DEVELOPMENT OF ELECTRICALLY INSULATING CaO COATINGS*

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OBJECTIVE

The objectives of this task are to (a) develop electrically insulating coatings, with emphasis on the basic understanding of the thermodynamic conditions and kinetics of coating development needed to achieve 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 defects and microstructure; (c) measure the electrical resistance of the coatings, before and after exposure external to Li; and (d) establish optimal procedures from the standpoint of sample preparation procedures, 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

A systematic study has been initiated to develop electrically insulating CaO coating by in-situ formation in a liquid Li environment. Twelve capsule tests were conducted at several temperatures and with different concentrations of Ca in Li-Ca mixtures. Specimens included in the run were annealed V-4Cr-4Ti alloy without and with a grit-blasted surface, O-precharged in 99.999 vol.% Ar environment, polished specimens precharged in a 99.999 vol.% Ar and 5000 vppm O_2-N_2 mixture. CaO coatings of 2-3 μm in thickness were obtained. Detailed mirostructural and compositional analyses were performed on the exposed specimens. The coatings exhibited a resistance of $\approx 44\Omega/cm^2$ on the surface of V-4Cr-4Ti alloys.

A systematic vapor transport study has been in progress to develop electrically insulating CaO coatings that are compatible with use in a liquid Li environment. Several additional experiments were conducted to study how the deposition of Ca on V-4Cr-4Ti substrate alloys is affected by variations in process temperature and time, and specimen location, surface preparation, and pretreatment. During this reporting period, several specimens were prepared with a coating of CaO by thermal/chemical deposition and the coatings were characterized before and after exposure to an Li environment.

EXPERIMENTAL PROGRAM

The present work on *in-situ* development of insulator coatings emphasizes a basic understanding of the thermodynamic conditions and kinetics of coating development in Li-Ca mixtures to achieve stable coatings of CaO *in-situ* in a Li/Li-Ca environment. Among the key variables that influence coating formation and its chemical and mechanical integrity are test temperature, test time, Li chemistry (including Ca content and trace element concentrations), and alloy chemistry and specimen

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surface preparation.

To understand the mechanism of in-situ formation of CaO coatings in an Li environment and to establish the optimal experimental conditions, a series of capsule experiments were performed with specimens of V-4Cr-4Ti alloy that were bare (identified as B) or pretreated by several methods: grit-blasted surface and O-precharged in 99.999 vol.% Ar (identified as G), polished specimens O-precharged in 99.999 vol.% Ar (identified as A) or in a 5000 vppm O_2-N_2 mixture (identified as O), and prealuminization and O-precharged in a 5000 vppm O_2-N_2 mixture (identified as L). The O precharging was done for 100 h at 500°C.

The pretreated V-4Cr-4Ti coupons, which measured 10 x 5 x 1 mm, were immersed in an Li-Ca mixture in a stainless steel capsule lined with V-alloy. To ensure flexibility in adjusting the Li-Ca chemistry in these experiments, capsules that contained ≈50-60 mL of Li-Ca mixture are used for specimen exposure. Table 1 lists the exposure conditions for different capsule experiments. Figure 1 shows the specimen assembly used in the capsule experiments in Li. The temperature of the in-situ coating varied from 800 to 450°C; the concentration of Ca varied from 40 to 85 wt.% (10 to 50 at.%) in the Ca-Li mixture. At Ca contents of >30 wt.%, the $CaLi_2$ phase is expected to deposit as the specimens are cooled, whereas at a Ca content of 10 wt.%, β-Ca and α-Ca deposits are expected. A furnace that could accommodate at least five capsules simultaneously at a given temperature was used for exposure of the capsules. The capsules were subjected to a rocking action to enable mixing of the Ca-Li mixture at elevated temperature. Upon exposure, the capsules were inverted at temperature to drain the specimens of Li and were then cooled to room temperature. Subsequently, the capsules were cut open, the sample holder was retrieved, the microstructures of the coatings were examined with a JOEL 6400 scanning microscope, and the compositions were analyzed by energy-dispersive X-ray (EDX) analysis. Resistances of the coated specimens were measured by a two-probe method.

Table 1. Exposure conditions for capsule tests

Capsule Number	Temperature (*C)	Exposure time (h)	Capsule condition	Wt.% Ca in Ca-Li mixture
1	800	500	rocking	40
2	800	500	rocking	60
3	800	500	rocking	85
4	800	210	rocking	85
5	650	1050	rocking	40
6	650	1050	rocking	60
7	650	1050	rocking	85
8	650	500	rocking	85
9	650/450	1004/1848	static	40
10	650/450	1004/1848	static	60
11	650/450	1004	static	85
12	650/450	1004/1848	static	85

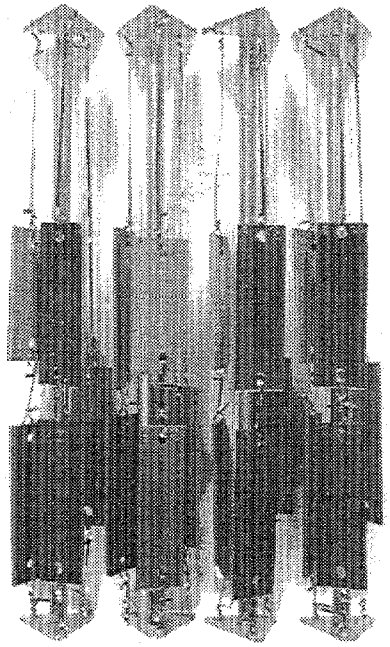

Fig. 1. Macrophotograph of specimen assembly used for in-situ coating development in liquid Li.

Experiments were also conducted to develop Ca-rich coatings by using the thermal/chemical deposition process. The experiments involved exposure of V alloy specimens to a pack of fine Ca pellets at 700-800°C. The specimens were either completely enclosed within the pack or hung above the pack material in a static Ar environment. Above 700°C, the vapor pressure of Ca is >0.1 torr and is sufficient to deposit a layer of Ca on the specimens. Several geometrical arrangements were examined to obtain a uniform coating of Ca on the specimens, which were typically coupons that measured 5 to 10 x 5 x 1 mm. Effort during this period concentrated on developing procedures to develop a thick adherent coating of CaO on a V-4Cr-4Ti alloy substrate and on measuring the electrical resistance of the coated specimens as a function of temperature up to ≈710°C.

RESULTS AND DISCUSSION

Coatings by in-situ method in Li

EDX analysis of the in-situ-developed coatings showed that the major elements in the coating are Ca, V, and O. Small amounts of Ti and Cr from the V-4Cr-4Ti alloy and Al from the prealuminized samples were also detected in the coatings. For the coating to be a good electrical insulator, a high Ca content is required. The Ca content of the present coatings increases with increasing Ca content of the Ca-Li mixture (see Fig. 2). Therefore, high Ca content in the Ca-Li mixture is advantageous in formulating a CaO coating. Several of the specimens were precharged with O. In these specimens, several surface interactions (which can lead to CaO coating) are possible upon exposure to the Ca-Li mixture:

$$VO_x + x\,Ca = x\,CaO + V \qquad (1)$$

Table 2. Ca concentrations in coated specimens, with different initial pretreatments, after exposure in Ca-Li mixtures

Capsule No.	Ca concentration (in at.%) in specimen				
	A	B	G	O	L
	29.7	1.1	43.8	31.4	4.9 (Al 0.4%)
1	34.5	1.1	25.0	16.9	14.4 (Al 0.4%)
	26	0.5	44.1	29.9	12.6 (Al 0.3%)
	46.7	4.4(Al 9.6%)	38.1	5.9 (Al 4.4%)	33.9 (Al 0.3%)
	26.2	7.7(Al 7.1%)	4.6	3.6(Al 4.6%)	28.9 (Al 0.48%)
2	38.8	3.1(Al 7.4%)	4.8	3.7(Al 2.8%)	28.4 (Al 0.4%)
	1.0	0.6	6.0	22.6	12.7
	4.8	0.3	6.6	24.6	5.2
5	2.1	1.2	6.9	22.4	4.7
	-	-	-	19.7	-
	-	-	-	17.1	-
	10.6	2.1	30.9	2.2	19.0
6	9.9	2.6	22.9	1.7	4.9
	6.6	0.5	20.7	1.7	9.7
	13.6	3.9	15.9	0.7	4.3
7	11.9	0.6	22.1	1.3	5.4
	19.1	2.0	18.6	0.5	7.7
	-	-	16.5	-	-
	10	0.55	4.7	0.4	-
9	25.9	0.82	9.1	0.4	-
	17.2		-	-	-
10	1.2	0.8	0.8	0.8	-
	12.6	-	30	-	-
	12.5	5.9	5.3	0.5	-
	39.4	3.6	12.1	1.5	-
11	18.1	0.7	8.7	2.3	-
	4	-	-	23.1	-
	-	-	-	37.6	-
	16.1	3.2	18.4	9.0	-
	16.4	-	7.7	9.6	-
12	14.6	-	1.3	11.7	-
	-	-	25.9	8.1	-
	-	-	3.7	-	-

$$VO_x + 2x\,Li = x\,Li_2O + V \tag{2}$$

$$Li_2O + Ca = CaO + 2\,Li \tag{3}$$

If Ca content is too low, VO_x may first react with the Li in the Ca-Li mixture. Then, Li_2O reacts with Ca to form CaO. However, in the two-step (Eqs. 2 and 3) exchange process, the volume change may lead to cracks in the coating. Higher Ca content can increase the chance of the one-step reaction, Eq. 1, and can lead to a coating with good mechanical integrity. Table 2 lists the Ca concentrations in the coatings developed on different specimens that were exposed in various capsules. Figure 3 shows the Ca content of the coatings that increases with an increase in exposure temperature. Higher exposure temperature may help increase the Ca content of the coating.

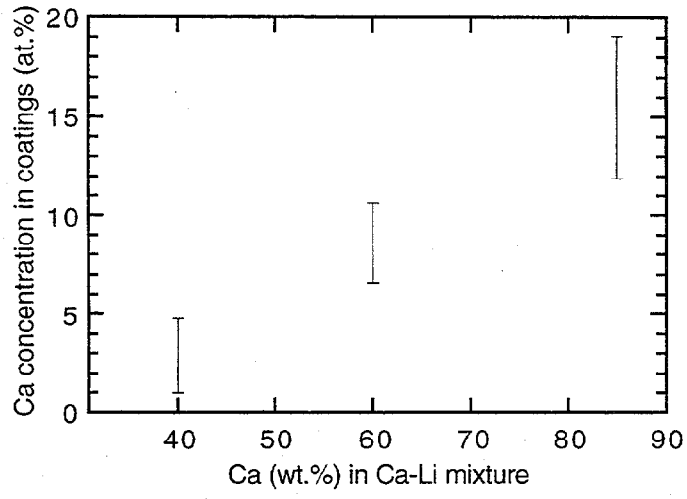

Fig. 2. Ca concentration in coatings, developed in-situ in Ca-Li mixture at 650-800°C, as a function of Ca content of the liquid.

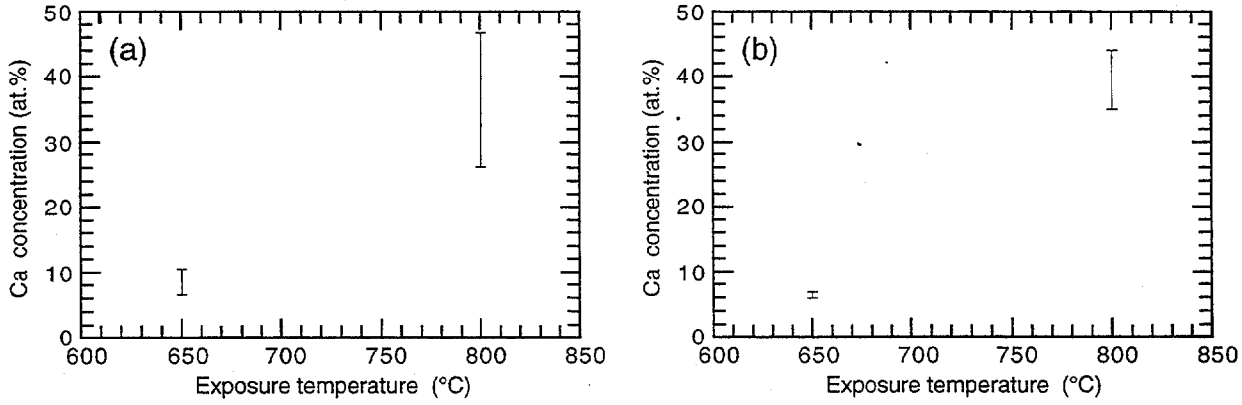

Fig. 3. Ca concentration in two coatings developed in-situ in Ca-Li mixture on V-4Cr-4Ti alloy: (a) polished surface, O-pretreated in 99.999 vol.% Ar at 650°C for 17 h and (b) grit blast surface, O-pretreated in 99.999 vol.% Ar at 650°C for17 h, as a function of exposure temperature.

The Ca content of the coating is strongly affected by the pretreatment of the specimens. The bare V-4Cr-4Ti samples always showed the lowest Ca content (Fig. 4). This is probably because the O content of the surface of the bare specimen is low enough that the reaction in Eq. 1 does not occur. The specimens pretreated at 650°C in 99.999 vol.% Ar exhibited higher Ca content in the coating when compared to specimens with other pretreatments. The oxygen in Ar gas formed a layer of oxide on the surface of the alloy, and the layer was converted to CaO coating according to Eq (1).

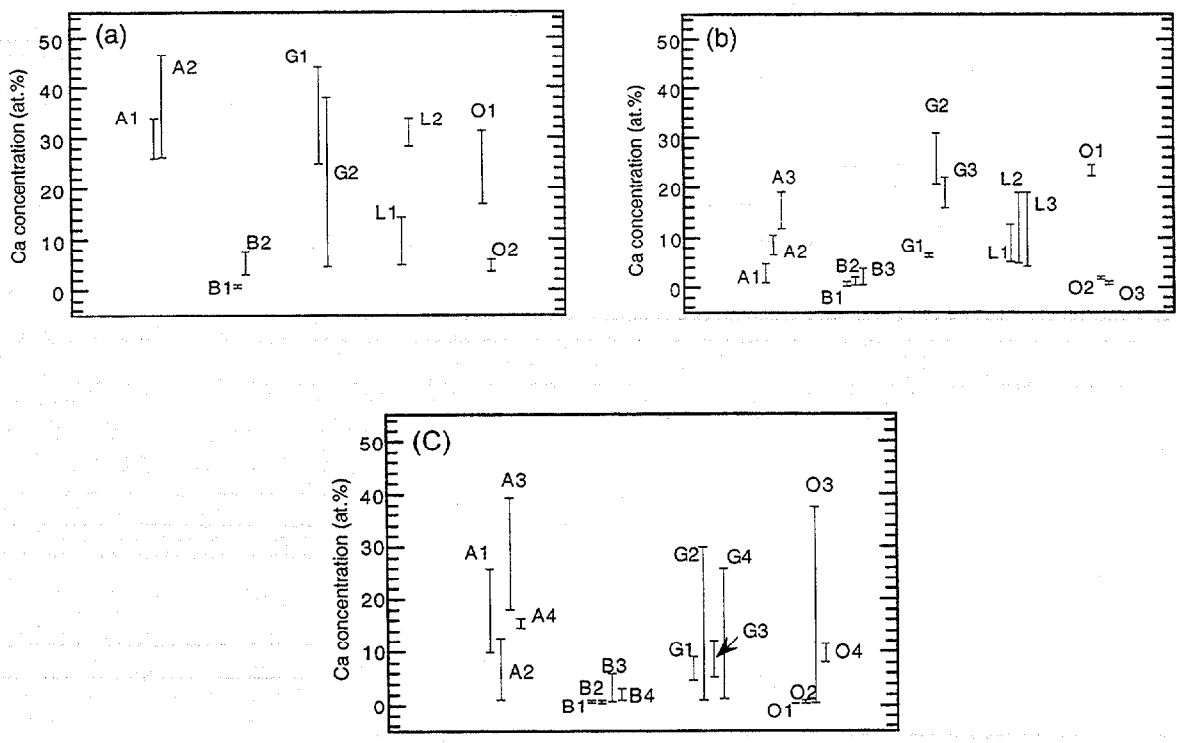

Fig. 4. Effect of specimen pretreatment on the Ca concentration in coatings developed in-situ in Ca-Li mixtures by exposure at (a) 800°C for 500 h, (b) 650°C for 1050 h, and (c) 650/450°C for 1004/1848 h. The letters A, B, G, O, and L signify specimen pretreatments of exposure in 99.999 vol.% Ar for 17 h, no treatment, grit blast, exposure in 5000 vppm O_2-N_2 mixture, and prealuminization, respectively. The numbers 1, 2, 3, and 4 signify exposure in Ca-Li mixtures containing 40, 60, 85, and 85 wt.%Ca, respectively.

Some areas of the sample treated by grit blasting exhibited a high Ca content but it was not uniformly high on the entire surface, indicating probable spallation of the coating. The results also indicated that surface roughness can play a large role in the adhesion of the coating to the substrate. An alternate approach, which involves chemical etching is being examined as a pretreatment for the specimens prior to exposure in a Ca-Li mixture.

The Ca content of prealuminized samples was higher than that of the bare samples, but lower than that in specimens pretreated in 99.999 vol.% Ar. Specimens pretreated in a 5000 vppm O-N gas mixture exhibited higher Ca content but also significant cracking of the coating; the cracked regions exhibited low Ca content. It is probable that the pretreatment led to a thick oxide layer that cracked upon reaction with Ca in the liquid mixture. The average thickness of the coating for the sample pretreated in 99.999 vol.% Ar is ≈3 μm. A sharp change in Ca and V content, shown in Fig. 5, is noted at the coating/substrate interface, indicating a lack of diffusion of Ca into the substrate alloy. Figure 6 shows the resistance of the coated specimen as a function of temperature. Resistance is ≈44 Ω/cm^2 at room temperature; it decreases with increasing temperature, but the values are much lower than desired for application in the first wall/blanket system.

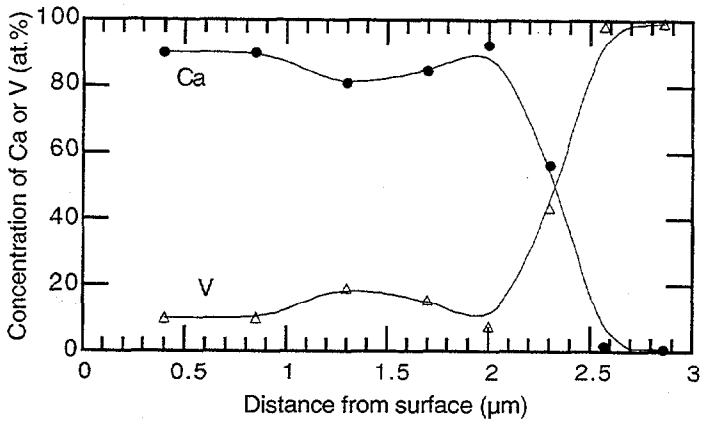

Fig. 5. Ca and V concentrations as a function of coating thickness for a typical in-situ-developed coating on a V-4Cr-4Ti alloy specimen.

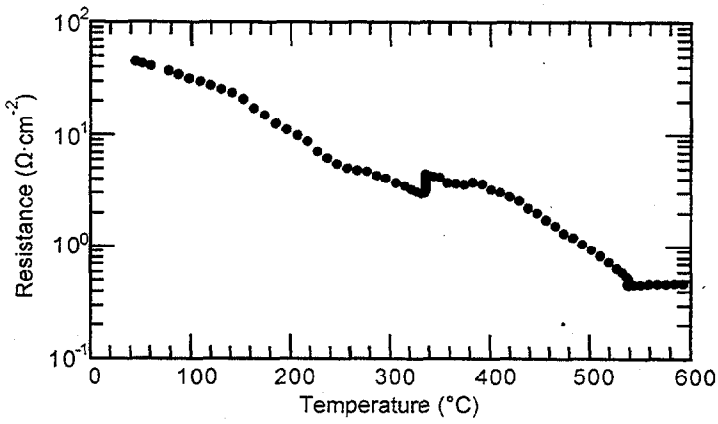

Fig. 6. Resistance of an in-situ-developed coating as a function of temperature, measured by a two-probe method.

In conclusion, CaO coatings on the surface of V-4Cr-4Ti alloy were made by in-situ coating. The results showed that specimen pretreatment had a strong influence on the composition, mechanical integrity, and thickness of the coating developed by exposure in a Ca-Li mixture.

Coatings by thermal/chemical vapor phase transport

In previous reports, we discussed the procedure for deposition of Ca by thermal/chemical vapor transport and subsequent oxidation to convert the Ca into CaO.[1,2] Based on an extensive analysis of the coated specimens, it was concluded that the coating thickness and the adhesive bonding of the coating to the substrate after a single deposition/oxidation procedure was not adequate to produce the desired insulating characteristics. Subsequently, a double Ca deposition/oxidation treatment was developed for producing CaO coatings.[3,4] During this reporting period, several additional specimens were coated by this procedure and the coatings were characterized for their chemical composition,

microstructure, and electrical resistance. Figure 7 shows typical scanning electron microscopy (SEM) secondary-electron and backscattered-electron images of cross sections of two V-4Cr-4Ti alloy specimens after a double Ca deposition/oxidation treatment. Coating thicknesses in these specimens were 30-34 μm. EDX analysis of the specimen surfaces showed the coatings to be CaO and also revealed the virtual absence of any elements from the substrate alloy. EDX analysis of the coating surface indicated primarily Ca and O peaks. Cross sections of several specimens were analyzed as a function of depth for constituent elements of the coating and substrate. Depth profiles for two of the coated specimens are shown in Figs. 8a and 8b. The coating composition was predominantly CaO in both specimens, and negligible amounts of substrate elements were detected in the coating region. The results also showed that consistently reproducible coatings with uniform thickness can be developed by this procedure.

Additional experiments are in progress to develop coatings on rod specimens with rounded ends (to minimize stress concentration and cracking of the coating at the corners of coupon specimens). These specimens will be used for in-situ measurement of resistance of the coating in an Li environment at temperatures up to 700°C. For this purpose, an Li facility is being built and is in the final stages of assembly.

REFERENCES

1. 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, Sept.1998.
2. K. Natesan, M. Uz, and S. Wieder, "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.
3. K. Natesan, M. Uz, and S. Wieder, "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, Sept. 1999.
4. 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.

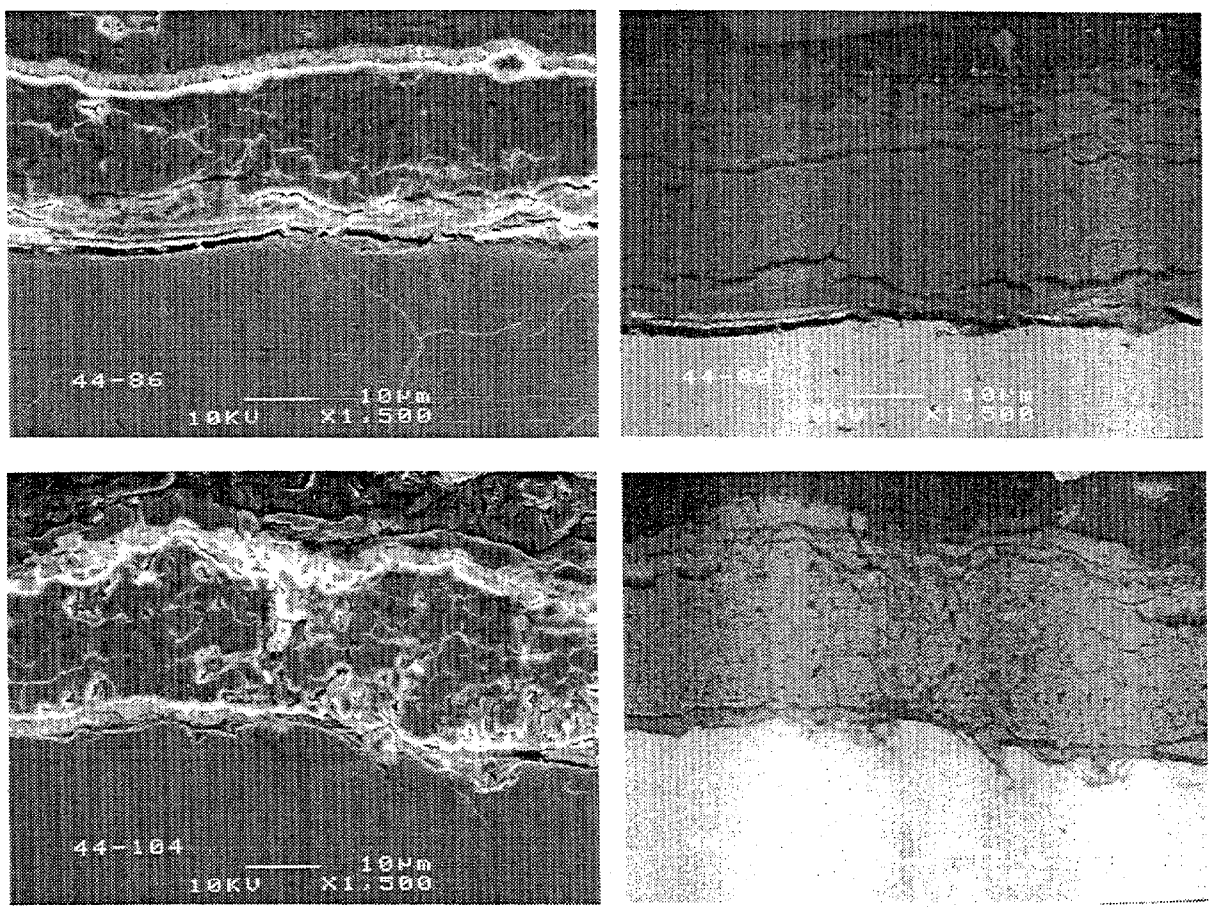

Fig. 7. SEM photomicrographs of cross sections of two V-4Cr-4Ti alloy specimens after double Ca deposition/oxidation treatment. Photographs on the left are secondary-electron images, those on the right are backscattered-electron images.

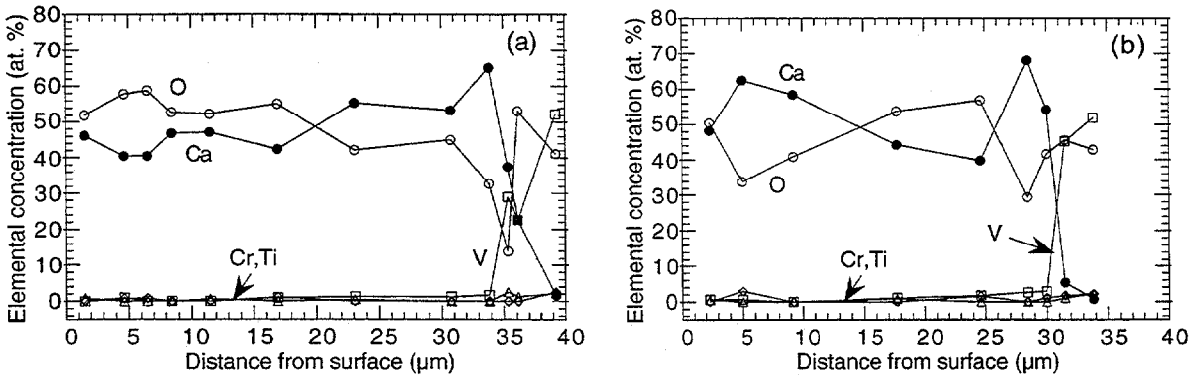

Fig. 8. Elemental concentrations as a function of coating thickness for V-4Cr-4Ti alloy specimens after (a) double Ca/deposition/oxidation treatment and (b) after exposure to Li at 500°C for 68 h.