

CaO INSULATOR AND Be INTERMETALLIC COATINGS ON V-BASE ALLOYS FOR LIQUID-LITHIUM FUSION BLANKET APPLICATIONS*

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SUMMARY

The objective of this study is to develop (a) stable CaO insulator coatings at the liquid-Li/structural-material interface, with emphasis on electrically insulating coatings that prevent adverse MHD-generated currents from passing through the V-alloy wall, and (b) stable Be-V intermetallic coatings for first-wall components that face the plasma. Electrically insulating and corrosion-resistant coatings are required at the liquid-Li/structural interface in fusion first-wall/blanket applications. The electrical resistance of CaO coatings produced on oxygen-enriched surface layers of V-5%Cr-5%Ti by exposing the alloy to liquid Li that contained 0.5-85 wt.% dissolved Ca was measured as a function of time at temperatures between 250 and 600°C. Crack-free Be₂V intermetallic coatings were also produced by exposing V-alloys to liquid Li that contained Be as a solute. These techniques can be applied to various shapes (e.g., inside/outside of tubes, complex geometrical shapes) because the coatings are formed by liquid-phase reactions.

INTRODUCTION

In the design of liquid-metal cooling systems for fusion-reactor blanket applications, major concerns are corrosion resistance of structural materials and the magnetohydrodynamic (MHD) force and its subsequent influence on thermal hydraulics. When the system is cooled by a liquid metal, an electrically insulating layer (e.g., CaO) is required on piping surfaces in contact with the coolant [1,2]. Because plasma-facing components are subjected to high operating temperatures and heat loads, they must exhibit high thermal conductivity and resistance to thermal shock, thermal erosion, and radiation damage [3,4]. Graphite, binary-element ceramics, refractory metals, and low-atomic-number elements, e.g., Be and B, have been considered for these applications [5]. Figure 1 depicts a V-alloy first wall with Be and CaO surface coatings that are capable of being formed on various shapes by exposure to liquid Li under controlled conditions. The coatings could also improve general corrosion resistance and act as a diffusion barrier for deuterium and tritium. This paper describes methods to fabricate both electrically insulating CaO and Be-V intermetallic coatings on V-alloys, which are being considered for the first wall/blanket in fusion reactors.

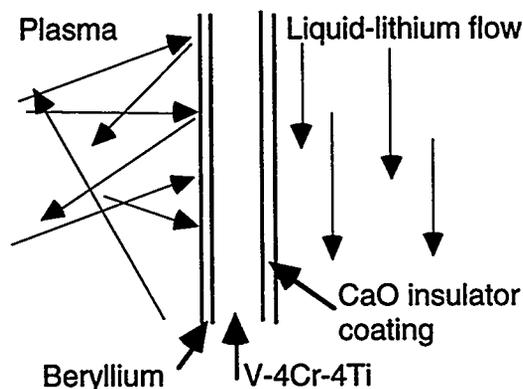


Fig. 1. Schematic diagram of first wall in a fusion reactor

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CaO Coating on V-Alloys in Liquid Li

According to previous studies [6,7], several ceramic materials that are thermodynamically stable in Li exhibit poor compatibility with the liquid metal because of thermodynamically unstable impurities that form at grain boundaries during fabrication. For example, sintered AlN disintegrated in liquid Li, but exhibited compatibility when yttrium, which acts as an oxygen getter and stabilizes the material (Y/Y_2O_3), was added before sintering [6]. Three types of experiments have been conducted to develop electrical insulator coatings for use in liquid Li: (a) in-situ fabrication of intermetallic layers for subsequent conversion to electrically insulating layers by oxidation, (b) reaction of an oxygen-rich surface layer in a V-base alloy with Ca dissolved in liquid Li to produce a ceramic insulator coating (CaO) on the material, and (c) in-situ electrical resistance measurements of insulator coatings on V-alloys as a function of time and temperature in Li. To fabricate a CaO coating on the alloy substrate, oxygen concentration in the near-surface region in V and Ca in liquid Li must be controlled. Oxygen can be incorporated into the interstitial sublattice in body-centered-cubic (bcc) V and its alloys. Thus, O that is present in the alloy (as a reactant) has a higher affinity for a solute (such as Ca dissolved in Li) than do the alloy elements. In the bcc lattice of a V-Cr-Ti alloy, O can occupy interstitial sites within a lattice up to several atomic percent. Samples of V-5%Cr-5%Ti were heat treated in flowing Ar at 670°C to charge the near-surface region of the alloy with O. The samples were then immersed in Ca-bearing liquid Li for ≈ 96 h at 420°C to investigate the formation of CaO.

In addition to thermodynamic stability in liquid Li and adherence of the coating to the V alloy under thermal cycling conditions, the in-situ self-healing behavior of defects (such as cracks in the coating) in liquid-Li environments is also an important consideration. Because the coefficient of thermal expansion of CaO is higher than that of V (12×10^{-6} vs. $9.2 \times 10^{-6}/K$), a CaO layer that forms in-situ on a V-5%Cr-5%Ti alloy will be subjected to tensile stress during cooling. Microcracks have been observed in CaO coatings after cooling of coated specimens to room temperature. Regions with diameters of ≈ 30 – $40 \mu m$ and crack widths of $\approx 2000 \text{ \AA}$ covered most of the CaO surface, which suggests that the cracks originate from a mismatch of thermal expansion coefficients during cooling, i.e., they are "crazing cracks." However, adhesion of the CaO film to the V-5%Cr-5%Ti substrate appeared to be quite good. Preliminary studies have been conducted to explore the self-healing properties of CaO coatings under temperature cycling [8]. Self-healing of CaO was investigated at temperatures between 300 and 740°C. At 300°C, self-healing did not occur in a 10-h period; at $\geq 360^\circ C$, cracks appeared to heal (e.g., at 450°C, resistivity was restored to its initial value within several hours, and at 500°C in < 1 h). When a CaO coating was subjected to compressive stress by increasing the temperature in a similar manner, no appreciable cracking was detected.

Be Coating on V-5%Cr-5%Ti

Beryllium forms intermetallic phases with many elements [9,10] including, Cr, Ti, and V. Consequently, this property can be potentially useful in forming Be intermetallic coatings on V-Cr-Ti alloys. According to the Be-V binary phase diagram, $Be_{12}V$ and Be_2V intermetallic phases are present. Similarly, Cr and Ti form $CrBe_2$ and $CrBe_{12}$, and $TiBe_2$, $TiBe_3$, Ti_2Be_{12} , and $TiBe_{17}$, respectively. Beryllium intermetallic coatings can form on structural alloys during exposure in a liquid-metal environment that contains Be as a solute element. In a liquid-Li environment, in contrast to vapor-phase deposition processes, contamination of the alloy surface by oxygen and other contaminants during the coating process does not occur and no other phases form at the Li/alloy substrate. Only dissolved Be at a relatively low concentration in Li reacts with the V alloy. The Be_2V intermetallic phase on the surface of a V-5%Cr-5%Ti specimen and a Be depth profile obtained by secondary-ion mass spectroscopy are shown in Fig. 2. The photomicrographs reveal good bonding and no cracks because the layer formed by inward diffusion of Be into V and then by a solid-state reaction to form the Be_2V phase. In general, it is difficult to prepare crack-free Be coatings by conventional methods.

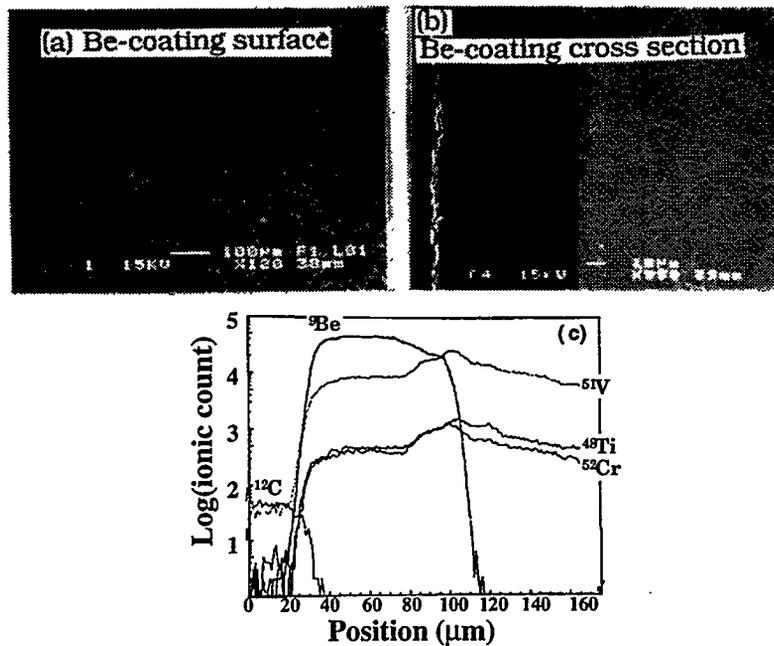


Fig. 2. (a, b) Be_2V intermetallic phase on V-5%Cr-5%Ti surface and cross section, and (c) Be depth profile obtained by secondary-ion mass spectroscopy

Be/V-Alloys/CaO/Li

Beryllium is used extensively for plasma-facing components in the design of the International Thermonuclear Experimental Reactor (ITER) because of the high fluxes of energetic particles and heat from the plasma [11,12]. Deuterium and tritium atoms from the plasma are implanted in the first wall, and neutron irradiation causes proton production within the materials by n,p reactions. The materials and material combinations (i.e., a layered structure, Fig. 1) influence hydrogen isotope recycling from the inner surface of the first wall to the plasma, as well as the magnitude of the hydrogen inventory in and permeation through the first-wall structure to the liquid-Li blanket/coolant [13,14]. Computer codes have been developed to assess the magnitude of hydrogen inventory, permeation, and recycling in the first wall because of (a) possible radiological hazards associated with tritium and (b) embrittlement of the structure by hydrogen isotopes [12-14].

Many factors contribute to transport and retention of hydrogen, namely, rates of release of hydrogen isotopes from the plasma-facing surface to the vacuum vessel, diffusivities and solubilities of hydrogen, densities of neutron-damage-induced traps, and thermodynamic distribution of hydrogen among the different materials in the blanket/structure. Radiation damage and diffusion/desorption behavior of tritium from irradiated Be have been reviewed [15,16]. Operating conditions such as duration of burn and recovery times, temperatures, and duty cycle also influence tritium inventory. Estimates of tritium inventory in the first-wall and permeation through the wall to the Li coolants (e.g., Fig. 1) vary over a wide range, depending on whether optimistic or pessimistic assumptions are invoked for the rate coefficient for recombination and release of hydrogen species back to the plasma, as well as effects of surface films thereon, neutron-induced trapping versus nontrapping of hydrogen in the structural materials, and presence or absence of a diffusion barrier (e.g., CaO) at the V-alloy/Li interface [11,13,14]. To reduce the uncertainty in these estimates, we are obtaining hydrogen solubility and permeability data in V-4%Cr-4%Ti in liquid Li, and in liquid Li-Ca alloys with and without CaO coatings [17].

CONCLUSIONS

Based on results of liquid-Li compatibility tests, information on the thermodynamic stability of ceramic materials in Li, and phase diagram considerations, we have developed methods for in-situ fabrication of CaO insulator and Be-intermetallic coatings on V-base alloys in a liquid-Li environment. Crack-free Be₂V intermetallic coatings and highly insulating CaO coatings were produced on a V-5%Cr-5%Ti alloy. The coating processes are facilitated in liquid Li because surface contamination by O or oxide films is virtually eliminated and the processes produce homogeneous coatings on various surface shapes through control of exposure time, temperature, and composition of the liquid metal. Additional work is underway to improve the mechanical stability of the coatings during thermal cycling and to establish the mechanisms for self-healing of the coatings.

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