**STUDY OF THE LONG-TERM STABILITY OF MULTI-LAYER MHD COATINGS FOR FUSION REACTOR APPLICATIONS**—B. A. Pint, P. F. Tortorelli, L. D. Chitwood, and H. M. Meyer (Oak Ridge National Laboratory, USA) and M. Fujiwara (Tohoku University, Japan)

## OBJECTIVE

The objective of this task is to assess the long-term, high-temperature compatibility of high electrical resistance, multi-layer coatings with lithium at high temperatures. Electrically insulating coatings on the first wall of magnetic confinement reactors are essential to reduce the magnetohydrodynamic (MHD) force that would otherwise inhibit the flow of the lithium coolant. A recent assessment of the crack tolerance for these coatings determined that a multi-layer coating with metal and ceramic layers was needed to prevent Li from wetting coating cracks or defects. Therefore, basic compatibility of a vanadium coating layer is now being assessed by studying the compatibility of vanadium alloys in static lithium.

## SUMMARY

Static lithium compatibility tests have been conducted on vanadium alloys at 800°C. Mass gains have been detected that are not consistent with prior static Li exposures of unalloyed vanadium and are difficult to interpret based on the impurity levels in the lithium specified by the manufacturer. A second test gave more reasonable results. Some of the mass gain could be attributed to N and C uptake from the Li but this should be countered by O loss from the alloy. Post exposure analysis of the specimens indicated a surface layer rich in O, C and Ca but no indication for the embrittlement observed.

## PROGRESS AND STATUS

### Introduction

A recent evaluation of the effects of cracks and defects on the performance of MHD coatings indicated that a very small fraction of through-thickness cracks could be tolerated with the assumption that Li will wet the cracks and thereby short the coating.[1,2] Even if cracks in the coating are not inherent from the fabrication process, tensile stresses are likely to cause periodic cracking in the brittle ceramic layer.[2] One strategy to address this issue is to use a two-layer or multilayer coating with a metallic layer adjacent to the Li to prevent wetting of cracks in the ceramic layer. Multilayer coatings have been suggested in several papers, e.g., Ref. 3. This strategy switches the focus of the compatibility work from the ceramic layer to the metallic layer. A likely candidate for the metallic layer is vanadium or a V-base alloy. The V-Li blanket system was originally proposed because of the reported good compatibility between vanadium and Li, e.g., Ref. 4. However, a review of the literature revealed that some studies showed relatively high dissolution rates of vanadium alloys with Li in loop tests.[1,5,6] while others found good compatibility.[7,8] This discrepancy suggests that more work needs to be done to understand the compatibility of vanadium alloys in Li before the multi-layer concept can be considered viable. This report presents results from three capsule experiments conducted at ORNL; the first two with specimens from Japan and the third with specimens from the US program.

### Experimental Procedure

Vanadium alloy coupons (≈250µm x ≈5mm x 25mm or ≈1mm x 10mm x 15mm) with various Cr and Ti contents and miniature tensile specimens (SS-3) of V-4Cr-4Ti (Heat#832665 made at Wah Chang, Albany, OR) were tested after a 1050°C, 1h vacuum anneal. The experimental procedure for static lithium capsule exposures has been outlined elsewhere.[9,10] Molybdenum capsules were used and all of the capsule tests were exposed for 1000h at 800°C. However, 5g of Li (≈9.4 $cm^3$) was used in each test and the

specimen volume was different in each test. After exposure, the vanadium alloy specimens were cleaned by a variety of techniques: (1) submerging them in methanol for 24h to dissolve the residual Li, (2) submerging them in ice water for 1h, (3) vacuum distillation for 10h at 550°C followed by 12h at 600°C in a specially developed rig with a water cooled copper coil and a base pressure of $10^{-6}$ Pa. The exposed SS-3 specimens were characterized using Auger electron spectroscopy (AES).

## Results and Discussion

Figure 1 shows the specific mass change results for three Mo capsule tests with vanadium alloy specimens exposed to Li for 1000h at 800°C. The first capsule contained seven vanadium alloy coupons with various Cr and Ti contents with a total volume of 1.00cm$^3$ and all of the specimens were cleaned in alcohol. The second capsule contained nine coupons of V-4Cr-4Ti (NIFS Heat #2) with a total volume of 0.31cm$^3$ which had the Li removed by different methods. In each test, the specimens gained an unexpectedly large amount of mass. Because the mass gain is associated with impurity (e.g., N and C) uptake from the Li, the higher mass gains for the V-4Cr-4Ti specimens may be due to the smaller specimen volume in that capsule. Figure 1a shows the results for the first two capsules for specimens cleaned with alcohol and compares the mass changes for different Ti and Cr levels. Specimens with higher Cr levels showed the lowest mass gains. However, all of the mass gains were relatively similar. Figure 1b shows the mass gains for the V-4Cr-4Ti specimens with different cleaning methods. The mass gain after distillation was the highest. This could be due to some O uptake during the 600°C vacuum distillation exposure. From the second capsule test, the lowest mass gains were for cleaning in water. In prior work, lithium removal in water has been associated with the dissolution of $Li_9CrN_5$.[11] For all of the cleaning methods, a thin surface film was observed on the specimens after exposure. Most of the specimens from these tests were sent to Japan for further characterization.

Because of the unexpected results, a third Mo capsule test was performed for the same time and temperature but using three SS-3 specimens of V-4Cr-4Ti with a total volume of only 0.18cm$^3$. After this exposure, the specimens were cleaned in alcohol and appeared shiny (as expected). However, Fig. 1b shows that the specimens still experienced a significant mass gain. However, the mass gain was much

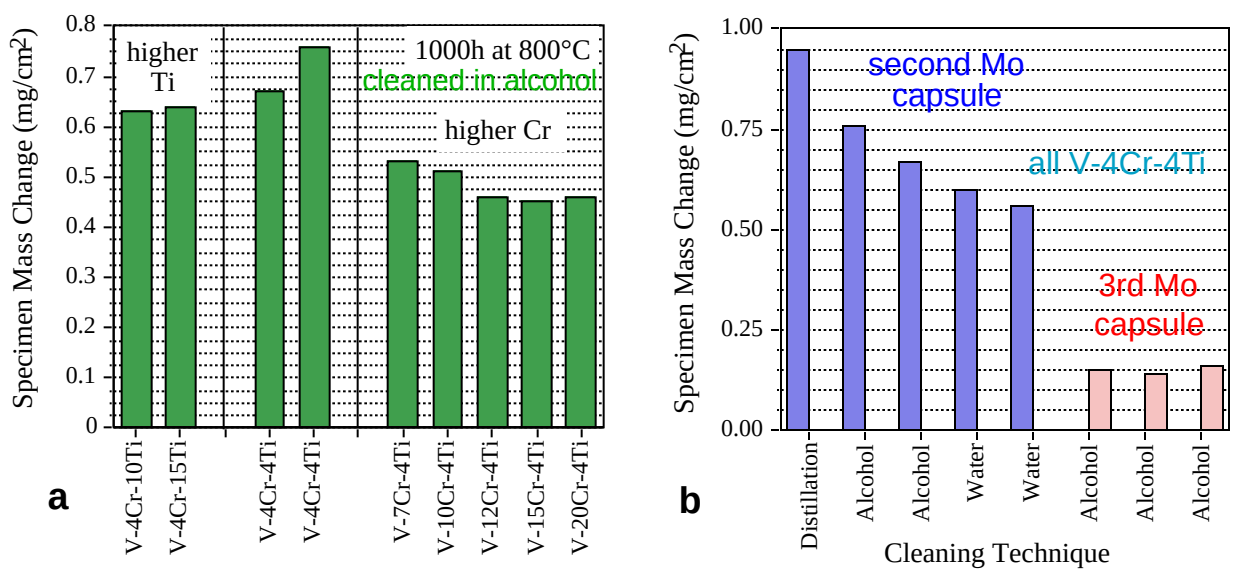


Fig. 1. (a) mass gain for various V-Cr-Ti alloy specimens after 1000h at 800°C in Li-filled Mo capsule and cleaned with chilled alcohol and (b) mass gain for V-4Cr-4Ti specimens after 1000h at 800°C in Li-filled Mo capsules and cleaned by various techniques.

lower compared to the previous tests. While drying one of the specimens in a lint-free cloth, it broke suggesting that all of the specimens were highly embrittled.

In all cases, the relatively high mass gains for so many samples cannot be explained. Vanadium alloys would be expected to getter N and C from the Li at this temperature. Each capsule contained ≈5g of Li with a manufacturers' analysis of 65ppmw N. No information is currently available on the C content. For the three specimens in the third capsule test, the N uptake could be as high as 0.06 mg/cm$^2$. However, a mass loss of 0.10 mg/cm$^2$ would be expected if the Li gettered 300ppmw O from each specimen (which has a starting O content of 310ppmw [12]). The starting Li oxygen content has not been determined but this element would be expected to remain in the Li based on thermodynamic stability. In order to explain the mass gain for these specimens, a large fraction of the N and C must have absorbed by the V-4Cr-4Ti while little O was lost. The Li chemical composition from the third capsule after exposure is currently being measured in order to determine if there was any significant change in the chemistry.

It also is possible that some Li was absorbed into the specimen or Li-containing compounds formed. After exposure and cleaning, the V-4Cr-4Ti specimen which broke during cleaning was characterized by AES. (As with most analytical techniques for vanadium alloys, there is great difficulty resolving the overlap between the V and O and Ti and N signals. However, AES is able to detect Li.) Figure 2 shows examples of the specimen surface. No surface preparation was performed prior to the test so the as-rolled surface morphology is present. The morphology in Fig. 2a was similar to that of a specimen from the same batch exposed to He indicating that no significant reaction occurred on the surface. However, at higher magnification, the surface appeared terraced, suggesting that some mass transfer or surface rearrangement occurred. No significant amount of Mo was detected by AES analysis, thus ruling out mass transfer from the capsule. Also, no Li was detected on the specimen surface. However, a non-uniform distribution of Ca was found on the surface in the form of a Ca-V-O layer, approximately 5-10nm thick. Apparently a modification of the native oxide on the specimen, which was 10-15nm thick, must have occurred. The Ca was likely due to the 53ppmw Ca impurity in the Li but this layer could not account for even 5% of the mass increase for this specimen. (If all of the Ca in the Li reacted to form an oxide on the surfaces of the three specimens, a mass gain of 0.046mg/cm$^2$ would be expected.) Isolated particles also were observed on the surface, e.g., Fig. 2b. These particles were often rich in V, Ti, C and N but also occasionally contained small amounts of Ca, O, Cu and Mo. The small number of these particles also could not account for much of the mass increase.

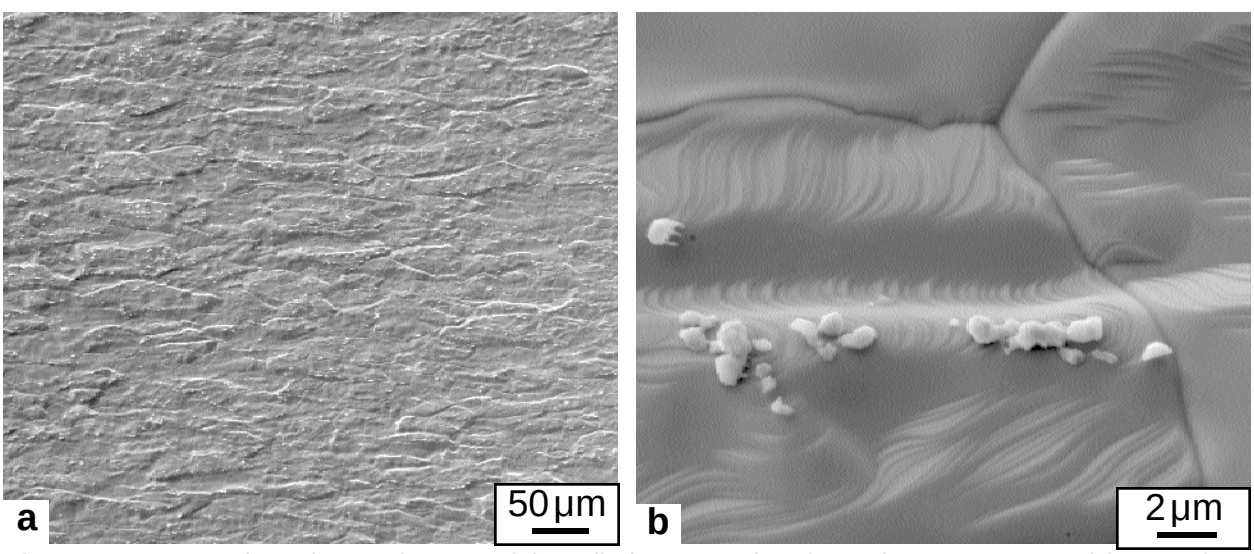


Fig. 2. SEM secondary electron images of the rolled V-4Cr-4Ti surface after exposure to Li for 1000h at 800°C. At higher magnification, (b), slight faceting or terracing of the surface was observed.

The fracture surface also was examined to determine the fracture mode. For this specimen, it appeared to be generally transgranular fracture, which indicates that the grain boundaries were not selectively embrittled, Fig. 3. This observation suggests that the matrix was embrittled by the exposure consistent with the mass gain.

To put the current results in perspective, Table I summarizes the results from a 1964 ORNL report by DiStefano of unalloyed vanadium tested in static Li capsule tests for 100h at 815°C.[13] Various levels of oxygen were added to vanadium using exposures at 850°C at an oxygen pressure of $10^{-2}$ Pa ($9 \times 10^{-5}$ Torr). Additions of O to Nb were known to increase its susceptibility to Li attack. However, for unalloyed vanadium, the O was selectively removed from the specimens resulting in a mass loss after exposure proportional to the O removed. No dissolution or attack of the vanadium specimens was observed. In this case, the specimens were cleaned by vacuum distillation.

Additional characterization is needed to further understand these results including measuring the impurity contents (N, O, C, H) of the specimens after exposure and obtaining more information on the Li chemistry. In general, future work will need to determine the role of Cr and Ti alloy additions on the compatibility of vanadium alloys with Li. However, capsule experiments can only be expected to produce a limited picture of V-Li compatibility. A loop experiment with a temperature gradient is needed to truly determine the compatibility in this system.

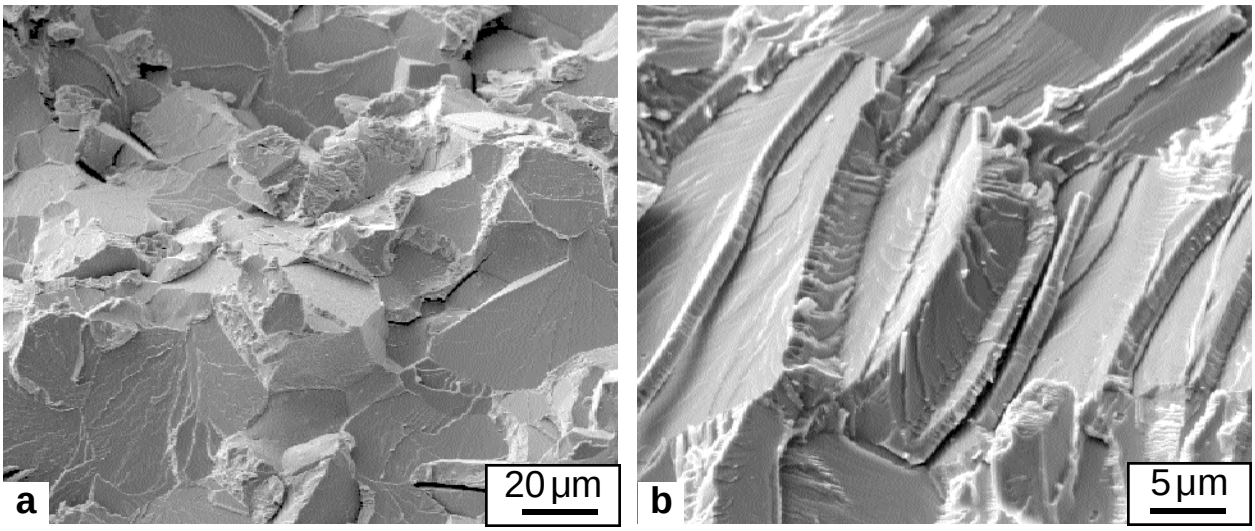


Fig. 3. SEM secondary electron images of the fracture surface of V-4Cr-4Ti which broke on handling after 1000h at 800°C.

Table 1. Summary of previous results of unalloyed vanadium exposed to Li for 100h at 815°C.[13]

| Oxygen Content (ppmw) | | |
|---|---|---|
| Before test | After Li exposure | Mass loss |
| 400 | 80 | 0.08 (mg/cm$^2$) |
| 800 | 110 | 0.20 |
| 1200 | 30 | 0.25 |
| 2200 | 180 | 0.52 |

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