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# Development of Electrically Insulating Coatings on Vanadium Alloys for Lithium-cooled Blankets*

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The self-cooled lithium blanket concept with a vanadium structure offers a potential for high performance with attractive safety and environmental features. Based on blanket design studies, it became apparent that electrically insulating duct walls would be required to reduce the magnetohydrodynamic (MHD) pressure drop for liquid metal-cooled blankets for high magnetic field fusion devices. As a result, development of insulator coatings was recommended as the most appropriate approach for resolving this issue. Oxides such as CaO, $Y_2O_3$, BeO, MgO, $MgAl_2O_4$, and $Y_3Al_2O_{12}$ and nitrides such as AlN, BN and $Si_3N_2$ were initially considered potential candidate coating materials. Based on results of scoping studies, CaO and AlN have been selected as primary candidates for further development. Progress on the development of CaO and AlN coatings, including in-situ formation and electrical properties measurements, are summarized in this paper.

## 1. INTRODUCTION

The self-cooled lithium blanket with a vanadium alloy structure offers a potential for high performance with attractive safety and environmental features [1-4]. Features include high heat load capability, high operating temperature, potential for long lifetime, design simplicity, low operating pressure and use of low activation materials. Key issues for the vanadium/lithium blanket include continued development of vanadium alloys, development of electrically insulating coolant channels to mitigate MHD effects, and tritium recovery from lithium. Development of the electrically insulating channels is perhaps the most challenging issue at this time. Development of electrically insulating coatings on channel walls is the preferred approach. Self healing of any defects in the coatings which might occur during operation is considered essential to provide acceptable reliability.

Design analyses and evaluation have been conducted previously in order to define performance requirements for insulator coatings under projected fusion system conditions. Use of insulator coatings in lithium cooled blankets will reduce the total pressure drop by a factor of 100 to 1000 compared to values for bare metal walls. These analyses indicate that only modest electrical resistivities or very thin coatings are adequate to suppress the MHD pressure drop. Design analyses have also indicated that some defects in the coatings would not seriously degrade the performance.

Oxide, nitride, and carbide coatings have all been considered. However, only a few oxides are stable in lithium and many nitrides, carbides and silicides do not exhibit adequate electrical resistivities. Although several oxides and nitrides are potential candidate coating materials, CaO and AlN are considered as the leading candidates at this time. Progress in the development of these two insulator coatings are summarized in this paper.

## 2. PRELIMINARY EVALUATION

The current focus of the insulator coating research is for the self-cooled lithium blanket with a vanadium alloy structure. Key considerations for selection of candidate coating materials include the following.

- chemical stability/compatibility with lithium at elevated temperatures
- reasonably high electrical resistivity
- potential for coating of complex channel geometries
- potential for *in situ* self-healing of any defects that might occur
- thermal expansion match with the vanadium alloys
- safety/environmental characteristics, e.g., low activation properties
- materials availability/cost
- Neutronic properties
- radiation damage

Oxides were generally considered initially as the preferred candidates to meet the specified criteria, however, only a limited number of oxides are stable

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in lithium [2]. Nitrides are generally more stable than the oxides in lithium; however, many of the nitrides do not exhibit high electrical resistivity. For example, both VN and TiN are stable in lithium; however, they do not exhibit high resistivity. Similarly, most carbides and silicides do not typically exhibit high resistivity. Therefore, oxides such as CaO, $Y_2O_3$, BeO, MgO, $MgAl_2O_4$, $Y_3Al_2O_{12}$, and nitrides such AlN, BN, and $Si_3N_2$ were considered as potential candidates based primarily on thermodynamic considerations and electrical resistivities of monolethic materials.

The initial focus of the development program involved scoping compatibility tests of selected monolithic ceramics in liquid lithium [5]. In general, results were mixed, with stability of the ceramic dependent on fabrication process and purity, e.g., bonding agents. Most ceramics were less stable than anticipated. Of the various candidate insulator materials, $Y_2O_3$, CaO, BeO, AlN and $Si_3N$ appeared to be the best candidates for further investigation.

Several methods for fabrication of the insulating coatings were considered [6, 7] e.g., physical vapor deposition (PVD) chemical vapor deposition (CVD), pack cementation (PC), and various approaches involving *in situ* formation by exposure in liquid metals. The more conventional approaches, e.g., PVD and PC, were investigated primarily for developing coatings for compatibility tests and as a possible application to the test module for conducting a proof-of-principle MHD test for the insulator coating concept.

The initial effort emphasized the $Y_2O_3$ followed by the AlN. An obvious approach for fabricating an $Y_2O_3$ coating on complex shapes and for providing a potential for self-healing was not defined. In addition, significant effects of hydrogen interactions were thought to affect the stability of the coating and to potentially present a tritium inventory problem. The current focus is on CaO with AlN as an alternate.

Theoretical and experimental investigations were conducted to evaluate the effects of insulated walls on the MHD flow characteristics for a variety of anticipated conditions. The theoretical investigations involved effects of magnetic field, channel geometry, insulator properties (resistivity, thickness, etc.) and integrity of the coating. Calculations indicated that very thin coatings (<1μm) with only modest resistivities (~$10^4$ Ω.m) were adequate to suppress the MHD pressure drop to negligible levels for projected blanket conditions. Candidate coatings, e.g., CaO and AlN, have electrical resistivities several orders of magnitude higher than required. Analyses have also been performed to evaluate the effects of defects in the coating [8, 9]. Results obtained indicate that channel walls with substantial defects (e.g., a few percent of the wall area) will have little effect on the pressure drop in the channel even if the effective resistivity of the defects is two-to-three orders of magnitude less than that required for the wall. In general, calculations indicate that thin insulator coatings (1-10μm) will effectively suppress MHD pressure drop in channels even with significant defects. Assuming self-healing of the coating occurs, it appears that the coating approach will be quite robust.

Experiments have also been conducted on the ALEX facility at Argonne to validate the effectiveness of coatings to suppress the MHD pressure drop in liquid metal systems [10]. For this experiment, an $Al_2O_3$ coating was produced on a type 304 stainless steel test section. Results obtained at 30°C approached the theoretical value, which is over a factor of 20 reduction in pressure drop from the values for a bare wall case. Higher temperature tests (85°C) gave pressure drops about twice those of the lower temperature tests. These results demonstrate the effectiveness of thin insulator coatings for reducing the MHD pressure drop in a liquid metal system.

## 3. AlN COATINGS

The AlN coating was investigated both by conventional fabrication methods and by possible *in situ* formation by additions of either Al or N to the lithium. Research on the AlN coating was focused primarily on formation by conventional processes. Physical vapor deposition (PVD) was one of the methods used to develop AlN coatings both on bare and pre-aluminized vanadium alloy specimens. PVD coatings were produced by Midwest Research Technologies (MRT) and by Basic Industrical Research Laboratory (BIRL). Coatings were also produced by reaction sputtering at Argonne (ANL) and by ion-beam-assisted reactive evaporation at Cametoid Advanced Technologies (CAT) of Canada. These processes provided coatings 8-12 μm thick, which generally exhibited high resistivity at room temperature. Initial compatibility tests in lithium resulted in significant cracking and/or spallation after exposure to lithium at 300°C [6, 11]. Substantial improvements in coating performance were obtained with further development involving thermal/chemical hardening of the coatings at temperatures of 700-900°C. Figure 1 shows a SEM photomicrograph of

the AlN coating on a vanadium alloy and the corresponding EDX profiles. Figure 2 shows the results of resistance measurements at room temperature for several specimens after exposure to Li at 300°C.

The AlN potentially offers a possibility for in-situ formation by either of two processes, i.e., aluminizing the vanadium surface and reacting with nitrogen from the lithium or by reacting nitrogen from the vanadium with aluminum dissolved in the lithium. Reacting nitrogen from the lithium with an aluminized vanadium alloy surface was selected as the best option for AlN, although scoping tests were conducted by adding both nitrogen and aluminum to the lithium. Only limited effort was provided for this approach with mixed results and with no definite conclusions regarding the feasibility of producing satisfactory AlN coatings by these processes.

## 4. CaO-BASED COATINGS

The primary effort related to *in situ* coating development has been focused on calcium oxide. This system offers a potential for superior performance compared to the other systems considered, e.g., high electrical resistivity, good thermal expansion match with vanadium alloys, chemical stability, low activation, and potential for *in situ* formation with self-healing potential. The primary mechanism of coating formation involves reactions of oxygen from the vanadium alloy with calcium dissolved in the lithium. Several variables involved in this reaction include temperature, time, oxygen concentration in vanadium alloy, and calcium concentration in lithium [5, 7, 12, 13]. Scoping tests were conducted by exposing small coupons of vanadium alloys at various temperatures to lithium containing various concentrations (2-50 at %) of calcium. It was generally found that increasing the oxygen concentration in this surface of vanadium by exposure to low pressure oxygen environments before exposure to the lithium-calcium alloy produced thicker oxide reaction products. A range of conditions (temperature, oxygen pressure, and time) were investigated to determine which conditions provided better coating characteristics. In the initial investigations "CaO" coatings were obtained by reacting vanadium alloy coupons in LiCa in small capsules (<100 cm3) at temperatures of 400-1000°C. CaO coatings ~10μm thick were successfully formed on vanadium alloys as shown in Figures 3 and 4. In this case microcracks were observed at room temperature; however, spallation of the coating was not observed.

An apparatus was constructed to obtain *in situ* electrical resistivity measurements from coated samples during exposure to lithium at elevated temperatures. In selected cases such as shown in Figure 5, high resistance measurements were obtained on specimens exposed to lithium - 0.5 wt% calcium for extended periods at elevated temperatures, e.g., >200 hr at 435°C. This coating was obtained by exposure to high purity argon (~ 10 ppm $\underline{O}$ ) at 650°C for 17 hours to oxygenate the surface followed by a 17 hour exposure to 50/50 at % Li/Ca alloy at 400°C in small capsule tests. The generally positive results were obtained in several tests of this type. Additional tests were conducted to evaluate the effects of thermal cycling/thermal shock resistance of these coatings. Results obtained by thermal cycling the Li-Ca vessel indicated ceramic resistivity behavior (increase in resistivity with a decrease in temperature) initially followed by a sharp decrease in resistivity. The decrease in resistivity was attributed to cracking of the coating (see Figure 6). An increase in temperature was followed by an increase in resistance, suggesting self healing of the cracks. These types of tests were duplicated with similar results. Significant resistances (R x A > 1000 $\Omega \bullet cm^2$) were achieved from these "self healing" experiments; however, the resistance values were typically much lower than the initial high resistance values.

Results obtained in these experiments were considered sufficiently encouraging to initiate tests on a larger scale, i.e., a static test vessel containing ~ 3 l of Li-Ca alloy. These tests were conducted with rod-type (pencil) specimens with rounded ends in an attempt to minimize residual liquid metal which adhered to the end of the specimens and possible cracking at sharp corners. Vanadium alloy specimens exposed to LiCa at temperatures of 400-500°C exhibited a modest increase in resistance with time as shown in Figure 7, indicating formation of a very thin insulating coating. A range of coating parameters (temperatures, exposure time, Ca content, and pre-exposure oxidation) were investigated. These tests were conducted primarily with only a few percent Ca ( $\leq 4$ $^{w}/_{o}$) in lithium; however, the general procedure remained the same; viz., oxygenate the vanadium alloy surface, expose the specimen to the Li-Ca alloy, gas phase oxidation of the Ca coating in most cases, and subsequent compatibility or resistance testing in the Li (usually with low Ca content to provide for self-healing). These test generally were less successful than the previous tests, typically exhibiting thinner coatings and much lower resistance values from the *in situ* measurements.

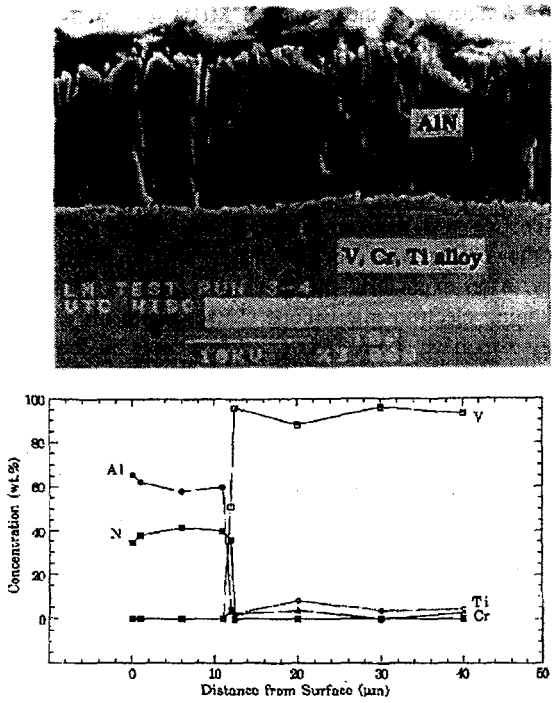



Figure 1. Cross-section SEM photomicrograph and EDX depth profiles for Al, N, V, Cr, and Ti for MRT-supplied, AlN-coated V-5Ti alloy specimen after 430-h exposure at 300°C to Li environment in which Ar-$N_2$ gas was bubbled for 24 h.

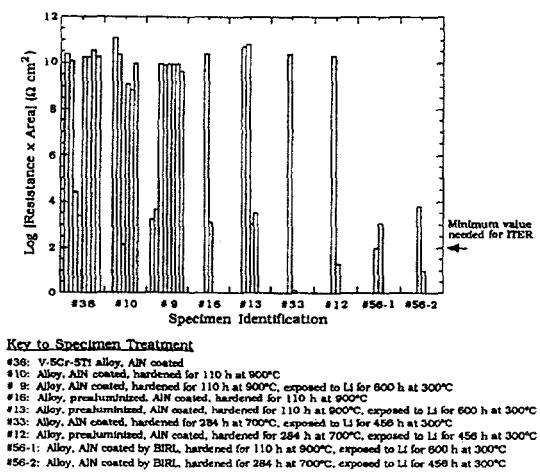



Figure 2. Electrical resistance data for several AlN-coated specimens in as-coated and hardened conditions and before and after exposure to Li

Resistance measurements by probes indicated high resistance over most of the surface at room temperature whereas many specimens exhibited very low resistance immediately upon insertion into the liquid. In several cases we were able to obtain relatively high resistance initially upon exposure to

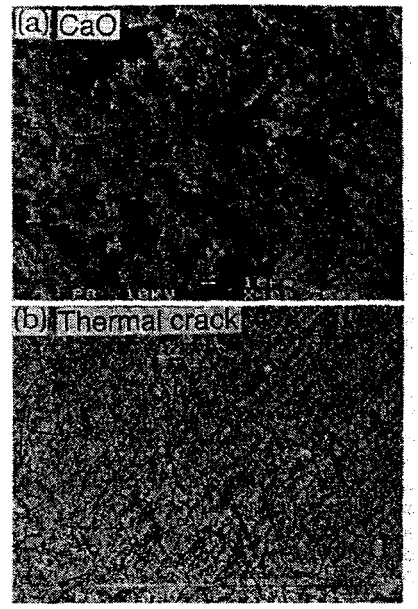



Figure 3. (a) SEM photomicrograph of surface of CaO coating, and (b) microcracks in coating shown in (a).

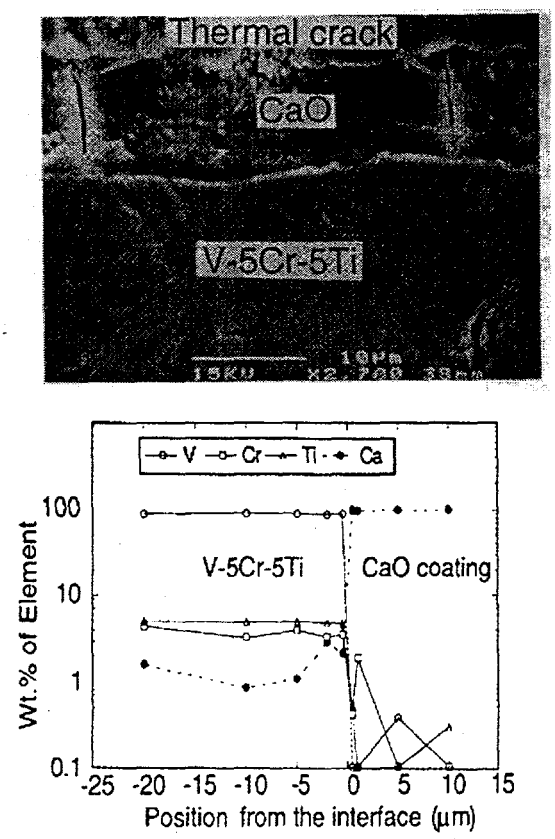



Figure 4. (a) SEM photomicrograph of cross section and (b) EDS depth profiles of V, Cr, Tia,a nd Ca at CaO/V-5Cr-5Ti interface of coating formed at 400°C.

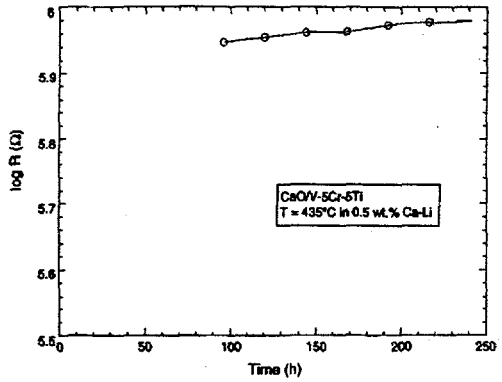



Figure 5. Log R(Ω) vs. time of CaO coating fabricated by exposure of V-5Cr-5Ti to Ar (99.999%) at 650°C for 17 h and to 85 wt. % Ca-Li at 400°C for 17h. Resistance measured in 0.5 wt. % Ca-Li at 435°C

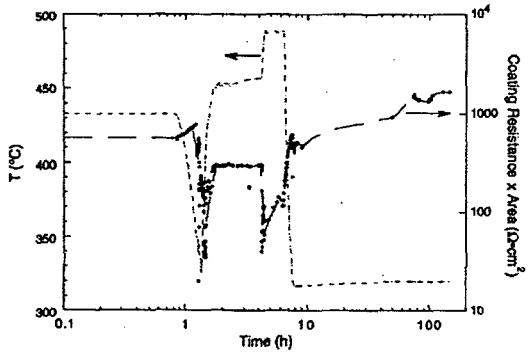



Figure 6. Temperature and ohmic resistance x area (R x A) vs. time during thermal cycling

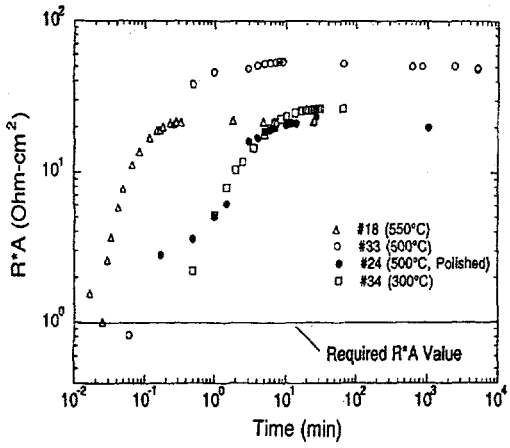



Figure 7. In-situ R*A measurement during Ca coating on the O-charged V-4Cr-4Ti

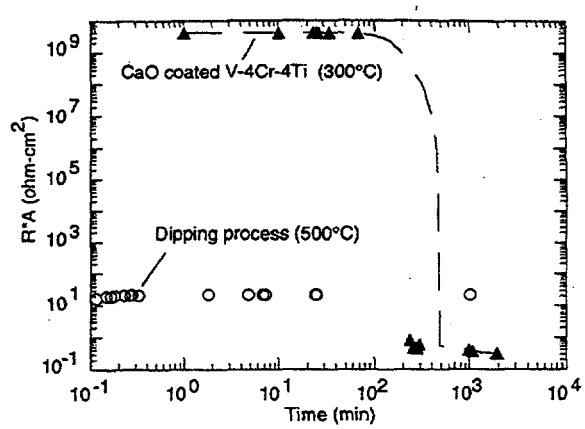



Figure 8. In-situ R*A vs. time for oxygen-charged (open symbol) and previously coated (closed symbol) V-4Cr-4Ti specimens in lithium with 2 at % calcium at 300°C

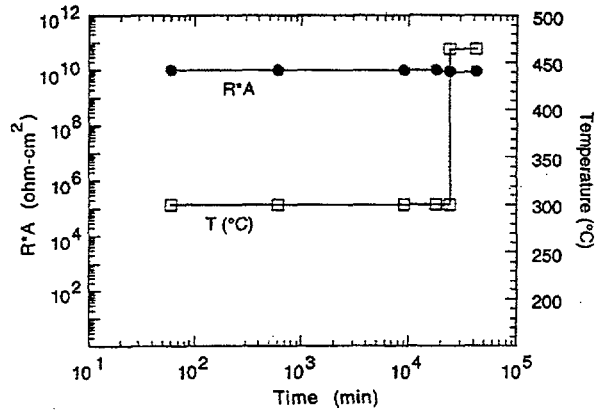



Figure 9. In-situ R*A (solid symbol) and tmerparute (open symbol) vs. time for CaO coating on V-15Cr-5Ti

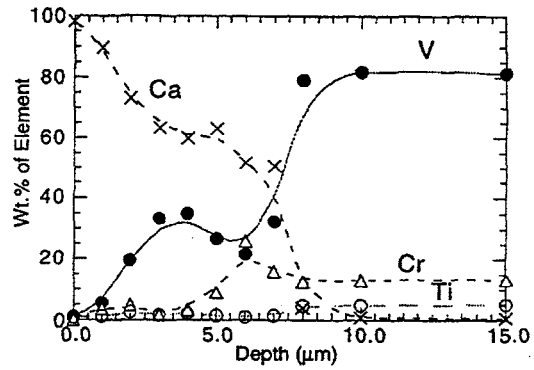
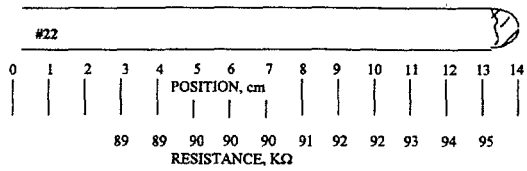



Figure 10. Chemical composition from ED analysis vs. depth for CaO/V-15Cr-5Ti specimen after exposure to lithium with 2 at % calcium for 700 h at 300-464°C

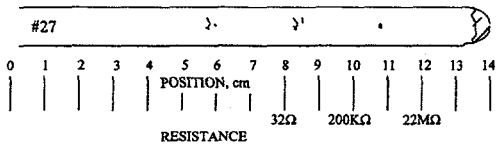
CaO Coated Vanadium Alloy Specimens




Resistance of CaO coated specimen(#22) in liquid Ga after defects in shaded end were separately insulated.

No defects observed by microscopic (low magnification) examination except at end.

Resistance of CaO coated specimen in liquid Ga was only 3.6 Ω without cementing spherical end.




Resistance of CaO coated specimen(#27) in liquid Ga after defects in shaded end were separately insulated.

Figure indicates location of defects. Localized defects at ~8 cm are ~70μm in size.

Resistance of CaO coated specimen in liquid Ga was low without cementing spherical end.

Figure 11. Pencil Specimens

LiCa with subsequent shorting (low resistance) after ~/1 hr exposure (Figure 8). In other cases, as shown in Figure 9, the insulator coatings exhibited high resistance ($R \cdot A \sim 10^{10}\ \Omega$ - $cm^2$) for periods of several hundred hours including changes in temperature. An EDX profile for this case is shown in Figure 10. Similar resistance measurements were made using a liquid gallium bath. Results were typically similar. For the case of gallium testing we were able to cover isolated defects in the coating with a resistive material. In these cases we obtained very high resistance (>100 kΩ) during testing in the gallium. In a few cases as illustrated in Figure 11, only a few very small defects were present over most of the specimens. Two positive results were the high resistivity of the coating and the sensitivity of the gallium continuity test procedure to extremely small defects. We have not resolved the cause of these defects but their presence is partially attributed to the thinner coatings (2-3 μm) compared to earlier experiments with coatings typically 5-10 μm thick.

An important result obtained in the analysis of the coatings involved the composition, in particular the amount of vanadium in the insulator coating. High resistivity was observed for Ca/V ratios above 0.8 whereas significantly lower resistivities were obtained for coatings when vanadium concentrations significantly exceeded 0.2 of the cation concentration.

## 5. CONCLUSION

Preliminary investigations have been conducted on the development of electrically insulating coatings for Li/V blanket applications. Several candidate insulator materials have been identified. CaO and AlN have been selected as the primary candidates with emphasis on CaO. Results obtained indicate that AlN coatings formed by PVD appear to be compatible with Li and they exhibit adequate resistivity at RT after exposure. CaO coatings have been formed on vanadium alloys by exposure to LiCa alloys. Although small defects in the coatings are observed in many cases, some specimens indicate high resistivity during extended exposure to lithium. Self-healing of CaO coatings is also indicated. Further research is required to reliably form high integrity coatings.

## REFERENCES

1. D.L. Smith et al., Fusion Technology 8, No. 1 (1985) 10-44.

2. CC. Baker et al., Tokamak Power System Studies FY 1985, Argonne National Laboratory Report ANL/FPP-85-2 (1985).

3. D.K. Sze et. Al., The ARIES-RS Power Core: Recent Developments in Li/V Designs, Presented at the 4th International Symposium on Fusion Nuclear Technology (ISFNT-4), Tokyo, April 6-11, 1997.

4. I.R. Kirillov et. Al., Liquid Lithium self-cooled Breeding Blanket Designs, Presented at the 4th International Symposium on Fusion Nuclear Technology (ISFNT-4), Tokyo, April 6-11, 1997.

5. J.-H. Park et. al., Fusion Energy and Design Volume 27 (1995) 683-695.

6. K. Natesan, J. Nucl. Mater. 233-237 (1996) 1403-1410.

7. J.-H. Park and W.D. Cho, in Surface Modification Technologies IX, eds T.S. Sudarshan et al., TMS (1996) 151-166.

8. T.Q. Hua and Y. Gohar, Fusion Engineer and Design 22 (1995) 696-702.

9. S. Malang and L. Buhler, MHD pressure drop in ducts with imperfectly insulating coatings, Argonne National Laboratory Report ANL/FPP/TM-269 (August 1994).

10. C.B. Reed, et al., Fusion Engr & Design Volume 27 (1995) 614-624.

11. K. Natesan, "Development of Aluminum Nitride Insulator Coatings for Fusion Reactor Applications," Argonne National Laboratory Report ANL/FPP/TM-290 (1996).

12. J.-H. Park and T.F. Kassner, J. Nucl. Mater. 233-237 (1996) 476-481.

13. R.F. Mattas, et al., Results of R&D for Lithium/ Vanadium Breeding Blanket Design," Presented at the 4th International Symposium on Fusion Nuclear Technology (ISFNT-4), Tokyo, April 6-11, 1997.