Contract No:

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Material Developments for 3D/4D Additive Manufacturing (AM) Technologies

Project highlight. Designed and created 3D/4D printed hydride materials via additive manufacturing that could be used as structural components for unmanned aerial vehicles (UAVs).

Awards and Recognition

Simona Murph: C3E Award Finalist in Research - The U.S. Clean Energy Education and Empowerment (C3E) Awards recognize outstanding mid-career researchers for exceptional leadership and achievements in clean energy. The US C3E program is an initiative of the Clean Energy Ministerial executed through collaboration between the US DOE and the MIT Energy Initiative.

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.

SRNL Legal Signature

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Signature **Date**

Material Developments for 3D/4D Additive Manufacturing (AM) Technologies

Project Team: Simona Hunyadi Murph (PI), Henry Sessions, Patrick Ward, John Bobbitt, and Ray Belliveau

Subcontractor: Applied Research Center

Project Type: Standard

Project Start Date: October 1, 2019
Project End Date: September 30, 2020

Additive Manufacturing (AM), or 3D printing, is a unique technology in which structurally complex objects can be easily manufactured. While AM allows for the creation of intricate 3D objects, these objects are inactive and motionless. With recent incorporation of a "pre-programmed functionality" to the 3D printed objects, a new concept has emerged, 4D printing. Specifically, the 4D printing technology enables a static 3D printed object to change its shape, functionality or property over time upon exposure to a specific stimulus such as heat, stress, light, pH, and moisture, etc. We designed and produced compact 3D/4D printable materials that can be used as (a) structural components of the unmanned aerial vehicles (UAVs), and (b) as hydrogen storage materials that supply hydrogen to a fuel cell to expand the operational reach, namely flight time, and endurance of the UAVs.

FY2020 Objectives

- Design and print 3D/4D hydride materials.
- Evaluate and optimize the 3D/4D printed hydride materials as hydrogen storage material.

Introduction

Additive Manufacturing (AM), or 3D printing **(Figure 1)**, is a unique technology in which structurally complex objects can be easily manufactured. While AM allows for the creation of intricate 3D objects, these objects are inactive and motionless. With recent incorporation of a "pre-programmed functionality" to the 3D printed objects, a new concept has emerged, 4D printing. Specifically, the 4D printing technology enables a static 3D printed object to change its shape, functionality or property over time upon exposure to a specific stimulus

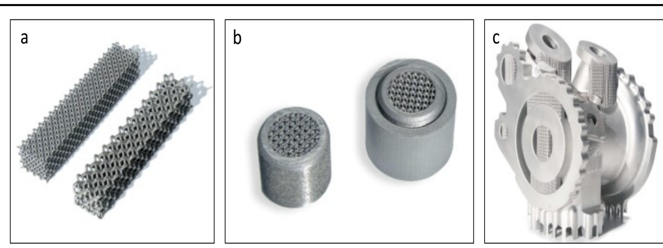

Figure 1. *3D printed objects via selective laser melting process.*

such as heat, stress, light, pH, and moisture, etc. One area of interest that can greatly benefit from the implementation of the 3D/4D printed objects is the field of unmanned aerial vehicles (UAV).

Unmanned aircraft systems (UASs) have experienced explosive growth in recent years and have proved to be an invaluable resource in military and first responders' missions, agricultural surveillance, deliveries, telecommunications, etc. In recent years, the need for improved UAS's operational reach and endurance has been echoed across all DOE's and DoD's levels of leadership. (Note: Operational reach is defined as the distance and duration across which a unit can successfully employ its capabilities).

The development and implementation of the 3D/4D hydride materials as structural components for hydrogen fuel cells operated UAV's proposed here will have a significant impact in expanding their operational reach and endurance (Figure 2). This project developed Smart/Enabling Tools, in the form of 3D/4D materials and components, that will enhance SRNL's drone and additive manufacturing programs while expanding SRNL's leadership role in scientific discovery and innovation. The research and development technologies addressed here will align with the SRNL's and DOE's and DOD's vision to encourage initiatives that will support national defense, and energy security programs.

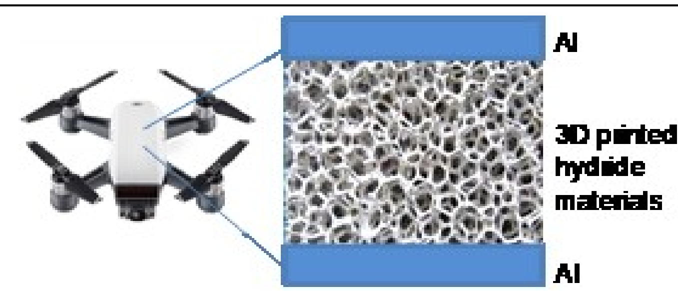

Figure 2. *Simple illustration of the concept of 3D/4D hydride material.*

Approach

- Design and produce a 3D/4D hydride materials via additive manufacturing technologies that could be used as parts of the unmanned aerial vehicles (UAV).
- 3D printing (e.g. selective laser melting) will be used to produce sandwich hydride foam materials (novel feeding stock materials) to create UAV parts, e.g. body, landing gear, and motor supports.

Results/Discussion

Hydrogen storage materials has been the subject of an intense research effort in the last decades. However, this is the first study demonstrating the successful creation of 3D printed hydride materials via additive manufacturing approaches.

The first task of the project focused on the design and material production of a library of 3D/4D hydride-based materials that could be used as structural components of the unmanned aerial vehicles (UAV). Metal hydrides selection is based on decades of intensive and extensive explorations at SRNL in this field. In the initial phase of this task, we engineered and designed hydride materials based on various composition additive metals. Aluminum served as an inert scaffolding material in these architectures. The following alloy compositions were explored: (a) powders: Al, Ti, Fe, Mn, V, Cr, Mg, Pd, Zr, Sc, Ni, Pd, Si, La, etc. and/or (b) nano-microscale additive: Ti, TiO_2, Pd, Fe2O3 as numerous studies shows improved strengths, kinetics, and favorable thermodynamics based on these compositions.

Selection of the hydride materials must meet the following specifications: (a) contains light metals as strength-to-weight ratio is important in aircraft applications, (b) has favorable hydrogen gas storage capabilities, (c) made of porous structures, e.g. foams, with regular/irregular arrays of pores having tunable dimensions at the microscale. Porous hydride materials are of particular interest because they can increase the penetration depth of hydride reaction and decrease the hydrogen absorption time. The pore size affects hydrogen storage capacity and kinetics, as well as thermal stability. Smaller pores impart larger surface areas of interaction at the gas/solid interface, allowing hydrogen to diffuse harmlessly out of the solid. The bulk hydride materials often decrepitate or break down into smaller particles under repetitive reaction cycles, usually hundreds of cycles. The reduced size material may be advantageous since previous studies show that nanophase metal hydrides have enhanced kinetics for reversible hydrogen storage relative to the bulk materials. The hydride material alloyed with specific additive of interest were successfully 3D/4D printed by a laser sintering 3D printing technique. The laser sintering 3D printing uses a high-power laser to fuse powdered material by scanning cross-sections on the surface of a powder bed which is the preferred technique for our materials (**Figure 3**).

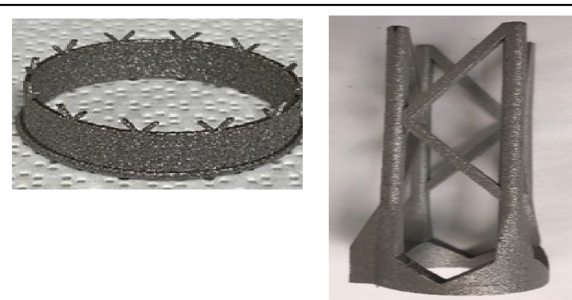

Figure 3. *3D/4D printed metal hydride objects.*

Once produced the 3D/4D printed materials were characterized by a series of analytical tools to evaluate their physico-chemical properties (**Figure 4**). This includes SEM, EDS, EDS mapping, ICP-MS, UV-Vis spectroscopy, surface charge, etc. Data shows that the materials retain their properties upon additive manufacturing. A number of the feeding stock materials were also produced and characterized by the aforementioned techniques (**Figure 5a** inset).

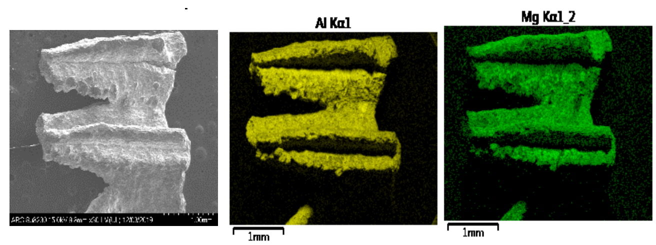

Figure 4. *EDS mapping of the 3D printed Mg-Al based alloys.*

Hydrogen absorption isotherms adsorption and desorption kinetics (**Figure 5 a, b**), capacity, thermodynamic were collected using the automated, patent pending Sieverts apparatus at various temperatures available in our lab at SRNL/ARC. This patent pending technology is based on a novel automatic gas absorption-desorption apparatus that can be used to collect isotherm measurements and evaluate the kinetics and thermodynamic behavior of hydride material at various temperatures and pressures. This automated apparatus is capable of collecting data on multiple absorption-desorption cycling experiments to study long-term cycling effects on capacity and kinetics. It is composed of automated valves that are remotely controlled using LabVIEW. The apparatus can process two samples concurrently for determination of equilibrium temperatures, pressures, and thermodynamics. It can be coupled with any PCTPro or magnetic induced heating systems available on

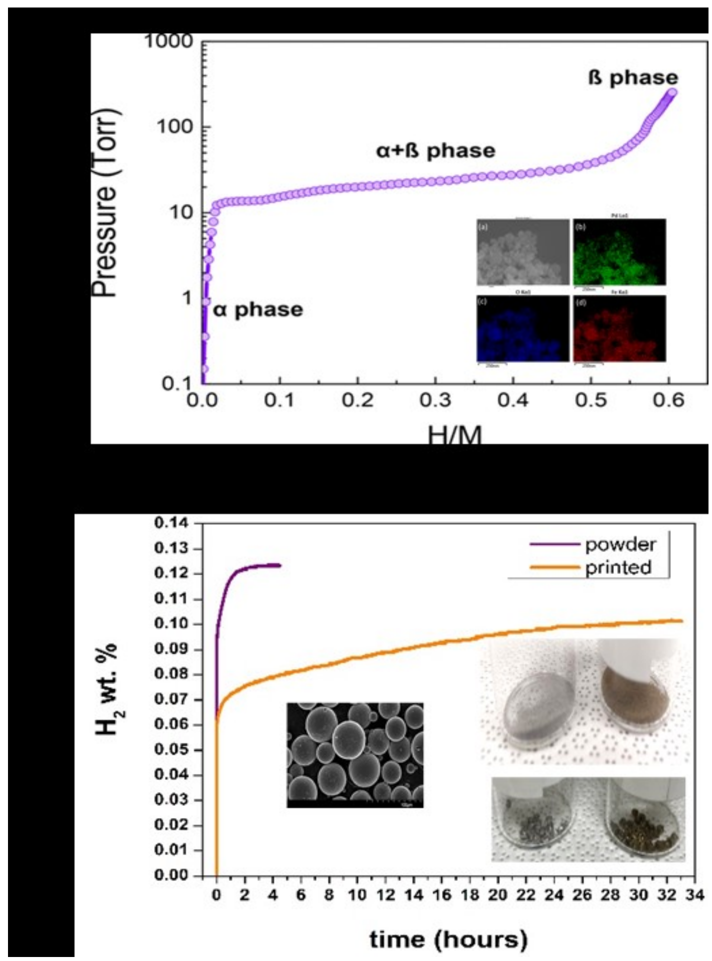

Figure 5. *Hydrogen absorption isotherm absorption on (a) Pd-Fe/FeOx; inset showing EDS mapping; and (b) TiAl6V4 alloy. Insert shows photograph of feeding stock alloy samples before (gray) and after (brown) hydrogenation. The kinetics are far slower for printed TiAl6V4.*

the market for automatization. Isotherms can be collected unattended in less than 8 hours on two hydride samples. The initial testing assessed the system's performance under a variety of process conditions (temperature, pressure, composition), physical design, transient heat and mass transfer. Data collected will be used to compare the material capacity and plateau pressure for the 3D/4D printed samples.

FY2020 Accomplishments

- Designed and produced 3D/4D hydride materials via additive manufacturing technologies that could be used as parts of the UAV;
- Acquired and/or 3D printed a number of hydride-based materials of various compositions: Al, Ti, Fe, Mn, V, Cr, Mg, La, and/or Pd - based materials coupled with other additives;
- Evaluated and characterized both hydrogen storage materials feeding stocks and 3D printed materials -isotherms, SEM, EDS, ICP-MS, EDS mapping, ICP-MS, UV-VIS, collected isotherms on selected feed stock & 3D printed hydride materials;
- Initiated modeling studies on hydride materials;
- Demonstrated for the first time that we can 3D print hydride materials for hydrogen storage capabilities. Preliminary measurements indicate small variation and responses in the hydride absorption kinetics;
- Developed a very unique automated, patent pending Sieverts apparatus at various temperatures available in our lab that can be used to collect isotherm measurements and evaluate the kinetics and thermodynamic behavior of hydride material at various temperatures and pressures;
- Two patent applications were filled with the US Patent and Trademark Office;
- Published one manuscript in the ACS Materials & Interfaces;
- A second manuscript was submitted to the International Journal of Hydrogen Research – Special Issue;
- One book chapter accepted for publication;
- Delivered two conference presentations – The Mineral, Metals and Materials Symposium and Technology and Environmental Business Association (ETEBA) Conferences.

Future Directions

- Continue to evaluate and optimize the 3D/4D printed hydride materials as hydrogen storage material.
- Produce structural components of the UAVs made of 3D/4D printed materials.
- Technology integration of UAV's components with the aircraft and maturation.

FY 2020 Peer-reviewed/Non-peer reviewed Publications

- Efficient Thermal Processes using Alternating Electromagnetic Field for Methodical and Selective Release of Hydrogen Isotopes, International Journal of Hydrogen Energy, Special Issue, 2020 submitted; SRNL – corresponding and first author.
- Controlled Release of Hydrogen Isotopes from Hydride-Magnetic Materials, ACS Applied Materials & Interfaces, 2020, 12, 9478-9488; SRNL – corresponding and first author.
- Analytical Method for Measuring Total Protium and Total Deuterium in a Gas Mixture Containing H_2, D_2, and HD via Gas Chromatography, 2020, Metal-Matrix Composites: Advances in Analysis, Measurement and Observations, Springer, accepted; SRNL – corresponding and first author.

Presentations

- Efficient Heating Processes Using Nanomaterials and Alternating Electromagnetic Fields, Energy, Technology and Environmental Business Association (ETEBA) Conference
- State-of-the-Art Materials at SRNL: From Innovation to Marketplace, TMS

Acronyms

ARC – Applied Research Center

SRNL – Savannah River National Laboratory

AM - Additive Manufacturing

3D – Three Dimensional

4D – Four dimensional

UAVs - Unmanned Aerial Vehicles

SEM – Scanning Electron Microscopy

EDS – Energy Dispersive X-ray Spectroscopy

ICP-MS - Inductively coupled plasma mass spectrometry

UV-Vis – ultraviolet - visible

ETEBA - Energy, Technology and Environmental Business Association

Intellectual Property

- Structural Components for UAVs Made of 3D/4D Printable Materials - U.S. Patent Application
- Automatic Gas Absorption-Desorption Apparatus - U.S. Patent Application

Total Number of Post-Doctoral Researchers

1 - Ray Belliveau (SRNL)