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Development of CaO coatings by thermal and chemical vapor deposition

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Abstract

We conducted several experiments to test electrically insulating CaO coatings on a V–4Cr–4Ti alloy for application in the Li environment of liquid metal blankets in fusion reactors. Two processes that involve double Ca deposition/oxidation steps were developed to successfully coat V–4Cr–4Ti alloy samples with stable CaO. During the study, we examined several geometrical arrangements, using tabs and/or rod specimens. After Ca deposition from the vapor phase, the specimens were oxidized in an Ar–10 vppm O_2 environment at ≈600 °C to convert the deposited metal into oxide, whereupon they exhibited insulating characteristics. Several coated specimens were then exposed to Li–2.8 at.%Ca at 500–700 °C to determine chemical compatibility and mechanical integrity. Depth profile analysis of the coatings was conducted to evaluate the compositional changes in the coatings and to assess the transport, if any, of substrate and coating constituents. Microstructural characteristics of the coatings were evaluated by scanning electron microscopy. The preliminary results indicate that CaO is a viable coating for V–Li advanced blankets.

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1. Introduction

Blanket-design studies revealed that electrically insulating duct walls will be required to reduce the magnetohydrodynamic (MHD) pressure drop in liquid-metal-cooled blankets used in high-magnetic-field fusion devices, and development of insulator coatings was recommended as the most appropriate approach to achieving the desired goal [1]. The major requirements for a viable insulator coating are

- chemical compatibility in liquid metal,
- chemical compatibility with structural metal,
- adequate electrical insulating characteristics,
- stability under irradiation environment,
- long-term stability, including self-healing, under thermal cycling conditions.

Based on a review of available information on electrical resistivity and Li compatibility, CaO has been considered a viable insulator coating for the V–4Cr–4Ti alloy in fusion first-wall applications [2]. Fig. 1 illustrates the thermodynamic stability of CaO in an Li environment. At temperatures in the range of 200–700 °C, of interest in the fusion application, the CaO coating will be thermodynamically stable over a wide range of O concentrations in Li, from a low value of 38 wppm in Li that is cold trapped at 200 °C, to values as high as 1000 wppm. Fig. 2 shows the temperature dependence of the electrical resistivity of CaO, indicating that the values at 200–700 °C are at least several orders of magnitude higher than needed for the first-wall application, based on the criterion that the product of the coating resistivity times the coating thickness should be $>100\ \Omega\,\mathrm{cm}^2$. This paper addresses the development and characterization of a CaO coating that was applied on V–4Cr–4Ti alloy by a vapor transport (or thermal and chemical vapor deposition) process. The results will be used to assess the applicability of these coatings in a V–Li self-cooled fusion reactor blanket.

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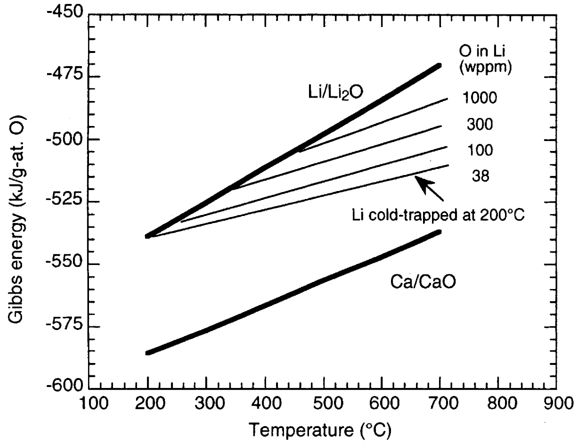

Fig. 1. Thermodynamic stability of CaO in Li.

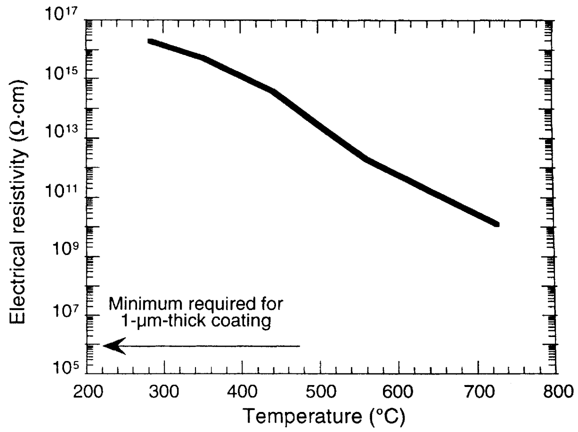

Fig. 2. Temperature dependence of the electrical resistivity of CaO.

2. Experimental procedure

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 tabs or 5 mm-diam rods. All of the specimens were annealed for 1 h at 1000 °C in a 1.3×10^{-5} Pa vacuum before use. The Ca metal was redistilled <6-mesh granules with a purity of 99.5% on the metals basis. A stainless steel wire screen with 1 mm square openings was used to fabricate the ≈20 mm-diam cylindrical inner specimen chamber. The outer chamber, ≈35 mm in diam, 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 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 a vacuum of 0.013 Pa during the Ca-deposition steps, and flowing Ar during the oxidation steps of the processes. Both He and Ar gases were 99.999% pure.

Calcium deposition by vapor transport relied on the relatively high vapor pressure of Ca metal at temperatures >700 °C. The vapor pressure of Ca metal is >0.13 Pa at 700 °C, and approaches 133 Pa at 800 °C. Evaluation, testing, and analysis of specimens showed that CaO produced by a single Ca deposition/oxidation process did not exhibit the desired insulating characteristics or stability in liquid Li. Therefore, two processes that involve double Ca deposition/oxidation steps, He-flow and vacuum, were developed to successfully coat V–4Cr–4Ti alloy samples with stable CaO.

He-flow process: In this process, the samples (tabs and/or rods) were hung vertically from the top of the wire screen inner chamber, which was placed inside the steel outer chamber, the top and bottom of which were porous. A 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 775–800 °C for 100–150 h. Calcium-coated specimens were subsequently oxidized in flowing Ar–10 vppm O_2 at ≈700 °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: In this process, the setup consisted of a wire screen sample chamber that was sealed in a quartz tube under a vacuum of 0.013 Pa. A granular Ca charge was placed around the inner chamber and in a cylindrical wire basket at the bottom. A wire basket filled with Ca granules was also placed above the 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. Ca-coated 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), the sample surfaces were examined by scanning electron microscopy (SEM) to characterize their microstructure. The chemical composition of the surface was determined by energy dispersive X-ray (EDX) and X-ray diffraction (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.

Two static liquid-Li systems were used to study the compatibility of the insulator coatings. The systems were filled with ≈15 l of high-purity (99.97 wt%) Li. The concentrations of trace impurities of Na, K, Fe, Si, and Cl in Li were <50 ppm, and the N concentration in the Li was 80 ppm. Ca was added to the Li to achieve a composition of Li–2.8 at.%Ca. The coupon specimens of CaO-coated samples were exposed in the liquid Li–Ca at 500–700 °C. The weight change was measured to establish corrosion rates of the coatings as a function of time. After exposure, the specimens were examined by SEM, EDX, and XRD analysis. The coated specimens were examined to evaluate coating integrity, microstructural changes in coatings, coating/substrate interactions, and electrical insulation characteristics of the coatings.

3. 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 publications [3–6]. It was reported that CaO coatings on V–4Cr–4Ti coupon samples remained intact after exposure to Li for 68 h at 500 °C [3,6]. An EDX spectrum of the coating surface showed 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 [5,6]. A depth profile for a typical coated specimen is shown in Fig. 3; the profile indicates a coating thickness of 34 μm. The coating composition was predominantly CaO, and negligible amounts of substrate elements were detected in the coating region. 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 in excess of the design requirements for a fusion device [5,6]. In this paper, additional results were obtained on coatings developed by both the He-flow and vacuum processes after exposure to Li–Ca for ≈137 h at 600 °C and for 145, 282, and 500 h at 700 °C (see Table 1). The Li used for all exposures contained ≈2.8 at.% dissolved Ca. 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 that held the samples were often self-welded during Ca deposition and/or oxidation steps.

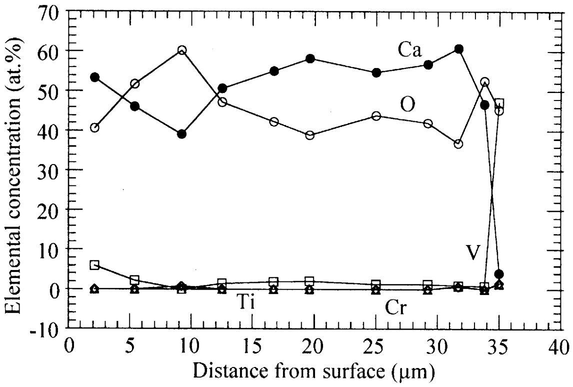

Fig. 3. Elemental concentrations as a function of coating thickness for V–4Cr–4Ti alloy specimen after double Ca deposition and oxidation treatment: coating thickness = 34 μm.

The histograms in Fig. 4 show the weight change data for the V–4Cr–4Ti tab samples after each step during the CaO coating process and also after exposure to Li–Ca at 600 and 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 exposure in Li–Ca indicates that CaO is stable in an Li–Ca environment, as predicted by thermodynamic data as long as the Ca activity in Li is maintained at some high level. Additional effort is needed to establish the threshold Ca and O levels in Li for maintaining a viable CaO coating in Li for extended time periods and in flowing systems with temperature gradients.

Fig. 5 shows XRD results of the two surfaces of the tab samples, 44Tab12 and 44Tab9, which were exposed to Li for 137 h at 600 °C and 145 h at 700 °C, respectively. Both patterns give strong indications of the presence of CaO (peaks identified as C1) on these samples after Li exposure. The $Ca(OH)_2$ phase (peaks identified as C2), observed in the sample tested at 600 °C, is the result of reaction in humid air during post-exposure handling of the specimen. The presence of the V peak (identified as V) in the patterns is predominantly 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 compatibility of CaO in a Li environment, was also verified by EDX analysis. 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 Fig. 6(a) and (b), respectively. These photomicrographs, which were typical of other samples listed in Table 1, indicate that the CaO coating maintained its integrity during exposure to Li.

Table 1
Experimental conditions for the Ca deposition and Li exposure

Sample ID and dimensions (mm)	Process step	Environment or method	Temperature (°C)	Time (h)
Exposure in 2.8 at.%Ca at 600 °C				
44Tab12/11.6 × 7.4 × 1	Anneal	$P \approx 1.3 \times 10^{-4}$ Pa	1000	1
	Ca step 1	He flow	795	140
	Ox step 1	Ar–10 vppm O_2	695	160
	Ca step 2	He flow	800	120
	Ox step 2	Ar–10 vppm O_2	692	140
	Li exposure	Liquid Li–Ca	600	137
44Rod13L/5 diam × 60 long	Anneal	$P \approx 1.3 \times 10^{-4}$ Pa	1000	1
	Ca step 1	He flow	795	140
	Ox step 1	Ar–10 vppm O_2	695	160
	Ca step 2	He flow	800	120
	Ox step 2	Ar–10 vppm O_2	692	140
	Li exposure	Liquid Li–Ca	600	137
Exposure in 2.8 at.%Ca at 700 °C				
44Tab9/12.8 × 7.5 × 1	Anneal	$P \approx 1.3 \times 10^{-4}$ Pa	1000	1
	O pre-charge	$P \approx 6.6 \times 10^{-2}$ Pa O_2	600	50
	Ca step 1	He flow	790	140
	Ox step 1	Ar–10 vppm O_2	690	160
	Ca step 2	He flow	775	146
	Ox step 2	Ar–10 vppm O_2	693	157
	Li exposure	Liquid Li–Ca	700	145
44Rod3S/5 diam × 20 long	Anneal	$P \approx 1.3 \times 10^{-4}$ Pa	1000	1
	O pre-charge	$P \approx 6.6 \times 10^{-2}$ Pa O_2	600	200
	Ca step 1	Vac./quartz	780	166
	Ox step 1	Ar–10 vppm O_2	705	190
	Ca step 2	Vac./quartz	775	146
	Ox step 2	Ar–10 vppm O_2	693	157
	Li exposure	Liquid Li–Ca	700	145
44Rod11S/5 diam × 20 long	Anneal	$P \approx 1.3 \times 10^{-4}$ Pa	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	Ar–10 vppm O_2	700	158
	Ca step 3	He flow	780	100
	Ox step 2	Ar–10 vppm O_2	675	120
	Li exposure	Liquid Li–Ca	700	500

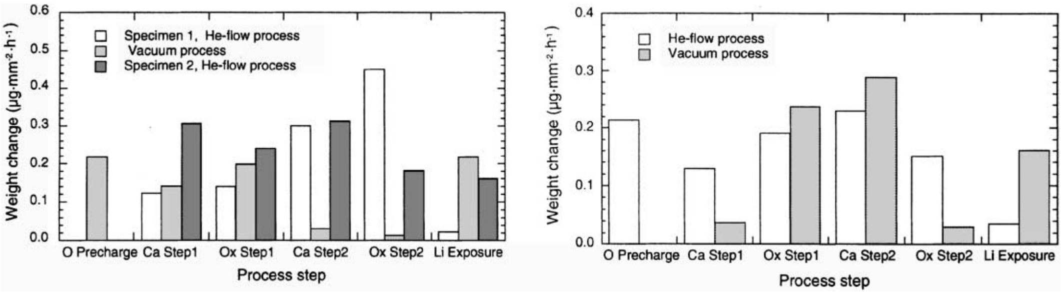

Fig. 4. Weight change in V–4Cr-4Ti alloy tabs during CaO deposition and Li exposure steps for (left) 137 h at 600 °C and (right) for 145 h at 700 °C.

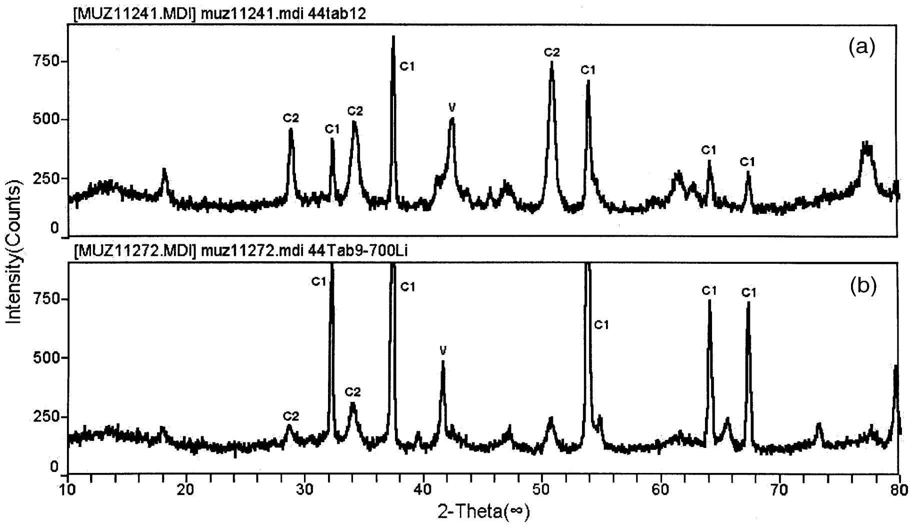

Fig. 5. XRD patterns obtained from both surfaces of CaO-coated V–4Cr–4Ti tabs after (a) 137 h Li exposure at 600 °C and (b) 145 h Li exposure at 700 °C.

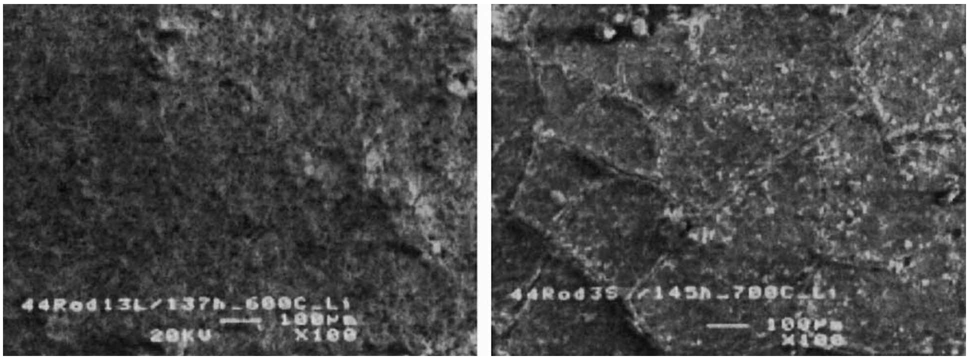

Fig. 6. SEM photomicrographs of V– 4Cr–4Ti rod samples after Li exposure, showing Li compatibility of CaO coating developed by double Ca-deposition/oxidation processes: (left) CaO-coated by He-flow process and exposed to Li for 137 h at 600 °C, and (right) CaO-coated by vacuum process and exposed to Li for 145 h at 700 °C.

The 44Rod11S sample was recently removed from Li after a 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 that CaO was still present on the sample. Other compounds detected on the sample included V, as sampled from beneath the coating, and some Li compounds because the sample was analyzed without removing all of the Li to avoid alterations on the coating that were due to exposure to the ambient environment. Coating scraped from various locations of the surface of this specimen was also analyzed with a Debye–Scherrer powder method and the results indicated the 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 the EDX spectrum (Fig. 7) obtained from the sample surface. 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 an Li–2.8 at.%Ca solution at 700 °C.

The next step in the development of these coatings is to evaluate their performance in a flowing Li system with controlled concentrations of Ca and non-metallic impurities such as O, N, and H. It is essential to establish whether the concentration of these elements can be controlled and maintained in a system with temperature gradients to maintain the chemical and mechanical integrity of the coatings and to retain their electrical insulating capacity.

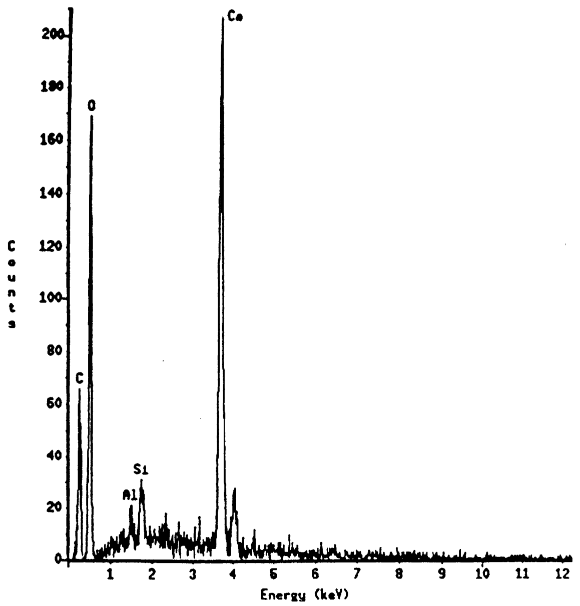

Fig. 7. EDX pattern obtained from surface of CaO-coated specimen of V alloy, after 500-h exposure to Li–2.8 at.%Ca at 700 °C.

4. Summary

We have developed CaO coatings that are applied by a thermal and chemical vapor deposition process. Several experiments were conducted to study how the deposition of Ca on a V–4Cr–4Ti substrate alloy is affected by variations in process temperature and time, specimen location, and surface preparation and pre-treatment. Results showed that thick adherent coatings can be fabricated by thermal/chemical vapor deposition, especially if a double Ca treatment is applied. Extensive microstructural analysis of the coatings showed almost 100% CaO over a coating thickness of 20–30 μm; electrical resistance (measured by the two-probe method) of the coatings was at least two orders of magnitude higher than the minimum required for blanket application. The results obtained in this study indicate that CaO is a viable coating for V–Li advanced blankets, but that significant additional effort is needed, especially from the standpoint of structure/composition relationship to its electrical resistance and the coating stability in a flowing Li environment. Furthermore, resistance must be measured in situ in Li to simultaneously evaluate coating integrity, resistance, and Li compatibility.

Acknowledgements

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