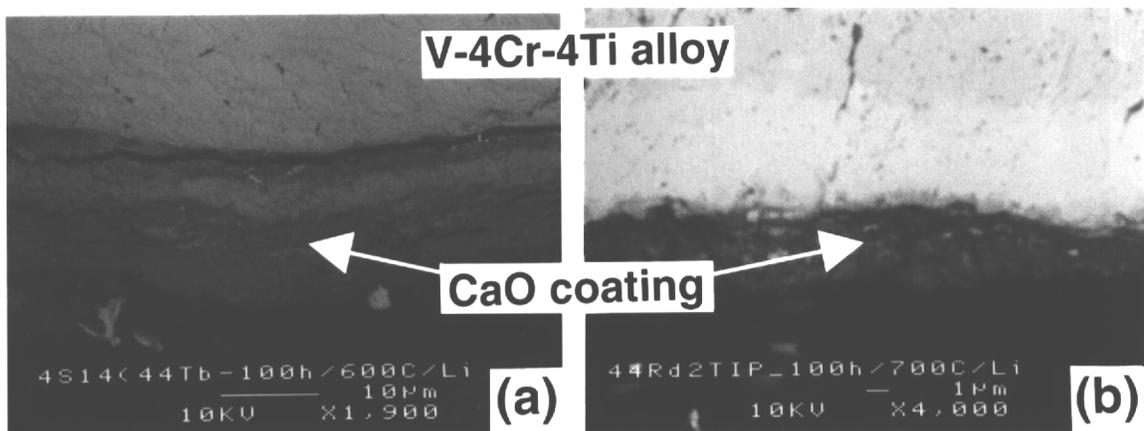


Fig. 7. SEM photomicrographs showing cross-sectional areas of V-4Cr-4Ti alloy specimens after exposure to liquid Li. (a) tab specimen exposed to Li-10 at.% Ca at 600°C for \approx 100 h; (b) rod specimen exposed to pure Li at 700°C for \approx 106 h. Both specimens were coated with CaO by double Ca-deposition/oxidation in He-flow process.

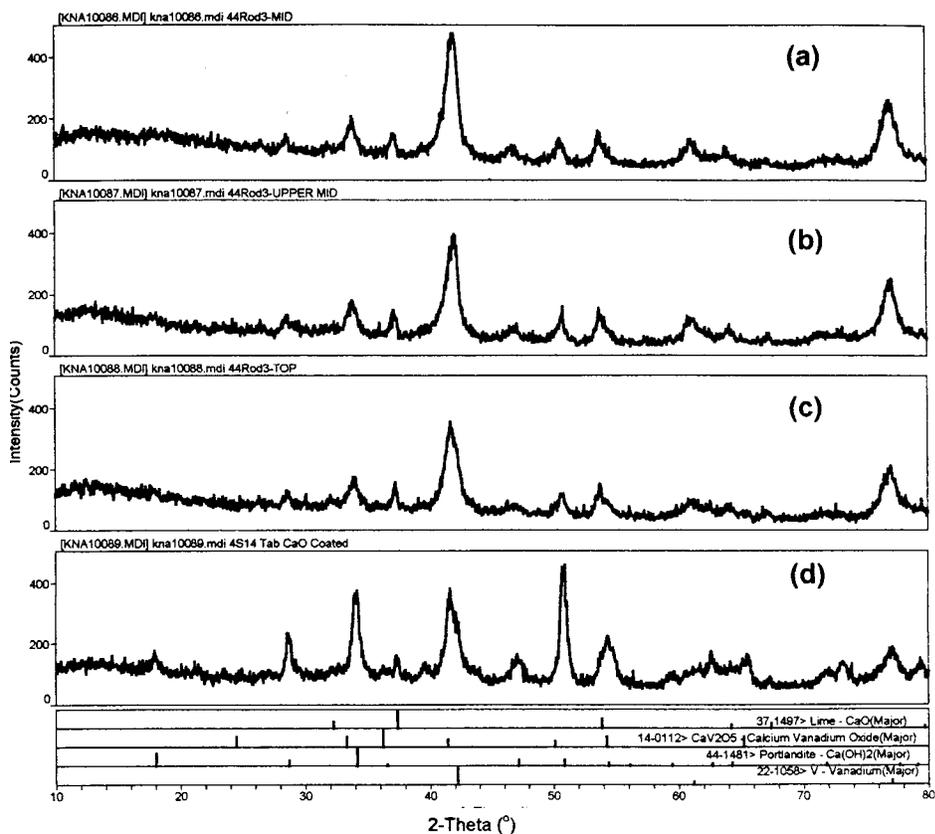


Fig. 8. X-ray diffraction patterns for surfaces of V-4Cr-4Ti samples after ≈ 100 h exposure to Li at 600°C . (a) Middle of rod, (b) upper-middle of rod, (c) top of rod, and (d) coupon.

analysis by SEM/XRD showed very little Ca on its surface (see Table 1), and the thickness of the coating was appreciably thinner than that of the others (see Figs. 6 and 7). X-ray diffraction analysis of the surface indicates the presence of various phases, including CaO, CaV_2O_5 , and V. These results indicate that Ca dissolved in Li may be an important consideration for the stability of electrically insulating CaO coating in liquid Li.

The goal of another series of studies initiated during the current reporting period is to develop the vacuum process described earlier in an effort to obtain a thicker coating by volatilizing a larger amount of Ca in vacuum. Also being investigated is the effect that O-precharging of the specimens exerts on the coating thickness, integrity, and stability in liquid Li. Most of the specimens from these experiments are in various stages of the double Ca-deposition/oxidation process. However, some of the preliminary results are provided in Table 2 and Fig. 10. Results indicate that either the He-flow or vacuum process may be used to coat V-4Cr-4Ti alloy with Ca, the vacuum system yielding a little higher amount of Ca and less oxygen. Also, there is a strong indication that O-precharging can lead to a measurably more uniform Ca concentration than the other two processes. Further results from these experiments will be provided in future reports.

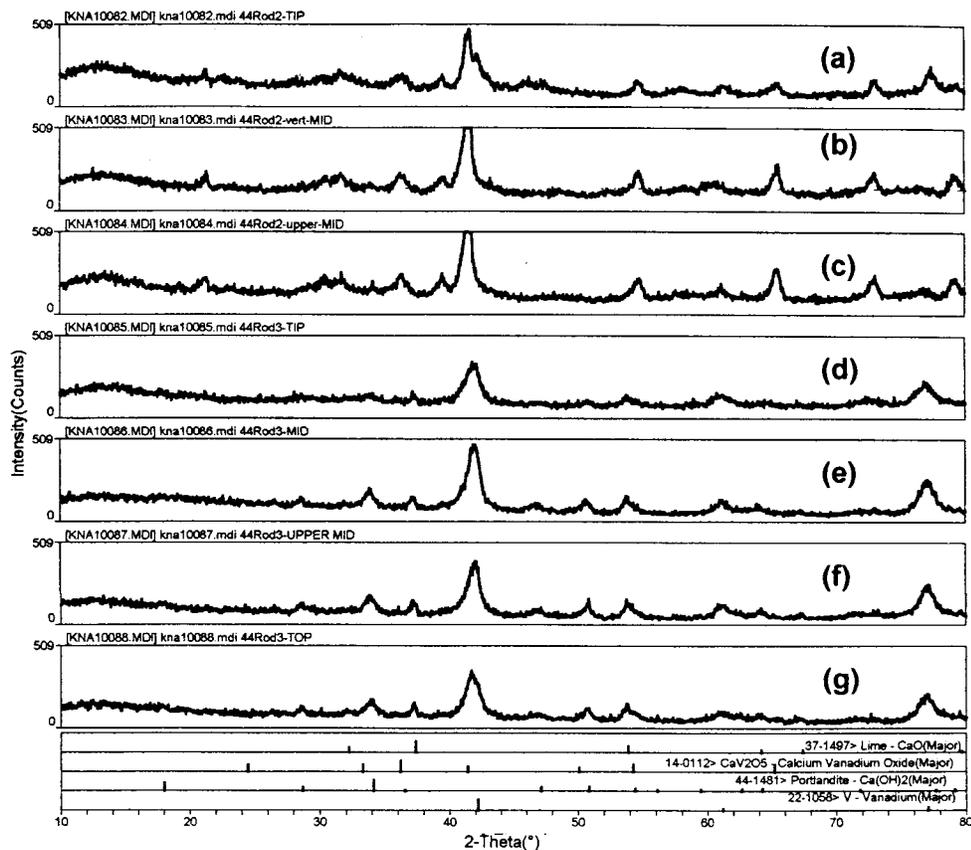


Fig. 9. X-ray diffraction patterns for surfaces at various locations along the length of 70-mm long V-4Cr-4Ti rod. (a)–(c): Rod after 106 h exposure to pure Li at 700°C and (d)–(g): Rod after \approx 100 h exposure to Li-10 at.% Ca at 600°C.

REFERENCES

1. K. Natesan, C. B. Reed, M. Uz, J. H. Park, and D. L. Smith, "Electrically Insulating Coatings for V-Li Self-Cooled Blanket in a Fusion System," Argonne National Laboratory Report ANL/TD/TM00-10, May 2000.
2. K. Natesan, Z. Zeng, W. E. Ruther, M. Uz, and D. L. Smith, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending June 30, 2000, Argonne National Laboratory, DOE/ER-0313/28, p. 30, September 2000.
3. K. Natesan, C. B. Reed, M. Uz, and D. L. Rink, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending June 30, 1998, Argonne National Laboratory, DOE/ER-0313/24, p. 82, September 1998.
4. K. Natesan, M. Uz, and S. Weider, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending December 31, 1998, Argonne National Laboratory, DOE/ER-0313/25, p. 69, April 1999.
5. K. Natesan, M. Uz, and S. Weider, "Development of Electrically Insulating CaO Coatings," Fusion Reactor Materials Progress Report for the Period Ending June 30, 1999, Argonne National Laboratory, DOE/ER-0313/26, p. 57, September 1999.

Table 2. Experimental conditions and Ca, O and V contents of V-4Cr-4Ti coupons after first Ca deposition step of double Ca-deposition/oxidation in He-flow and in vacuum processes.

Sample ID and pretreatment	Process Environment	T (°C)	T (h)	Ca-Range ^a (Area) (at.%)	Ca _{min} ^a (Spot) (at.%)	O ₂ -Range ^a (Area) (at.%)	V-Range ^a (Area) (at.%)
44-7 Pre-ox. ^b	Vacuum	775	120	60 - 90	50	1 - 50	0.5 - 2
44-31 As-is ^c	Vacuum	780	165	27 - 40	5	10 - 50	1 - 70
44-11 As-is ^c	He-flow	800	166	34 - 78	4	20 - 50	1 - 52

^aObtained from energy-dispersive x-ray analysis of areas or spots on sample surfaces.

^bCoupon preoxidized for 200 h at 600°C in 5×10^{-4} torr O₂.

^cCoupons with no pre-treatment of surfaces.

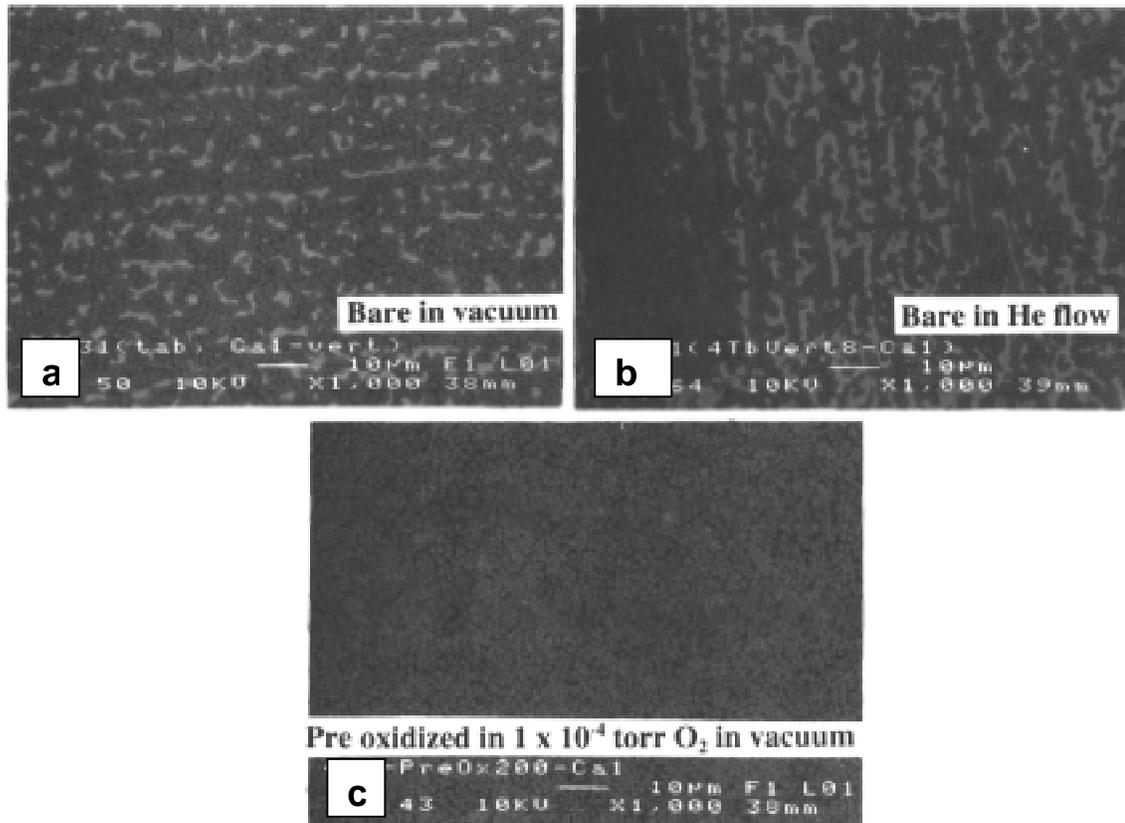


Fig. 10. SEM photomicrographs of surfaces of tab specimens after single Ca-deposition step. (a) tab with no pretreatment after Ca-deposition in vacuum; (b) tab with no pretreatment after Ca-deposition in He flow; (c) tab with O-precharge in 5×10^{-4} torr O₂ environment, and subsequently exposed for Ca-deposition in vacuum.