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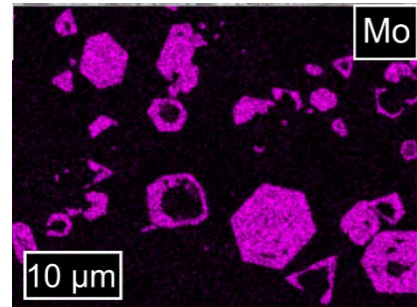
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MAX phase materials and MXenes as hydrogen barrier coatings

Project highlight. Hydrogen isotope permeation barriers are a key supporting technology for both next generation fusion reactors and the national security enterprise. This project seeks to develop MAX phase and MXene based hydrogen isotope permeation barriers for use in neutron environments. Furthermore, routes to lower temperature deposition of MAX phases and MXenes were also explored.



Awards and Recognition

None

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publicly published in its current form.

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Date

MAX phase materials and MXenes as hydrogen barrier coatings

Project Team: D. Hitchcock, T. Krentz, M. Drory, B. Garcia-Diaz (SRNL)

Subcontractor: E. Vogel and K. Young (GA Tech)

Project Type: Standard

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Project End Date: September 30, 2021

Hydrogen and its isotopes play an important role in nuclear applications, but their permeation and radioactivity lead to degradation of materials. Therefore, hydrogen isotope permeation barriers are an important supporting technology. Unfortunately, most permeation barriers that perform well in the laboratory fail when placed in radiation environments. The goal of this work is to begin the development of next generation permeation barriers with materials known to have good stability under neutron irradiation, and then tailor their composition and structure to maximize their barrier properties. In particular MAX phase materials and their two-dimensional analogues (MXenes) have been chosen due their excellent stability under neutron irradiation.

FY2020 Objectives

- Coating deposition
- Structural characterization of deposited films
- Permeation measurements

Introduction

Hydrogen and its isotopes play an important role in nuclear applications, but their permeation and radioactivity lead to degradation of materials. During tritium production, permeation release rates from Tritium Producing Burnable Absorbing Rods (TPBARs) exceed expected levels. Moreover, surface interactions, particularly with stainless steel, demand high performance hydrogen isotope permeation

barrier coatings (HIPBs). Additionally, tritium retention in both plasma facing and process components is a major issue facing the demonstration and widespread use of fusion energy. The development of permeation barriers capable of operation in a fusion environment would greatly alleviate this concern.

Barrier materials display bulk hydrogen isotope permeabilities as low as 10 orders of magnitude below structural materials. Therefore, very thin coatings, on the order of microns, can reduce the permeation through structural materials drastically. Current candidates for HIPBs include oxides such as Al_2O_3 or Er_2O_3 , carbides such as SiC , and aluminides. Previous work has shown that though some hydrogen isotope permeation barrier materials display very low permeability² most barrier materials which perform well in laboratory experiments fail when placed in radiation environments.³ Furthermore, permeation reduction factors (PRFs) vary significantly in literature. For example oxide and carbide barriers have PRFs varying from ~ 10 - 1000 ⁴ while aluminide PRFs can also span 10 - $10,000$ (though the general PRF value for gaseous H_2 is <1000).⁵ In-reactor permeation measurement on aluminides show PRFs as low as 3.4 and as high as 80.⁶ SiC coatings are another alternative, but are brittle which leads to coating failure during thermal cycling and delamination issues.

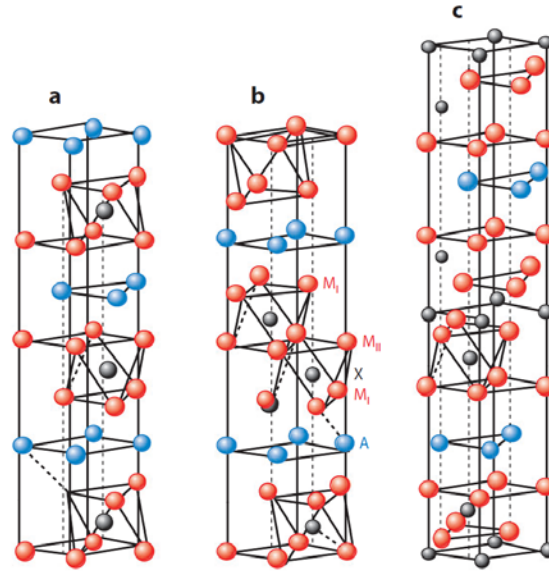


Figure 1: MAX phase unit cells: (a) 211, (b) 312, and (c) 413 phases. Taken from¹.

MAX phase materials have a layered structure with the general formula $\text{M}_{n+1}\text{AX}_n$ where M is an early transition metal, A is an A group element from group 13-16, and X is carbon or nitrogen. The carbide or nitride octahedra layers are alternated with single atomic layers of metallic A atoms (Figure 1). MAX phases are currently being investigated for fission applications due to their excellent stability under neutron irradiation. These materials have mixed ceramic and metallic characteristics due to their layering and have displayed excellent barrier properties to hydrogen and stability under elevated temperature, aggressive chemistries, and high neutron fluence, making them attractive for cladding materials in nuclear reactors.⁷

Approach

The goal of this work is to begin the development of next generation permeation barriers with materials known to have good stability under neutron irradiation, and then tailor their composition and structure to maximize their barrier properties. In particular MAX phase materials and their two-dimensional analogues (MXenes) have been chosen due their excellent stability under neutron irradiation.

In addition to studying the barrier mechanisms for MAX phase/MXene materials and identify/synthesizing specific formulations which are hydrogen/irradiation resistant in extreme environments, routes to lower temperature depositions were also explored. Current deposition strategies for MAX phases and MXenes,

namely sputtering followed by high temperature annealing, are not suitable for structural materials in many nuclear environments due to the need for heat treatments outside of the operating temperatures of the alloys of interest. Strategies for deposition of MAX phases at moderate temperatures are an important innovation which will enable the use of MAX phases in wide range of commercial applications.

Results/Discussion

Recent work has explored the use of chemical vapor deposition on liquid metal substrates to controllably synthesize transition metal carbides^{8,7} and early results from this work confirmed that Mo_2C can be grown on Cu substrates at temperatures above 1000 °C. However, this elevated temperature is unacceptable for many applications which has led to recent studies using Cu alloy substrates such as Cu-Sn to lower the growth temperature.⁹ In this work the effects of using a Ag-Cu alloy as a substrate for Mo_2C synthesis by chemical vapor deposition were systematically analyzed. The results conclusively demonstrated that synthesis of Mo_2C is controlled by Mo diffusion through the liquid alloy (Figure 2). Utilizing a Ag-Cu alloy as a substrate successfully reduced the necessary synthesis temperature below the melting point of Cu; however, Mo_2C coalescence was limited and directly proportional to Cu content due to the separation of the Ag and Cu components in the alloy upon cooling (Figure 3). Ag alone is not a suitable substrate for Mo_2C synthesis, likely due to the inability of Ag to dehydrogenate methane effectively. Thus, an optimal substrate for Mo_2C synthesis should be able to dehydrogenate methane, have a low melting temperature, and, if an alloy, demonstrate solid solubility.¹⁰

Though the Mo_2C synthesis temperature is decreased when using a Ag-Cu alloy vs Cu-alone, there were still some challenges with the Ag-Cu alloy as a substrate. One of the major challenges with using a Ag-Cu alloy as substrate for Mo_2C synthesis is that there is separation of the alloy components upon cooling. This prevents the Mo_2C from coalescing fully. Thus, an alloy that can remain mixed or that does not separate except at low temperatures, could solve this problem. In-Cu alloys have greater mixing, even at lower temperatures, than Ag-Cu alloys. Though uniform coverage across the entire sample is still a challenge, there is much higher Mo_2C coalescence for an In-Cu alloy substrate (Figure 3) compared to the Ag-Cu alloy substrate.

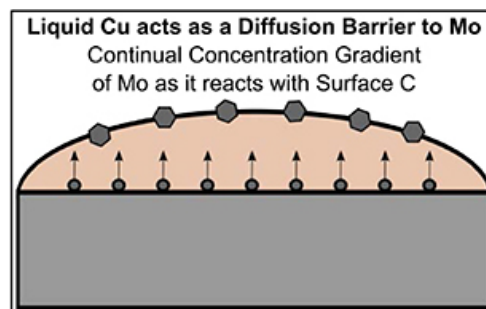


Figure 2: Proposed mechanism where Cu melts on the Mo foil surface. Mo atoms diffuse through the liquid Cu until they reach the surface, where they either react with surface C or CH_4 to form Mo_2C .

Another challenge with using Cu alloy substrates for Mo_2C synthesis as a substitute for Cu-alone is that the alloy may not dehydrogenate CH_4 as effectively as Cu. The inability of Ag to efficiently dehydrogenate CH_4 is likely what causes a decrease in Mo_2C flake size with increasing Ag composition in the alloy substrate. Unlike Ag, In substrates have had some success in dehydrogenating CH_4 for CVD graphene synthesis. Thus, alloys with lower Cu composition could still successfully synthesize Mo_2C with large flake sizes and/or coalescence. In the case of In-Cu alloys, the melting temperature tends to decrease with increasing In composition. Thus, synthesis temperatures that are even lower than 1000°C may be possible. Chaitoglou, et al., were able to synthesize Mo_2C at 880°C using a Sn-Cu alloy substrate; however, no Mo_2C was synthesized at temperatures below 880°C (Stefanos Chaitoglou et al 2019 *Nanotechnology* 30 125401). However, in the current study, Mo_2C was synthesized at 800°C when using an alloy with 40 wt% In and 60 wt% Cu (Figure 4). Though the flakes are smaller and less coalesced, these are promising results for synthesizing two-dimensional transition metal carbides by CVD at lower temperatures.

To test the ability of the SRNL permeation system to resolve the effects of monolayer coatings on bulk substrates, permeation measurements were performed on monolayer graphene coated copper samples synthesized using CVD. Since the graphene was synthesized directly onto the Cu, the permeation

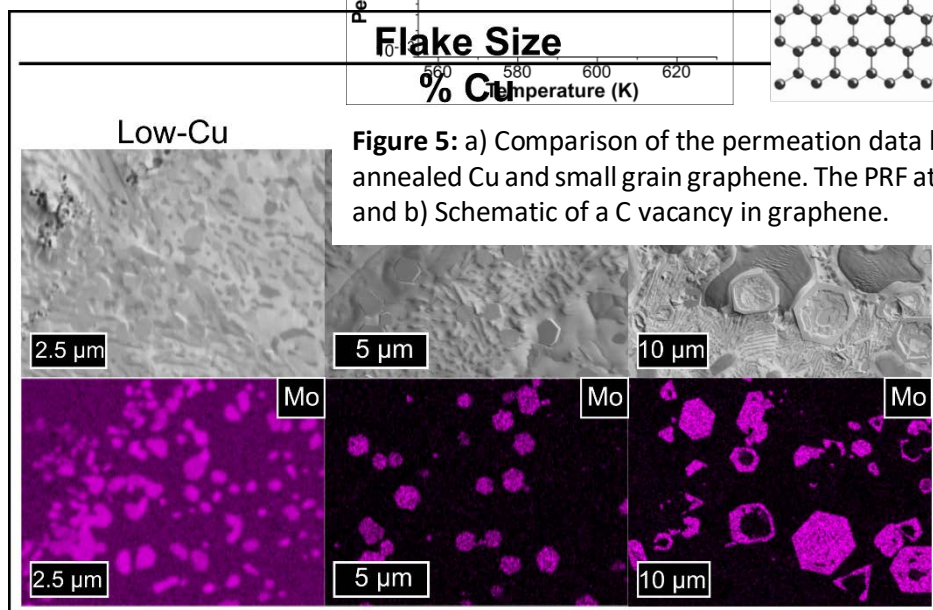
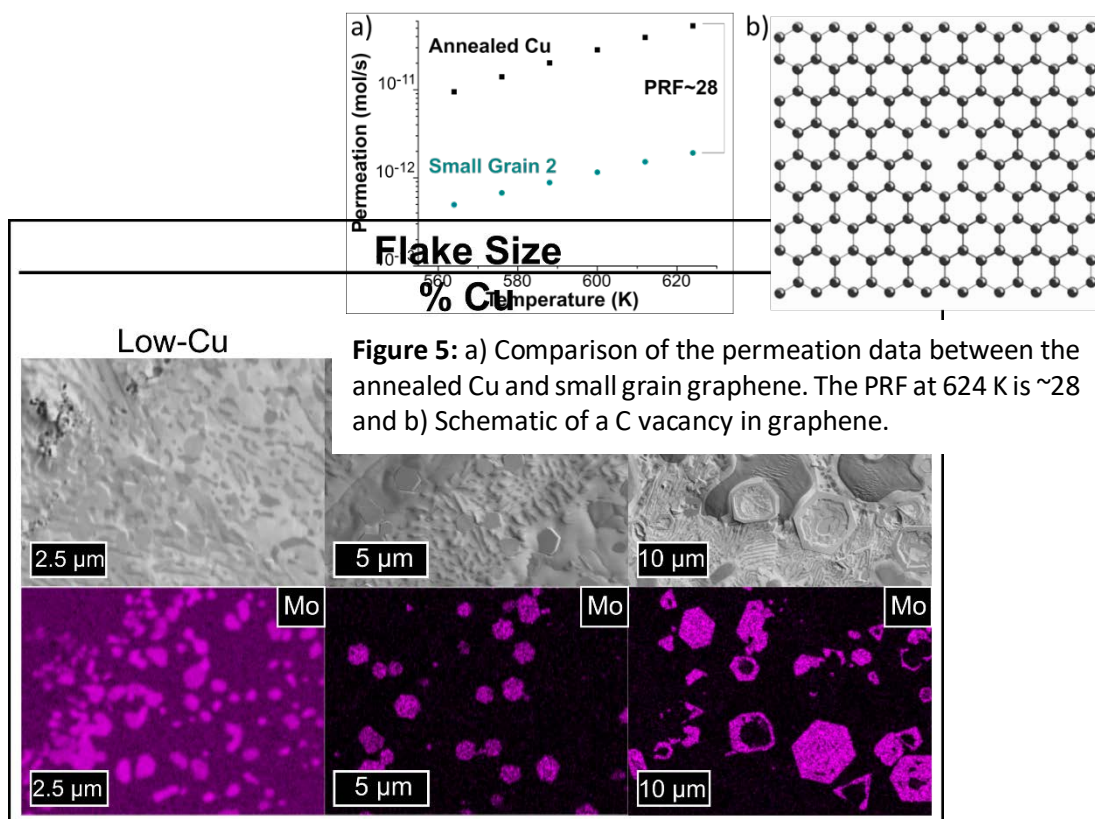


Figure 3: SEM images and EDS maps comparing the Mo_2C flake sizes on Low-, Medium-, and High-Cu alloys

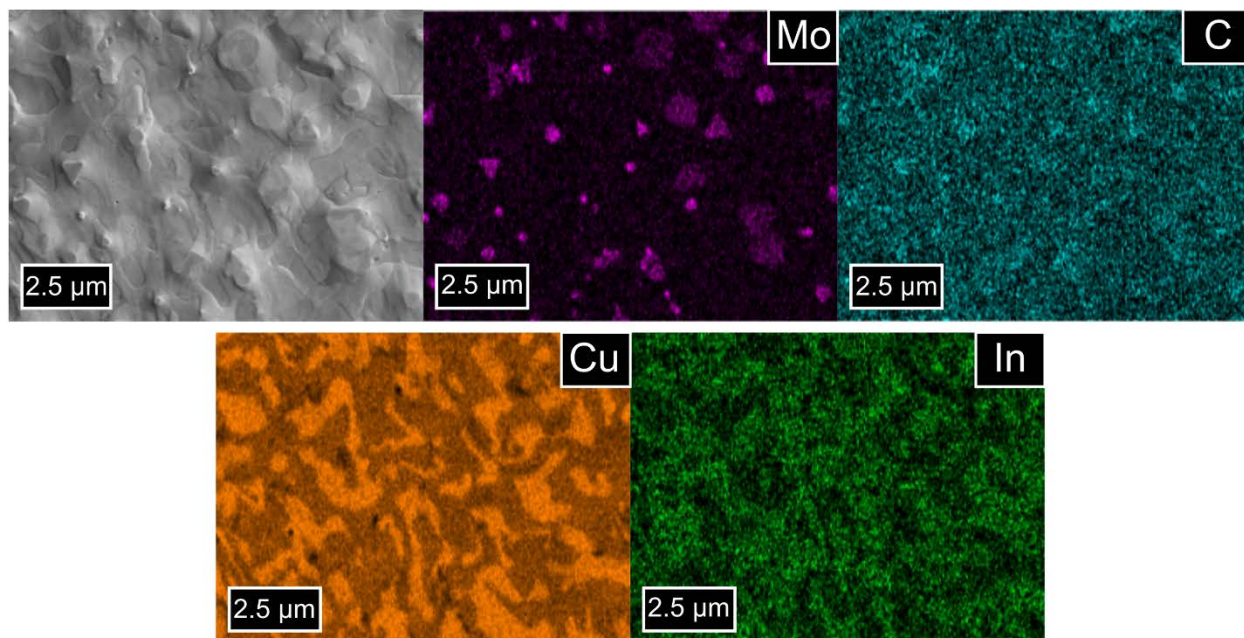


Figure 4: Mo₂C synthesis on an In-Cu alloy substrate at 800 °C.

experiments were able to be performed over a large area (16.62 mm²) without the detrimental impact of transfer-induced tears and holes that is common in previous studies. Thus, permeation through intrinsic defects of the chemical vapor deposited graphene was probed. The graphene-coated copper showed a reduction in permeation by a factor of ~28 compared to copper alone (Figure 5a). The permeation results were modeled with a composite permeation model where the graphene coating is in series with the Cu. The permeation through the composite system displayed surface-controlled behavior, and the graphene permeance followed Arrhenius behavior, suggesting permeation is in the activated regime. The room temperature pore permeation coefficients for the small and large grain graphene samples are $\sim 7.0 \times 10^{-28} \pm 5.0 \times 10^{-28}$ and $\sim 1.9 \times 10^{-27} \pm 1.4 \times 10^{-27}$ mol/s MPa, respectively, which are lower than what is normally observed in literature. The experimental results and associated modeling strongly suggest that single C vacancy intrinsic defects (Figure 5b) are limiting permeation through the graphene. Thus, the results provide a fundamental understanding of the intrinsic permeation of chemical vapor deposited graphene, as well as the use of graphene in hydrogen isotope permeation barrier applications.

FY2020 Accomplishments

- Deposition of Mo₂C on multiple substrates
 - Deposition on Cu-In alloy at 800 °C is the lowest reported growth temperature for Mo₂C using CVD
- Permeation measurement system configured to work with thin film permeation barriers
- Permeation measurements performed on graphene coated Cu
 - Mention that the PRF may be the highest reported if scaled for thickness

Future Directions

- Magnetron sputtering of MAX phase coatings
- Atomic Layer Deposition of MAX phases
- Permeation measurements on MAX phase and MXene coated substrates

- Transfer of MXenes films

FY 2020 Peer-reviewed/Non-peer reviewed Publications

1. “The Synthesis Mechanism of Mo₂C on Ag-Cu Alloy Substrates by Chemical Vapor Deposition and the Impact of Substrate Choice”, K. Young, C. Smith, D. Hitchcock, T. Walters, C. Voigt, and E. Vogel *2D Materials* 7 (3), 035022
2. “Graphene Synthesized by Chemical Vapor Deposition as a Hydrogen Isotope Permeation Barrier” K. Young; C. Smith; T. M. Krentz; D. A. Hitchcock, and E. M. Vogel *Carbon* submitted, SRNL co-corresponding author
3. “Measurement of Gas-Concentration-Driven Permeation for the Examination of Permeability, Solubility, and Diffusivity in Varying Materials” K. Young, T. Krentz, A. d'Entremont, E. Vogel, and D. Hitchcock *Review of Scientific Instruments* submitted SRNL corresponding author

Presentations

1. “The Effects of Graphene and its Defects on Hydrogen Permeation in Cu” Katie Young, MRS Fall Meeting, Boston MA Dec. 2019
2. “Fusion Fuel Cycle Science and Technology” Dave Babineau, Steve Xiao, and Dale Hitchcock, Technical Seminar, MIT Plasma Science and Fusion Center, Cambridge MA Dec. 2019

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Acronyms

Hydrogen Isotope Permeation Barriers HIPBs
Permeation Reduction Factor PRF
Tritium Producing Burnable Absorbing Rods (TPBARs)

Intellectual Property

None

Total Number of Post-Doctoral Researchers

None

Total Number of Student Researchers

Graduate student: Katie Young, Georgia Institute of Technology, Advisor: Dr. Eric Vogel

External Collaborators (Universities, etc.)

Dr. Eric Vogel, Department of Materials Science and Engineering, Georgia Institute of Technology