DEVELOPMENT, CHARACTERIZATION, AND Li COMPATIBILITY OF AN ELECTRICALLY INSULATING CaO COATING ON V-4Cr-4Ti ALLOY

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OBJECTIVE

The objectives of this study include (a) development of an electrically insulating CaO coating on V-4Cr-4Ti alloy; (b) evaluation of the coating's long-term Li compatibility; (c) characterization of the coating before and after exposure to Li; and (d) establishment of optimal processing procedures from the standpoint of sample preparation, exposure time and temperature, and sequence of operations in order to obtain reliable and reproducible coatings with adequate electrical resistance for use in an Li environment.

SUMMARY

Vanadium (V), alloyed with chromium (Cr), and/or titanium (Ti), V-4 Cr-4 Ti alloy in particular, has been the primary candidate for various fusion reactor structural applications, including the first-wall structure/blanket. The outside of 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 of the conducting liquid in the magnetic field. Hence, it is essential that a coating be applied to the alloy, and that it be electrically insulating and compatible with a liquid Li environment at temperatures of 400-700°C. More information on the material requirements of fusion reactors is reported in Ref. 1.As part of the U.S. Department of Energy's Fusion Program, research is being conducted to develop an electrically insulating and liquid-Li-compatible CaO coating on V-4Cr-4Ti alloy. CaO has been identified as the primary coating candidate for this application, based on its high electrical resistivity and thermodynamic stability in Li at the temperatures of interest.[1] This report deals with the development and characterization of a CaO coating deposited on V-4Cr-4Ti alloy specimens by a vapor transport process that uses double Ca-deposition/oxidation steps. The specimen surfaces were analyzed after each step during the process, and the surfaces, along with their cross-sections, were analyzed after exposure to liquid Li. The analysis and characterization were done by one or more techniques, including scanning electron microscopy, energy-dispersive X-ray analysis, X-ray diffraction, and measurement of electrical resistivity external to Li. Here, we present the new developments and results obtained since the last reporting period that ended on December 31, 2000.

EXPERIMENTAL

Details of the experimental aspects of the processes utilized in depositing a CaO coating on V-4Cr-4Ti alloy specimens, including materials, system details, and procedure are provided in Ref. 2. Therefore, only brief information on materials and experimental procedure is discussed below.

Two approaches, an He-flow process and a vacuum process, were successfully used to coat V-4Cr-4Ti alloy coupons and rods with CaO. Both processes utilized transport of Ca through the vapor phase and deposition onto the samples.

In the He-flow process, the samples (tabs and/or rods) were hung vertically from the top of the wire screen inner chamber, which was placed inside a steel or alumina outer chamber with a porous bottom and top. A granular Ca charge was placed between the inner and outer chambers. The first Ca deposition step was carried out by heating the entire assembly in a flowing He environment at 775-800°C for 100-150 h. The resulting Ca-coated specimens were then oxidized in a vertical quartz tube furnace in a flowing Ar environment at ≈700°C for 130-200 h. The sequence of Ca deposition followed by oxidation was repeated to complete the double Ca deposition/oxidation process in He flow to fully coat the samples with CaO.

In the vacuum process, the samples held inside a cylindrical wire screen basket were sealed in a quartz tube with a pressure $\approx 10^{-4}$ torr. A granular Ca charge was placed around the inner chamber and in a cylindrical wire basket at the bottom. The entire assembly was then heated for 100-150 h at 775-800°C in a muffle furnace. The resulting Ca-deposited samples were oxidized as described in the He-flow process above. Development of stable CaO on sample surfaces via double Ca deposition/oxidation in vacuum was accomplished by repeating the Ca deposition and oxidation steps.

The alloy used in this study had a nominal composition of V-4 wt.% Cr-4 wt.% Ti. The samples were either 1-mm-thick tabs or 5-mm diameter rods. All specimens were annealed for 1 h at 1000°C at a pressure $\approx 10^{-7}$ torr before use. The Ca metal was redistilled -6 mesh size granules with a purity of 99.5% on metals basis.

Results obtained from the CaO-coated samples exposed to Li at 500, 600, and 700°C for up to ≈100 h were reported in Refs. 1-5. During the current reporting period, several samples coated with CaO by either the He-flow or vacuum process were exposed to Li at 600 and 700°C for up to 500 h. Tables 1 and 2 show the experimental conditions and the process details for samples exposed to Li at 600°C and 700°C, respectively. It will be noted from Table 1 that the sample 44Tab29 was given an Mg step instead of the second Ca step. Also, the sample 44Rod11S in Table 2 was given a third Ca deposition step followed by a third oxidation step. The reasons for these deviations in processes and their effects are discussed below in the Results and Discussion section. All other samples listed in these tables were coated by the double Ca-deposition/oxidation processes.[2]

RESULTS AND DISCUSSION

In earlier reports,[2-6] it was noted that the CaO coatings on the V-4Cr-4Ti coupon and/or rod samples remained intact after exposure to Li at 500 and 600°C for ≈100 h. It was also reported that the electrical resistivity measurements (external to Li) on these samples showed that they had electrical insulation properties in excess of the design requirements of a fusion device that uses an Li blanket at temperatures of up to 700°C.[1]

During the present reporting period, V-4Cr-4Ti specimens in the form of both tabs and rods were coated with CaO via the He-flow or vacuum process and exposed to Li for ≈137 h at 600°C (see Table 1) and for about 145, 282 and 500 h at 700°C (see Table 2). The Li used for all exposures

Table 1. Experimental conditions for the Ca deposition and Li exposure at 600°C

Sample ID	Process Step	Environment or Method	Temperature (°C)	Time (h)	Tab Dimensions (mm)
44Tab12	Anneal	P ≈10^{-6} torr	1000	1	11.6 x 7.4 x 1
	Ca Step 1	He flow	795	140	
	Ox. Step 1	UHP Ar	695	160	
	Ca Step 2	He flow	800	120	
	Ox. Step 2	UHP[2] Ar	692	140	
	Li Exposure[1]	Liquid Li	600	137	
44Tab14SB[3]	Anneal	P ≈10^{-6} torr	1000	1	11.9 x 7.65 x 1
	Ca Step 1	He flow	795	140	
	Ox. Step 1	UHP Ar	695	160	
	Ca Step 2	He flow	800	120	
	Ox. Step 2	UHP[2] Ar	692	140	
	Li Exposure[1]	Liquid Li	600	137	
44Tab29	Anneal	P ≈10^{-6} torr	1000	1	12.1 x 9.4 x 1
	O Precharge	P ≈ $5x10^{-4}$ torr O_2	600	50	
	Ca Step 1	Vac./Quartz	790	140	
	Ox. Step 1	UHP[2] Ar	690	160	
	Mg Step 1	Vac./Quartz	600	116	
	Ox. Step 2	UHP[2] Ar	410	120	
	Li Exposure[1]	Liquid Li	600	137	
44Rod13L[4]	Anneal	P ≈10^{-6} torr	1000	1	
	Ca Step 1	He flow	795	140	
	Ox. Step 1	UHP[2] Ar	695	160	
	Ca Step 2	He flow	800	120	
	Ox. Step 2	UHP[2] Ar	692	140	
	Li Exposure[1]	Liquid Li	600	137	

[1]Li-2 wt.% Ca solution maintained at 600°C during exposure.
[2]Argon gas used was ultrahigh purity (UHP) grade with a 99.999% purity.
[3]This tab was slightly sandblasted.
[4]L designates long rod ≈60 mm in length.

contained ~2.8 at.% Ca dissolved in it. It was possible to obtain data on the weight change after each step during the CaO coating of the tab samples, and also after their exposure to Li. This was not possible for the rod samples because the screws used to hold the samples were often self-welded in during the Ca deposition and/or oxidation steps.

The bar graphs in Figure 1 show the weight change data for the V-4Cr-4Ti tab samples after each step during the CaO coating process and also after Li exposure at 600°C. The bar graphs in Figure 2 show similar data for samples exposed to Li at 700°C. From these figures, it is not

possible to compare the rate of weight change during similar steps of the He-flow and vacuum processes. However, it is clear that either process can be used to successfully coat V-4Cr-4Ti alloy samples with stable CaO. The lack of weight loss after Li exposure in Figures 1 and 2 indicates that CaO is stable in an Li/Li/-Ca environment, as predicted by thermodynamic data.

Table 2. Experimental conditions for Ca deposition and Li exposure at 700°C

Sample ID	Process Step	Environment or Method	Temperature (°C)	Time (h)	Tab Dimensions (mm)
44Tab9	Anneal	P ≈10^{-6} torr	1000	1	12.8 x 7.5 x 1
	O Precharge	P ≈5x10^{-4} torr O_2	600	50	
	Ca Step 1	He flow	790	140	
	Ox. Step 1	UHP[2] Ar	690	160	
	Ca Step 2	He flow	775	146	
	Ox. Step 2	UHP[2] Ar	693	157	
	Li Exposure[1]	Liquid Li	700	145	
44Tab24	Anneal	P ≈10^{-6} torr	1000	1	11.9 x 8.9 x 1
	Ca Step 1	Vac./Quartz	780	150	
	Ox. Step 1	UHP[2] Ar	700	140	
	Ca Step 2	Vac./Quartz	775	146	
	Ox. Step 2	UHP[2] Ar	693	157	
	Li Exposure[1]	Liquid Li	700	145	
44Rod1S[3]	Anneal	P ≈10^{-6} torr	1050	1	
	O Precharge	P ≈5x10^{-4} torr O_2	600	124	
	Ca Step 1	Vac./Quartz	780	150	
	Ox. Step 1	UHP[2] Ar	700	140	
	Ca Step 2	Vac./Quartz	775	146	
	Ox. Step 2	UHP[2] Ar	693	157	
	Li Exposure[1]	Liquid Li	700	145	
44Rod3S[3]	Anneal	P ≈10^{-6} torr	1000	1	
	O Precharge	P ≈5x10^{-4} torr O_2	600	200	
	Ca Step 1	Vac./Quartz	780	166	
	Ox. Step 1	UHP[2] Ar	705	190	
	Ca Step 2	Vac./Quartz	775	146	
	Ox. Step 2	UHP Ar	693	157	
	Li Exposure[1]	Liquid Li	700	145	
44Rod10L[4]	Anneal	P ≈10^{-6} torr	1000	1	
	O Precharge	P ≈5x10^{-4} torr O_2	600	50	
	Ca Step 1	Vac./Quartz	790	140	
	Ox. Step 1	UHP[2] Ar	690	160	
	Ca Step 2	Vac./Quartz	775	142	
	Ox. Step 2	UHP[2] Ar	700	161	
	Li Exposure[1]	Liquid Li	700	282	
44Rod11S[3]	Anneal	P ≈10^{-6} torr	1000	1	
	Ca Step 1	Vac./Quartz	780	135	
	Ox. Step 1	UHP[2] Ar	700	145	
	Ca Step 2	Vac./Quartz	775	142	
	Ox. Step 2	UHP[2] Ar	700	158	
	Ca Step 3	He flow	780	100	
	Ox. Step 2	UHP[2] Ar	675	120	
	Li Exposure[1]	Liquid Li	700	500	

[1]Li-2 wt.% Ca solution maintained at 700°C during exposure.

[2]Argon gas used was ultrahigh purity (UHP) grade with 99.999% purity.
[3]S designates short rod ≈20 mm in length.
[4]L designates long rod ≈60- mm in length.

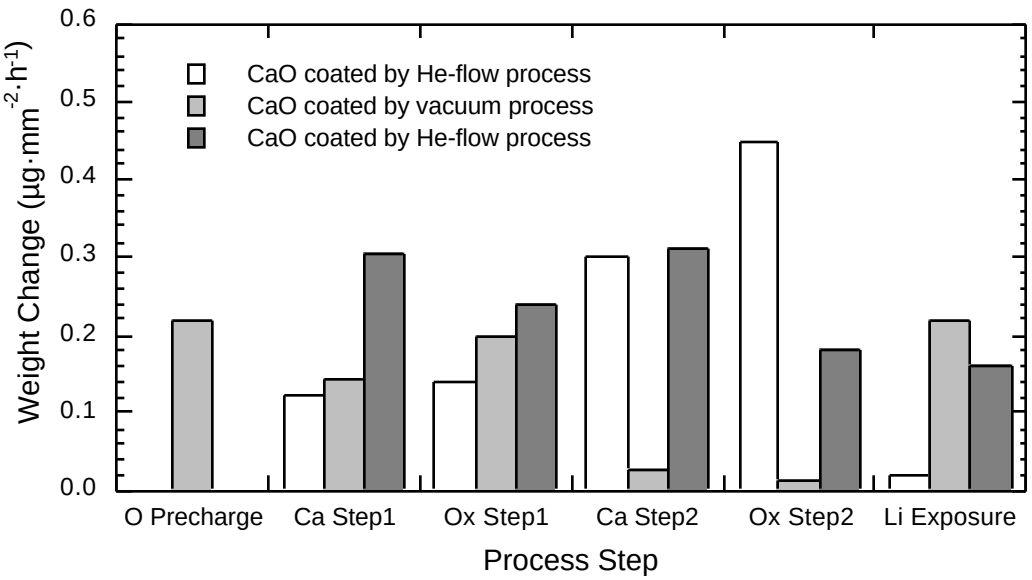

Fig. 1. Weight change during CaO deposition steps and 137-h Li exposure at 600°C of V-4 Cr-4 Ti alloy tabs coated by He-flow or vacuum process (also see Table 1).

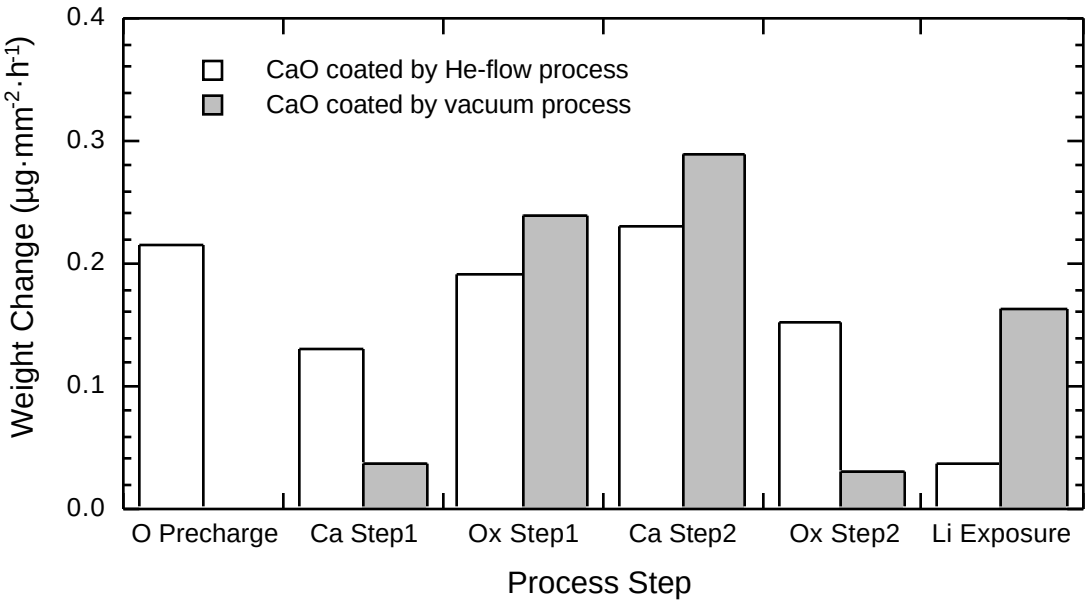

Fig. 2. Weight change during CaO deposition steps and 145-h Li exposure at 700°C for V-4 Cr-4 Ti alloy tabs coated by He-flow or vacuum process (see Table 1).

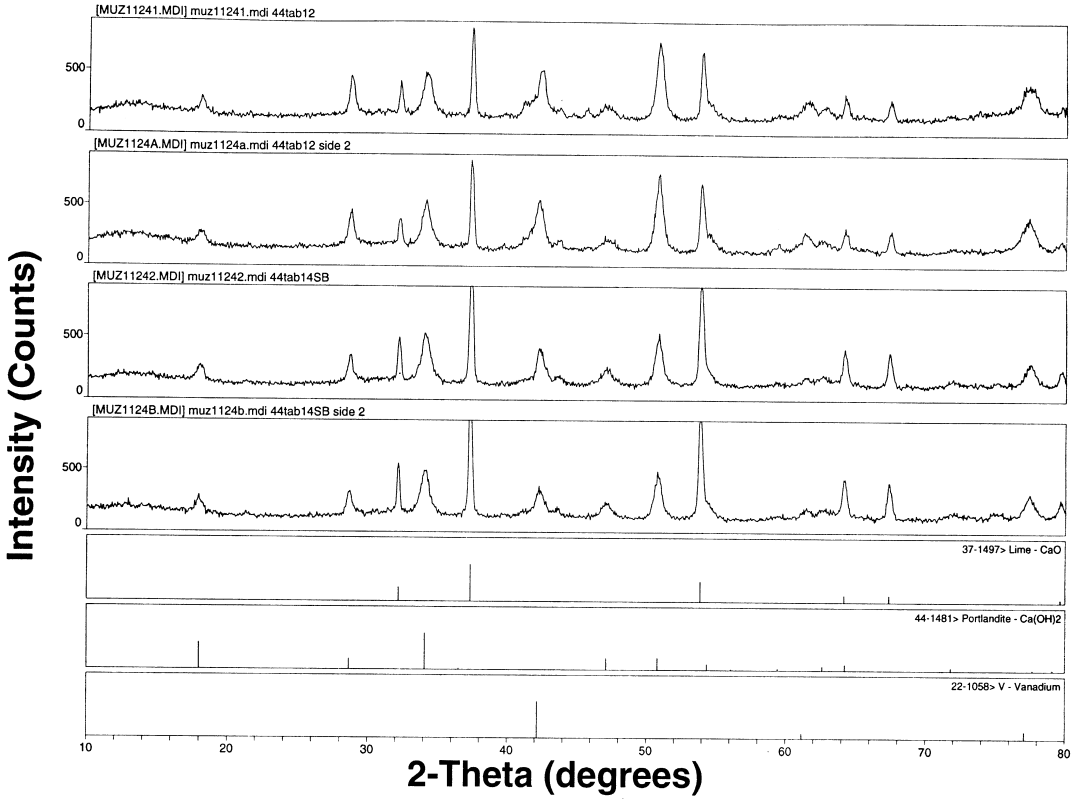

Fig. 3. X-ray diffraction patterns obtained from both surfaces of CaO-coated V-4 Cr-4 Ti tabs after 137-h Li exposure at 600°C (both samples were coated by He-flow process; see Table 1 for process histories of samples).

Figure 3 shows X-ray diffraction (XRD) results of the two surfaces of the tab samples (44Tab12 and 44Tab14SB), that were exposed to Li for 137 h at 600°C. Figure 4 shows similar results for 44Tab24 and 44Tab9, which were exposed to Li at 700°C. All patterns in both figures give strong indications of the presence of CaO on these samples after Li exposure. $Ca(OH)_2$ is expected because it forms readily from CaO in a humid environment. The presence of the V peak in all these patterns (less so in samples exposed to Li at 700°C) should be due to sampling of the matrix during the X-ray analysis. The presence of CaO in these tabs, as well as in other samples exposed to Li, and hence indicating Li compatibility with CaO, was also verified by energy-dispersive X-ray analysis (EDX) using scanning electron microscope (SEM). The photomicrographs of 44Rod13L after exposure to Li for 137 h at 600°C and of 44Rod3S after exposure to Li for 145 h at 700°C are shown in Figures 5 a and b, respectively. These photomicrographs, which were typical of other samples listed in Tables 1 and 2, indicate that the CaO coating maintained its integrity during exposure to Li.

Characterization of the ≈60-mm-long rod 44Rod10L (see Table 2), which was exposed to Li for 282 h at 700°C, is in progress. This sample will have to be cut before it can be analyzed by XRD. However, preliminary examination of this sample by SEM and SEM/EDX indicate that CaO is still present on the sample surface.

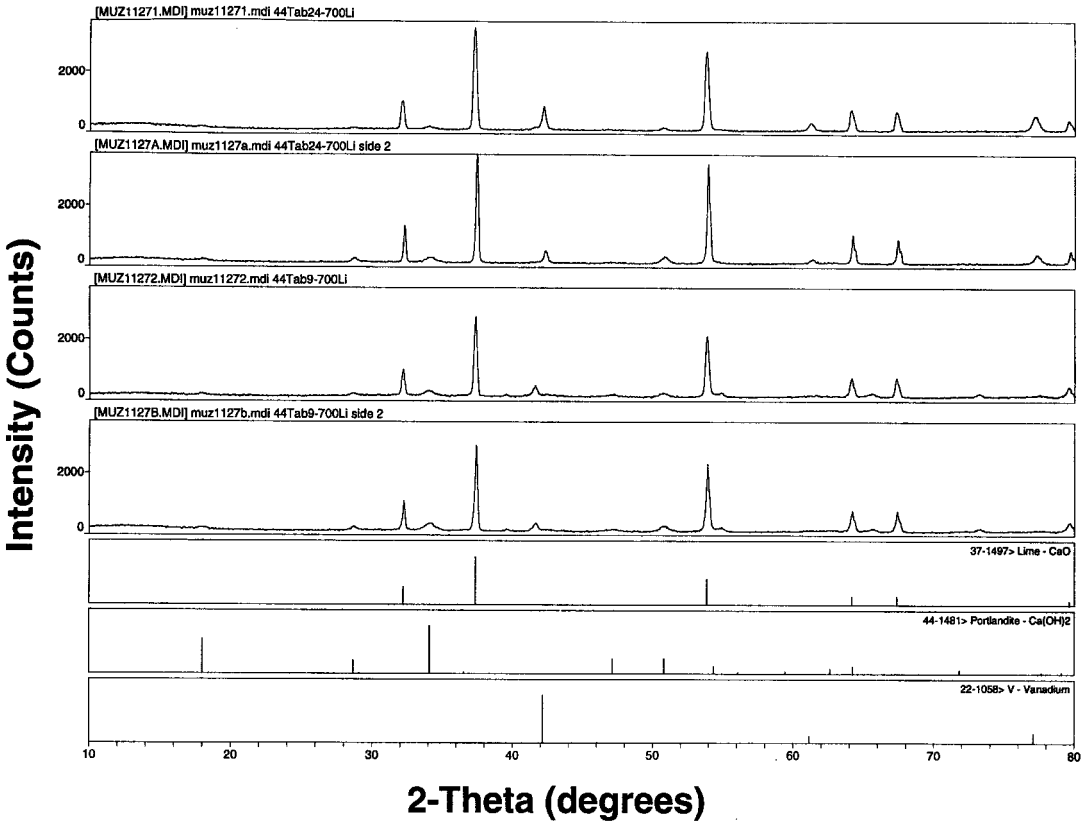

Fig. 4. X-ray diffraction patterns obtained from both surfaces of CaO-coated V-4 Cr-4 Ti tabs after 145-h Li exposure at 700°C. (44Tab9 was coated by He-flow , and 44Tab24 was coated by vacuum process; see Table 1 for process histories of samples).

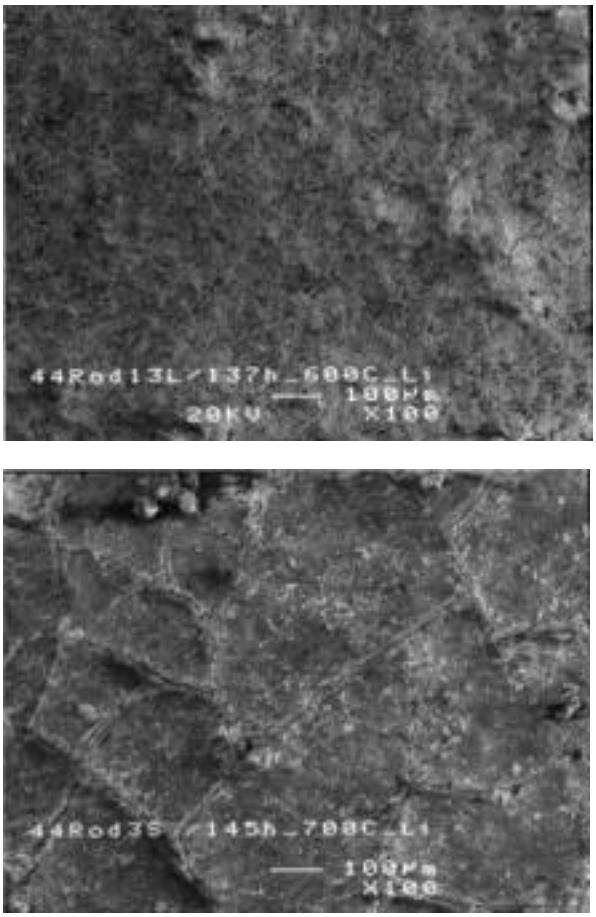

Fig. 5. SEM photomicrographs of V-4 Cr-4 Ti rod samples after Li exposure, showing Li compatibility of CaO coating developed by double Ca-deposition/oxidation processes: (left) 44Rod13L CaO coated by He-flow process and exposed to Li for 137 h at 600°C, and (right) 44Rod3S CaO coated by vacuum process and exposed to Li for 145 h at 700°C.

The 44Rod11S sample was recently removed from Li after 500-h exposure at 700°C. To minimize the deleterious effects of the humid ambient environment, this sample was analyzed by XRD at several spots on its surface. The peaks were not sharp due to the curvature and uneven nature of the sample surface. But there was clear evidence of CaO in this sample. Other compounds detected on this sample included V, as sampled from beneath the coating, and some Li compounds because the sample was analyzed without removing all the Li in order to avoid alterations on the coating due to exposure to ambient environment. Environmental effects on the coating after removal from Li was accomplished to some extent as evidenced by the absence of $Ca(OH)_2$ in this sample. Coating scraped from various locations on the surface of this specimen was also analyzed with a Debye-Scherrer camera and the results indicated presence of CaO. Further evidence of the presence of CaO on this sample after 500 h in Li at 700°C can be seen in Figures 6 a and b. These patterns are obtained from EDX analysis at two different locations on the sample surface using SEM. The Ca and O peaks are sharp, and there seems to be no

appreciable V peak. Along with other results, this indicates that CaO is stable in Li-2 wt.% Ca solution at 700°C.

WORK IN PROGRESS

Cross sectional areas of the samples listed in this report will be further analyzed by SEM and SEM/EDX. Depth profiles for various elements, including Ca, O, V, Cr, and Ti, will be determined from the outer surface of the coating to the interior of the substrate alloy.

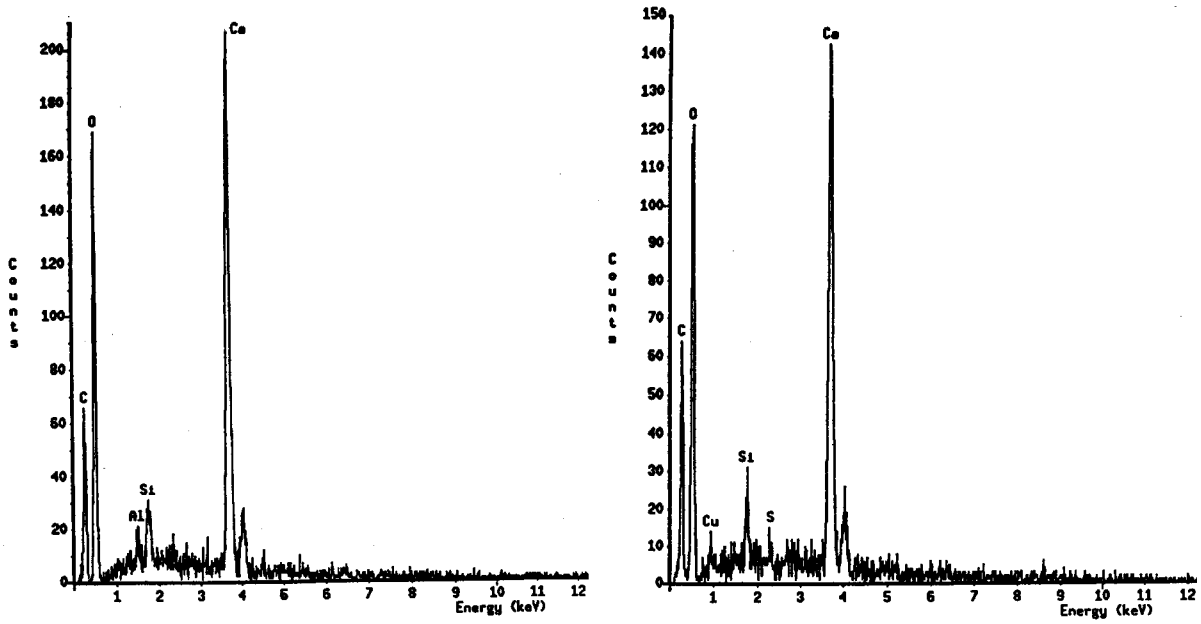

Fig. 6. Energy-dispersive X-ray patterns obtained from (left) light gray area, and (right) dark gray area on surface of 44Rod11S after 500-h Li exposure at 700°C (see Table 2 for processing history of sample).

REFERENCES

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