PRF Project number: 59251-ND-10
Project Title: Discovery of New Petroleum Reforming Catalysts via Investigation of Complex Metallic Alloys Aided by Deep Learning Methods
Principal Investigator: Michael Shatruk, Florida State University

Summary of the 1st-year progress

In the first year of the project, we have embarked on the synthesis of several layered-structure intermetallics (LIMs) and complex metallic alloys (CMAs), using the guidance of a machine-learning algorithm developed in our labs to identify atomic sites with similar "fingerprints" of the local atomic structure. In particular, we focus on devising alternative synthetic pathways to inexpensive LIMs materials, AlM_2B_2 (M = Cr, Mn, Fe), which might prove to be active in various catalytic reactions. We have successfully achieved the synthesis of $AlFe_2B_2$ by direct arc-melting and induction (RF) melting, both of which have been reported before. Importantly, however, we also synthesized this material by a reaction in a microwave oven, which allowed to simplify the synthetic protocol and achieve the complete reaction in 3-5 min (Figure 1). The convenience of the microwave protocol is not only the speed of the reaction. With this method, we do not need to use protective environment around the reaction vessel, such as Ar-filled atmosphere used during arc- or RF-melting. A short-term treatment of the microwave-melted product with dilute HCl removes a minor impurity of $Al_{13}Fe_4$ and affords a phase-pure $AlFe_2B_2$. In the second year of the project, we will apply a similar procedure to the synthesis of $AlMn_2B_2$ and $AlCr_2B_2$ which, thus far, we have not been able to obtain in sufficiently pure state by arc- or RF-melting.

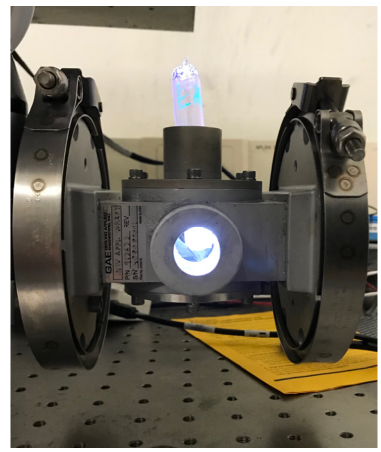

Figure 1. The microwave setup used for the synthesis of $AlFe_2B_2$.

To prepare the materials for catalytic testing, we applied high-energy ball milling to reduce the particle size. We found that $AlFe_2B_2$ can be successfully ball-milled, without the loss of phase purity (except for a minor impurity peak of alumina (Al_2O_3) – see Figure 2). The broadening of the X-ray diffraction lines indicates the decrease in the particle size after 1 hour of ball-milling under inert atmosphere.

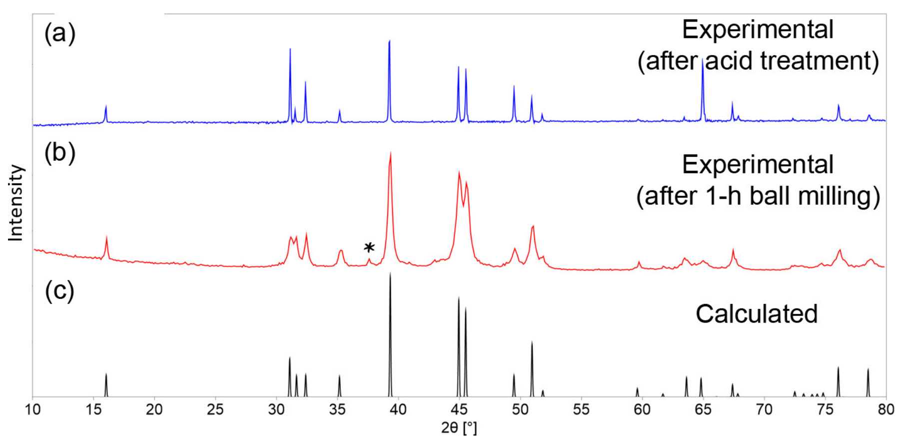

Figure 2. Powder X-ray diffraction patterns of $AlFe_2B_2$ after removal of the $Al_{13}Fe_4$ impurity by acid treatment (a) and after ball-milling (b), in comparison to the calculated pattern (c). The asterisks marks a minor Al_2O_3 impurity.

We have provided a part of this sample to our collaborators in the Iberian Nanotechnology Laboratory (INL) in Portugal, who have demonstrated that $AlFe_2B_2$ acts as a remarkable pre-catalyst for the oxygen evolution reaction.[1] Our interest, however, as relevant to the present proposal, is in the use of this and related LIMs for the reactions involved in catalytic reforming. We have also provided a sample of $AlFe_2B_2$ to Dr. Angeles-Boza at University of Connecticut for testing some of these reactions. If the tests prove successful, we will collaborate with the UConn group to establish a similar testing setup in our labs.

This past year we also focused on synthesizing several so-called MAX phases and exploring HF-free exfoliation techniques to make thin sheets of these materials, referred to as MXenes. We have successfully synthesized phase-pure Cr_2GaC, Cr_2AlC, and Cr_2GeC, using arc-melting and conventional high-temperature annealing techniques. To use these materials as catalysts, our idea is to increase the exposure of basal planes by leaching out the main-group element (Al, Ga, or Ge), i.e., converting the MAX phases to MXenes. We aim to achieve HF-free exfoliation by utilizing the NaOH–KOH eutectic. The preliminary results show the conversionof Cr_2AlC to semi-exfoliated flakes under these conditions (Figure 3). Over the next year, we will concentrate on testing catalytic and electrocatalytic activities of these materials.

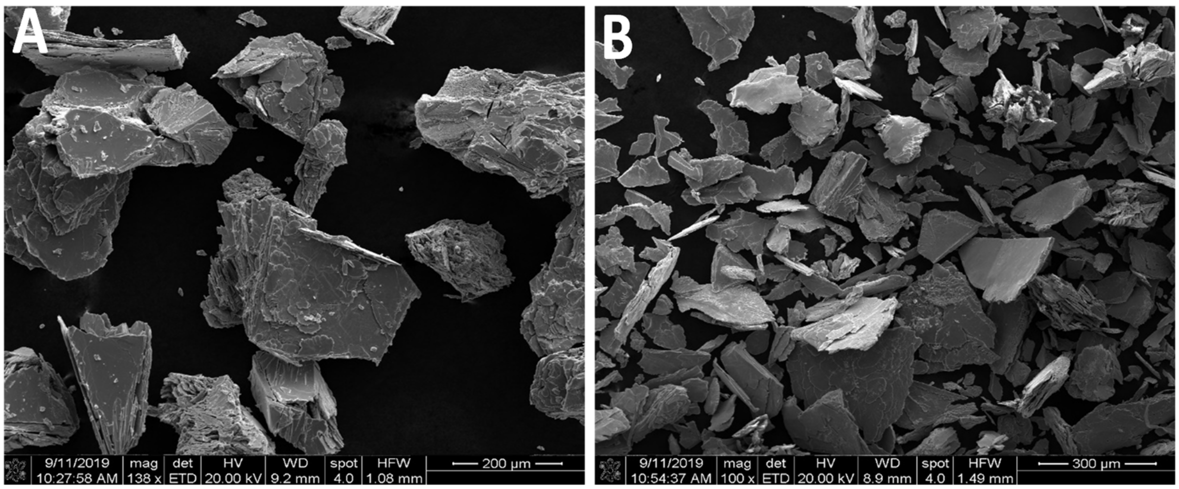

Figure 3. SEM images of MAX phases before (a) and after (b) the treatment in the alkali eutectic.

Impact on the research lab and the student

This PRF grant has allowed us to explore a drastically new research direction in our labs – heterogeneous catalysis. While we have just begun some catalytic tests, the initial materials synthesis results are promising, and one of the solids has already demonstrated catalytic activity.[1]

With the support of this grant, the graduate student participant traveled to Portugal to learn various catalytic testing techniques from our collaborators at the Iberian Nanotechnology Lab. The student learned to design/formulate electrocatalytic experimental set-ups and became proficient in testing a variety of different catalytic properties and analyzing the data. In the second year of the project, the student will guide the efforts to implement a catalysis testing station in our labs at Florida State University.

1. Mann, D.; Xu, J.; Mordvinova, N.; Yannello, V.; Ziouani, Y.; González-Ballesteros, N.; Sousa, J.; Lebedev, O.; Kolen'ko, Y.; Shatruk, M. Electrocatalytic water oxidation over $AlFe_2B_2$. *Chem. Sci.* **2019**, *10*, 2796-2804.