Calcium Oxide Coating on Vanadium Alloys in Liquid Lithium[*]

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ABSTRACT

We have fabricated CaO coatings on vanadium metal and various vanadium alloys (V-10Cr, V-1Ti, V-4Cr-4Ti, and V-5Cr-5Ti), for use in liquid metal blankets of fusion reactors. Initially, by monitoring weight change as a function of time, oxygen was charged into the vanadium alloys (rectangular sample, 2 x 1 x 0.1 cm) at 710°C by flowing Ar-O_2 gas. Oxygen-charged samples were exposed in 2.8 at.% Ca-Li at temperatures of 600 and 700°C for times between 50 and 120 h. The thickness of the in-situ-formed CaO was 13 to 30 μm in the experimental conditions. Thicker CaO films were formed at higher oxygen contents and 700°C, while thinner CaO films were formed at lower oxygen contents and 600°C. The data show promise for in-situ formation of CaO layers on V alloys for the fusion blanket application.

INTRODUCTION

Corrosion resistance of structural materials and magnetohydrodynamic (MHD) forces and their influence on thermal hydraulics and corrosion are major concerns in the design of liquid-metal blankets for magnetic fusion reactors (MFRs). The objective of this study is to develop in-situ coatings at the liquid-metal/structural-material interface, with emphasis on coatings that can be converted to an electrically insulating film to prevent adverse currents generated by MHD forces from passing through the structural walls [1].

Several electrically insulating oxides such as binary oxides (CaO, BeO, MgO and Y_2O_3), ternary perovskite ($CaZrO_3$), spinel ($MgAl_2O_4$), and nitrides (e.g., AlN) can be applied as coatings to V/Li MFR-blanket systems. We have chosen to pursue development of in-situ CaO film deposition on the vanadium alloys because CaO is thermodynamically stable in liquid Li, has the highest electrical resistivity desirable for a thin film, forms in-situ, and is greatly beneficial for healing of defects, such as microcracks and open pores [2,3].   Based on its high thermodynamic stability CaO can be formed in-situ to heal most of the defects on insulator coatings. Therefore, this study of the in-situ CaO-forming process is very important in developing electrical insulator coatings for MFR applications in the V/Li system.

The main process can be stated as Ca + O = CaO, where Ca dissolves in liquid Li and then reacts with O near the surface of V alloys to form CaO. The CaO layer grows based on the inward ambipolar diffusion of Ca^{2+} ion and the two electrons through the CaO layer to react with the O in the V alloys at the CaO/V interface. The O accepts two electrons to form O^{2-} ions, and reacts with Ca^{2+} ions to form CaO. As a result, the CaO layer is dynamically adhesive, and O levels decrease in the V alloys. It is expected that the rate of the process will increase under netron fluency. Additionally, CaO has low activation with neutron bombardment. Both Li and Ca-Li are liquid metals that do not interact heavily with V alloys. The present studyinvolved in-situ CaO film fabrication at 600 and 700°C in 2.8 at.% Ca-Li on vanadium metal and the alloys, V-10Cr, V-1Ti, V-4Cr-4Ti, and V-5Cr-5Ti. We investigated detailed step-by-step procedures for O charging and homogenization, and determined O-migration profiles before and after Ca-Li exposure in O-charged V alloys.

EXPERIMENTAL DETAILS

Samples of V V-10Cr, V-1Ti, and V-5Cr-5Ti were prepared in a rectangular shape (2 x 1 cm) with a 1 mm-diameter hole for the attachment. Sample thickness were 1.15 mm for V, 1.20 mm for V-10Cr, 1.16 mm for V-1Ti, and 0.65 mm for V-5Cr-5Ti. Samples were vacuum-annealed at 1000°C for 2 h, heated at 710°C in Ar-O_2 to reach a proper amount of O charge [2-4], and O-homogenized in a vacuum-sealed (quartz) cell for 17 h at 750°C.   Several samples were arrayed together, dipped into a Ca-Li pot at 450°C, and then heated to 600°C for 120 h or 700°C for 50 h. The sample tree was raised above the liquid Ca-Li level and shaken to

minimize residual Ca-Li around the samples. The excessive Ca-Li around the samples was dissolved in methanol to investigate the surface and cross section by scanning electron microscope (SEM), X-ray diffraction (XRD), and microhardness measurements. For the 700°C run, only the O-charged V-4Cr-4Ti sample was prepared and analyzed. Vickers hardness (VH) was measured before and after the Ca-Li exposure and also on the as-received sample for reference. Ex-situ electrical conductivity measurements were performed for the several samples after removal of the residual Ca-Li in the ethanol. As electrodes metallic gallium was used on two platinum discs in the top and bottom position. Liquid gallium on the coating was not wet at room temperature, but the gallium was well adhered on the platinum discs for the electrical conductivity measurement. However, when the CaO-coated V alloys were placed between two gallium electrodes and a spring load applied, the excessive gallium was extruded out around the sample-platinum edge. This excess gallium was removed. The electrical conductivity measurements were performed in 99.996% Ar gas at $25 \leq T \leq 500°C$, and supplied the current, i, was $\leq 1\times10^{-6}$ ampere.

DISCUSSION

During O charging, a blue surface layer of thin vanadium oxide appeared. However, with O homogenization, the sample surface became shiny and metallic looking. It can be assumed that surface oxygen diffused into the V alloys by solid-state diffusion. A small amount of oxygen was added during the O-homogenization process. Figure 1 shows VH values versus normalized thickness for V, V-10Cr, V-1Ti, and V-5Cr-5Ti before and after Ca-Li exposure at 600°C for 120 h. Because hardness was lower near the surface of the V alloys, it is related to the lower oxygen concentrations near the surface. In V-5Cr-5Ti (Fig.1d), most of the oxygen was present near the surface, and the oxygen in this region was evacuated during the CaO forming process. Figure 2 shows the elemental Ca and V fractions obtained by the energy dispersive scpectrometry (EDS) versus distance near the interface of the CaO/V alloys. For the EDS analysis, O in the V-alloy system cause a problem if the vanadium concentration (or Ti and Cr) is too high. Since the oxygen k energy level and the V-(Cr-Ti) l energy level are too close for separation in the EDS analysis, analysis of O is possible only when the vanadium concentration is low enough for comparison with oxygen. In the near future, we will do O-analysis by secondary ion mass spectroscopy (SIMS).

600°C exposures

According to the cross-sectional EDS analysis in Fig. 2 and the SEM photomicrographs in Fig. 3 for the CaO coating layers, the thicknesses of the underlined adhered CaO layer formed at 600°C for 120 h are 14 μm for , 3 μm for V-10Cr, 6 μm for V-1Ti, and 18 μm for V-5Cr-5Ti. The SEM view (Fig. 3e) and back-scattered electron image (Fig. 3f) reveal the uniform thickness of the in-situ-formed CaO film on the V-5Cr-5Ti. A high-magnification SEM view (Fig. 4a) and EDS analysis with distance (Fig. 4b) were obtained near the CaO/V-5Cr-5Ti interface. A higher oxygen concentration is apparent near the interface, but the EDS data will not be reported here (including O) because we do not have calibrated data yet. However, the EDS analysis indicated that the interface area has somewhat higher O concentration than that in the overall CaO layer. This higher O concentration is quite understandable because the O source is the metallic site, and calcium reacts with the oxygen provided by the V alloy. This trend is promising for in-situ formation of CaO layers on the V alloys because the higher O concentrations mean that higher electrical resistivity is expected in this system.

700°C exposures

Figure 5a shows VH versus normalized thickness at low O levels (561 wppm) as-received samples (without O charging or exposure in Ca-Li) and for V-Cr-Ti samples exposed in 2.8 at.% Ca-Li at 700°C for 50 h. The VH values increased in the near-surface area of 40-50 μm depth. Figure 5b and c indicate that the oxygen is consumed in the 200 μm region for the high oxygen sample (9725.5 wppm), and in the 80 μm region for the low oxygen sample (4452.3 wppm). According to Fig. 5a-c, when the O content is low in the V-4Cr-4Ti, its surface region becomes hardened after exposure in the Ca-Li environment. In the higher O-bearing V-alloys, the in-situ-forming CaO film behaves as a barrier to environmental impurities, such as C and N whose incorporation into the V-4Cr-4Ti increases the alloy hardness.

Figure 6 shows cross-sectional and surface SEM/EDS for the samples exposed at 700°C for 50 h in 2.8 at.% Ca-Li. A 30-μm thick CaO layer was formed in such conditions for the 9359 wppm-O-charged sample,

and a 17-μm layer for the 5021 wppm-O-charged sample. Also, we see similar O-enrichment at the interfaces for both the 600 and the 700°C runs.

Figure 7 shows the X-ray diffraction analysis for various CaO-film fabrication processes. As can be deduced from Fig.7, the PVD film formed on the V-4Cr-4Ti has a CaO crystal structure (NaCl-type structure)[4], but the in-situ films formed by exposure to Ca-Li environments do not present a clear CaO crystal structure. Presumably, an amorphous CaO film was a formed in-situ Ca-Li environment.

The in-situ Ca-Li film (or Li exposed oxide, e.g., Y_2O_3 in lithium) contains lithium based on our previous SIMS work.   Lithium will be oxidized when exposed to oxygen, carbon dioxide, or moisture by the reaction, $2Li + 1/2\ O_2 = Li_2O$, $2Li + 1/2O_2 + CO_2 = Li_2CO_3$, or $2Li + 1/2\ O_2 + H_2O = 2Li(OH)$, respectively.   The generated Li ion is highly mobile in the solid state. Therefore, the Li ion under an electric field becomes very sensitive to field polarity and will be polarized through the film layer. When polarized, the Li makes an open circuit and follows a strong DC dry-battery behavior. The Li ion remains through the electrochemical potential gradient buildup by the DC field. Figure 8a shows the polarization behavior when switching the polarity over 10-s interval. Figure 8b shows the temperature and iR-drop [dc i = ± 1 μa] potential monitored as a function of time during the conductivity measurement. However, when the system is controlled in a as steady state (current vs. applied potential) with inert electrodes, then we are measuring the electrical conductivities only for the electrons or electron holes (not ions), which might be suitable for the MFRs condition. However, under the same condition, hydrogen isotopes (H, D, or T) or protons will be affected by the electric fields or the EMF (electromotive force). Even in our current electrical resistivity measurement, we expect that some fraction of the proton conduction could be included due to few parts per million moisture in the measuring system.

Figure 9 shows the electrical conductivity and resistivity vs. reciprocal temperature for the oxygen-charged-V-4Cr-4Ti exposed in 2.8 at.% Ca-Li at 600°C for 50 h, after the excess Ca-Li had been dissolved from the CaO-coated samples were dissolved the excess Ca-Li by means of gallium metallic electrodes supplying a switching polarity of 1 μa (dc) in flowing 99.996 % Ar. In the near future, electrical conductivity will be measured on in-situ-formed CaO films in Ca-Li with other V-4Cr-4Ti. The measured electrical resistivity for the in-situ formed CaO layers on V alloys provided that the promising on the magnetic fusion blanket applications [2].

CONCLUSIONS

The CaO coatings were produced on oxygen-charged vanadium (V, V-10Cr, V-1Ti, V-4Cr-4Ti, and V-5Cr-5Ti) by exposure to liquid Li that contained 2.8 at.% Ca. The thickness of in-situ formed CaO layers increased with increased oxygen charging. In the experimental conditions, the thickness of the grown CaO films was 13-30 μm. The measured electrical resistivity data and the microstructure of the in-situ formed CaO layers on V alloys tested in this study show promise for the magnetic fusion blanket application.
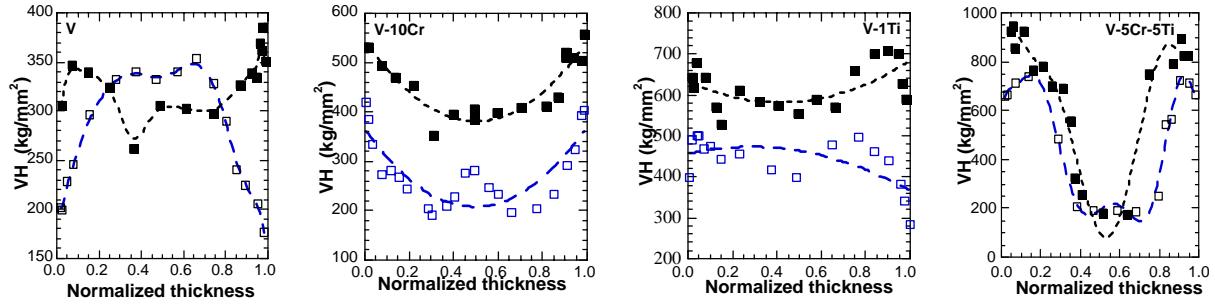

ACKNOWLEDGMENTS

Figure 1. Vickers hardness vs. normalized thickness for before (closed symbol) and after (open) exposure in 2.8 at.% Ca-Li at 600°C for 120 h (from left to right, V, V-10Cr, V-1Ti, and V-5Cr-5Ti.)
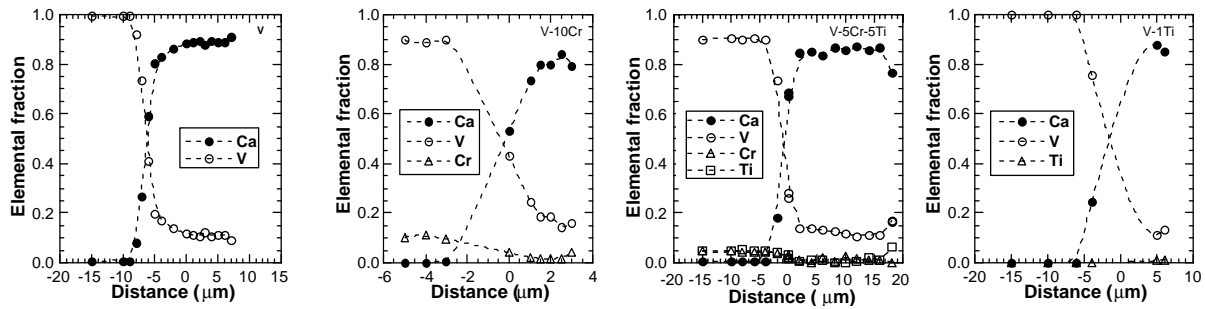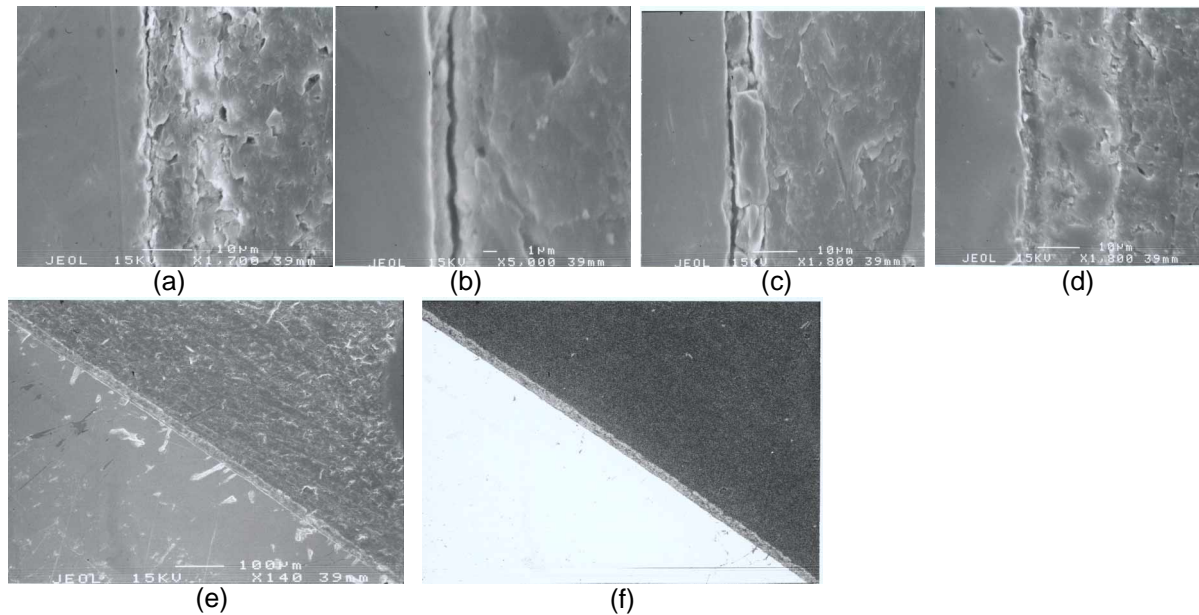

Figure 2. EDS analysis vs. normalized thickness for before (closed symbol) and after (open) exposure in the 2.8 at.% Ca-Li at 600°C for 120 h (from left to right, V, V-10Cr, V-1Ti, and V-5Cr-5Ti.)

(a) (b) (c) (d)

(e) (f)

Figure 3. Cross section SEM photographs near coating/V-alloy interface for sample exposed in 2.8 at.% Ca-Li at 600°C for 120 h: (a) V,(b) V-10Cr, (c) V-1Ti, and (d) V-5Cr-5Ti. Also shown are (e) the extended area SEM view with low magnification from (d) and (f) the back-scattered-electron image (BEI).
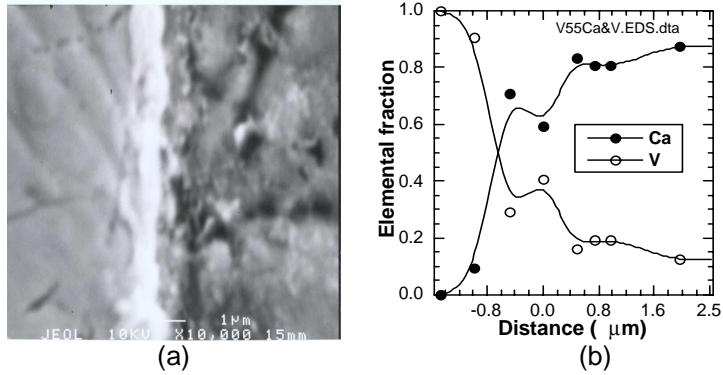
Figure 4. Cross-section (a) SEM photomicrograph and (b) EDS analysis near interface region for CaO/V-5Cr-5Ti sample exposed in 2.8 at.% Ca-Li at 600°C for 120 h.
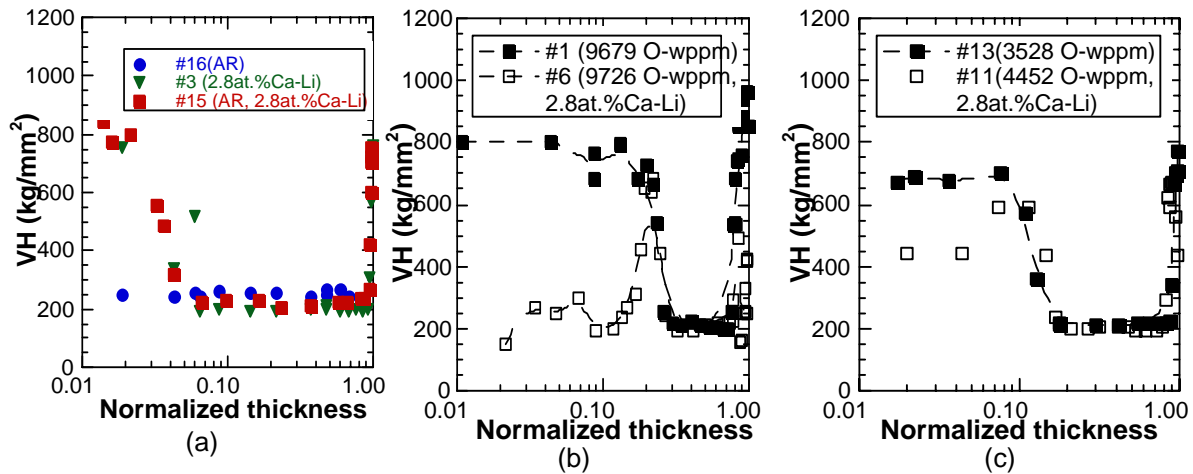

Figure 5.
VH vs. normalized thickness for (a)as received samples (AR) and sample exposed and 561 O wppm; (b) samples exposed 9679.2 O wppm and 9725.5 O wppm, and (c) sample exposed 4452.3 O wppm and 3527.7 O wppm. Conditions: V-4Cr-4Ti in 2.8 at.% Ca-Li at 700°C for 50 h.
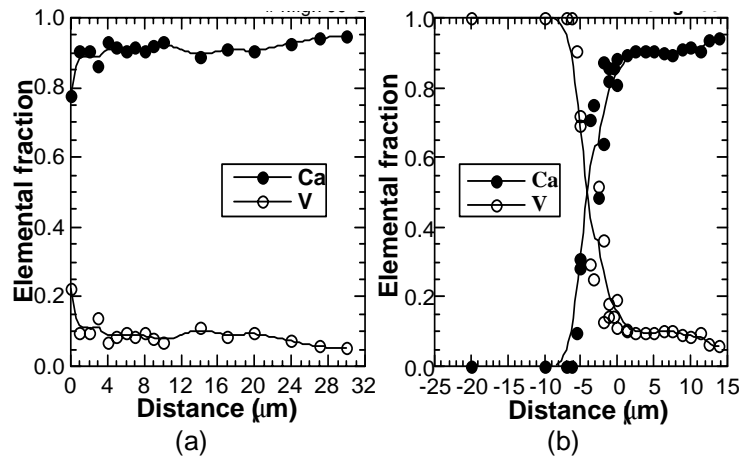

Figure 6. EDS profile for V-4Cr-4Ti samples exposed to (a) 9359 wppm O and (b) 5021-wppm O. Formed at 700°C for 50 h in 2.8 at.% Ca-Li.
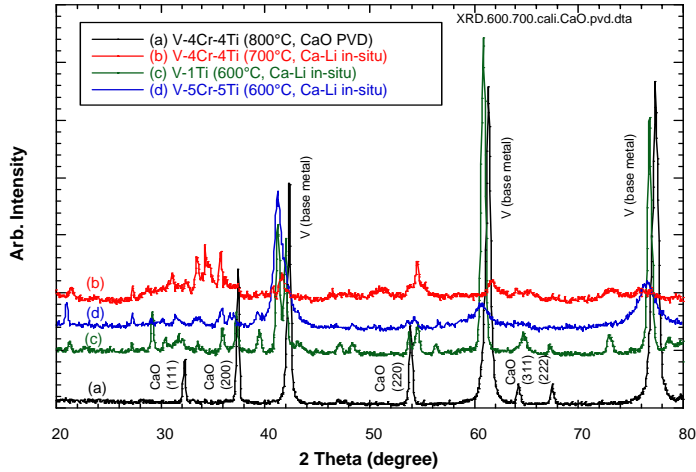
Figure 7. X-ray diffraction analysis for various CaO-film fabrication processes:

(a) Physical vapor deposition (PVD) of CaO on O-charged V-4Cr-4Ti,[4];
(b) (b) V-4Cr-4Ti formed at 700°C for 50h,
(c) V-1Ti formed at 600°C for 120 h, and
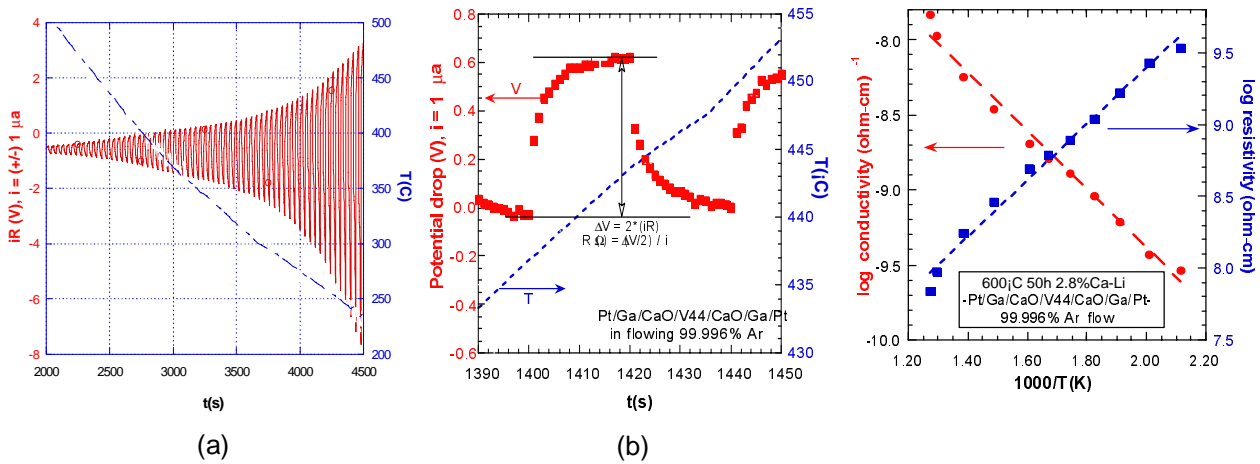(d) V-5Cr-5Ti formed at 600°C for 120 h, respectively. In b-d, O-charged V alloys exposed to 2.8 at.% Ca-Li.

(a)

(b)

Figure 8. (a)Temperature and iR-drop potential monitored as function of time during conductivity measurement (b) for detail.

Figure 9

Electrical conductivity and resistivity vs.1000/T for the O-charged-V-4Cr-4Ti exposed in 2.8 at.% Ca-Li at 600°C for 50 h.

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