Protective and High-temperature Coatings
Room Palm 3-4 - Session MA3-1-TuM

High Entropy and Other Multi-principal-element Materials I

Moderators: Frederic Sanchette, Université de Technologie de Troyes, France, **Frédéric Schuster**, CEA, France

8:00am **MA3-1-TuM-1 A Combinatorial Approach to Develop Sputter-Deposited Lanthanide-Containing High Entropy Alloys for ICF Applications**, ***Daniel Goodelman [goodelman1@llnl.gov]***, Lawrence Livermore National Laboratory, USA; *Minsuk Seo,* Lawrence Livermore National Laboratory, Republic of Korea; *Gregory Taylor, Alison Engwall-Holmes, Swanee Shin, David Strozzi, Brandon Bocklund, John Chesser, Jimmy Aut, Sergei Kucheyev, Leonardus Bimo Bayu Aji,* Lawrence Livermore National Laboratory, USA

In indirect-drive inertial confinement fusion (ICF) experiments at the National Ignition Facility (NIF), the hohlraum plays a critical role in achieving increased implosion yield, as it drives the fuel capsule's compression. Our simulations with the radiation hydrodynamics code LASNEX suggest that the fusion yield can be improved by using hohlraums made of high entropy alloys (HEAs) containing rare-earth (RE) elements. Here, we present results from a systematic study using combinatorial radio-frequency magnetron co-sputtering to develop a family of Gd-Ta-W-Au-Bi coatings with properties favorable for ICF applications, including high electrical resistivity for consideration in magnetically-assisted ICF schemes. These results provide a framework for the future development of RE-HEA hohlraum materials.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract AC52-07NA27344 and was supported by the LLNL-LDRD Program under Project No. 26-ERD-011.

8:20am **MA3-1-TuM-2 Lanthanide- and Actinide-Containing High-Entropy-Alloy Coatings for Inertial Confinement Fusion Hohlraums**, ***Leonardus Bimo Bayu Aji [bayuaji1@llnl.gov]***, Lawrence Livermore National Laboratory, USA

A hohlraum, centimeter-scale sphero-cylindrical heavy-metal cans with wall thicknesses of 10–100 μm, is a key component of indirect-drive inertial confinement fusion (ICF) targets, as they determine the x-ray drive that implodes the fuel capsule. Our simulations predict that hohlraums made from rare-earth-containing high-entropy alloys (RE-HEAs) or depleted-uranium-containing high-entropy alloys (DU-HEAs) can achieve significantly higher x-ray coupling efficiencies than the best-performing single-element hohlraums made from Au or DU. Here, we present our progress in developing sputter-deposited RE- and DU-HEAs with material properties compatible with ICF target fabrication processes.

This work was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344 and LDRD project 26-ERD-011.

8:40am **MA3-1-TuM-3 Machine Learning Assisted Design of Complex and High Entropy Alloys by Hybrid Hipims/Pulsed Dc Pvd Process for Low Carbon Energy Applications in Extreme Environments**, ***Frederic Schuster [frederic.schuster@cea.fr]***, *Paul Foulquier, Jean-Philippe Poli, Fanny Balbaud, Ryma Haddad,* CEA, France **INVITED**

Materials and Data sciences convergence is the new paradigm governing the discovery acceleration of new materials, always more complex and integrating, in a virtuous approach, new durability and sovereignty requirements. Every great transitions are concerned : towards a sustainable future and energies, towards frugal digital applications, towards a medicine of the future always more customized/personalised. In France, this dynamic is organised at the national level by the PEPR DIADEM, a program gathering universities and research institutes to shape and promote this trend.

In this race to the discovery acceleration of materials, artificial intelligence may play a significant role in always more complex synthesis and shaping processes proficiency. Among these high impact generic processes for many industrial sectors, thin film deposition technologies play a key role, in particular driven towards excellence by constraints and specifications imposed by the requirements always more specific of microelectronics applications.

Consequently, highly ionized PVD processes like HiPIMS emerged in this dynamic and now are being developed in many other domains like sustainable energies, in particular in nuclear applications, and also for green hydrogen via electrolysis, photovoltaics and marine energy.

We will present two developments using a hybrid pulsed-DC/HiPIMS multi cathode system :

1. a new refractory HEA diffusion barrier layer for nuclear claddings on one hand : To prevent loss of coolant accident, fuel claddings in zirconium alloys are now coated with PVD chromium, but at 1320°C an eutectic phase may occur. Hence, we are developing a refractory V-Nb-Mo-W diffusion barrier to avoid the formation of this eutectic phase (ASTERIX project of PEPR DIADEM).
2. new HEA coatings for corrosion in molten salt dedicated to Small Modular Reactors, on the other hand : we will explore the feasibility of Ni-Al-Cr-Mo alloys (A-DREAM project of PEPR DIADEM).

Combinatorial approaches made possible by instrumented multi-target PVD technologies, coupled to artificial intelligence allowing the extraction of inter-parametric relations between processes parameters, are at the heart of this study dedicated to the development of a hybrid pulsed-DC/HiPIMS PVD process digital twin for the deployment of complex coatings for extreme media.

9:20am **MA3-1-TuM-5 Refractory High Entropy Nano-layered Alloy Thin Films For Oxidation Resistance**, ***Abdelhakim Bouissil [Abdelhakim.bouissil@utt.fr]***, *Sofiane Achache, Djallel Eddine Touaibia,* Université de Technologie de Troyes, France; *Jaafar Ghanbaja,* IJL - Université de Lorraine, France; *Pavel S. Postnikov,* Tomsk Polytechnic University, Russian Federation; *Mohamed M. Chehimi,* Université de paris, France; *Benoit Panicaud, Fabrice Parent, Frederic Sanchette, Mohamed El Garah,* Université de Technologie de Troyes, France

Refractory high entropy TiTaZrHfW-N/Si_3N_4 nano-layered alloy thin films are investigated to study the effect of nano-layered architecture and silicon (Si) mean content on their structural, mechanical, thermal properties and oxidation behavior. The films are deposited using direct current (DC) magnetron sputtering of separate Si and TiTaZrHfW targets. The Si mean content is controlled by tailoring the power discharge applied to the Si target. The deposition process led to a nano-layered architecture where Si_3N_4 (amorphous) and TiTaZrHfW-N (nano-crystalized NaCl FCC type structure) are alternated. By increasing the thickness of Si_3N_4 nano-layers, the Si mean content increases. All coatings are found to have good thermal stability after annealing under vacuum at 900 °C. Increasing Si mean content reduces the film's hardness; however, the annealing treatment at 900 °C improves it. A super-hardness of 41 GPa is found for the post-annealed Si-free film. Si_3N_4 nano-layers enhance the oxidation resistance at elevated temperatures of 600, 700, and 800 °C. This oxidation resistance is further enhanced by increasing the nano-layer's period and also by increasing the density of the films.

9:40am **MA3-1-TuM-6 Solid-State Synthesis and In-Situ XRD Analysis of Titanium-Based Composite Oxides for Lithium-Ion Battery Anodes and Application**, ***Guan-Hong Lin [m56144031@gs.ncku.edu.tw]***, *Hsing-I Hsiang, Yu-Min Shen,* National Cheng Kung University (NCKU), Taiwan

The rational design of multi-component oxide systems provides an effective pathway to balance high capacity and structural robustness in lithium-ion battery anodes. In this study, TiO_2–SnO_2 composite solid solutions were synthesized via a controlled solid-state reaction to explore the interplay between structural evolution and electrochemical performance. Structural analyses (XRD and TEM) confirmed the partial incorporation of Sn^{4+} into the rutile TiO_2 lattice, accompanied by limited phase segregation into SnO_2-rich domains at higher Sn contents. The coexistence of solid-solution and segregated regions generated a nanoscale heterostructure that enhanced Li^+ diffusion and mitigated volume fluctuation during cycling. Among the synthesized samples, ST1450 initially delivered the highest capacity of 635.5 mAh g^{-1} at 0.2 C, but gradually declined to 231.9 mAh g^{-1} after 100 cycles, corresponding to the lowest degree of phase segregation. Electrochemical impedance spectroscopy (EIS) and distribution of relaxation time (DRT) analyses revealed that coherent TiO_2/SnO_2 interfaces effectively facilitated charge-transfer kinetics while preserving mechanical integrity. The optimized ST1450 sample exhibited an extremely low charge-transfer resistance of 3.85 Ω, reflecting improved electronic transport pathways. Furthermore, in-situ XRD measurements directly captured phase transitions during lithiation and delithiation, providing crucial insight into the dynamic reaction mechanism. The observed spinodal decomposition within the TiO_2–SnO_2 system forms a self-organized nanoscale microstructure that reinforces both ionic transport and structural stability. These results elucidate the lithiation pathway of TiO_2–SnO_2 composite oxides and highlight spinodal decomposition as a promising strategy for developing structurally adaptive, high-performance oxide anodes for next-generation lithium-ion batteries.

Keywords: **Composite oxides**, **Anode materials**, **Fast-charging materials**, **In-situ XRD**, **Solid-state reaction**

10:00am **MA3-1-TuM-7 EELS study of Fe–Co–Ni Phosphides electrocatalysts for Hydrogen Evolution Reaction***, Chun-Te Chiang* ***[tony25477210@gmail.com]**,*

Southern Taiwan University of Science and Technology, Taiwan*; Yu-Min Shen,* Center for Resilience and Intelligence on Sustainable Energy Research, National Cheng KungUniversity, Taiwan*; Yu-Tsung Lin, Jow-Lay Huang,* National Cheng Kung University (NCKU), Taiwan*; Sheng-Chang Wang,* Southern Taiwan University of Science and Technology, Taiwan

Abstract

Hydrogen is widely recognized as a promising clean energy carrier, with the hydrogen evolution reaction (HER) serving as a crucial step in sustainable hydrogen production. Transition-metal phosphides have attracted considerable attention owing to their excellent electrical conductivity and catalytic activity. In this study, Fe–Co–Ni phosphides were synthesized via a solution-based precursor route followed by phosphorization, forming nanostructured multimetallic phases with uniform morphology. Transmission electron microscopy (TEM) revealed nanoscale features, while energy-dispersive X-ray spectroscopy (EDS) confirmed the homogeneous distribution of Fe, Co, and Ni.

Electron energy loss spectroscopy (EELS) played a central role in elucidating the electronic structure evolution of the catalysts. The spectra revealed distinct edges corresponding to O (538.5 eV), Fe (712.0 eV), Co (783.0 eV), and Ni (857.0 eV), clearly reflecting the hybridization between metal 3d and P 2p orbitals and providing direct evidence of charge redistribution among the transition-metal sites. These findings demonstrate the strong correlation between the local electronic configuration and catalytic performance.

Electrochemical analysis further confirmed that Fe–Co–Ni phosphides exhibit remarkable HER activity, requiring only -0.176 V overpotential to reach -10 mA cm^{-2}. The polarization (I–V) curves showed rapid current response and low activation energy, while a Tafel slope of 109 mV dec^{-1} indicated a favorable Volmer–Heyrovsky mechanism. Long-term chronoamperometric measurements verified excellent durability, and subsequent durability and accelerated cycling tests lasting up to 100 hours will be conducted to comprehensively evaluate structural and electrochemical stability under realistic conditions.

This work not only demonstrates the successful synthesis of multimetallic phosphides but also highlights EELS as a powerful tool for probing the structure–property relationship, offering valuable insights for the rational design of efficient and durable hydrogen electrocatalysts.

Keywords: NiCoFeP ; EELS; electrocatalyst

10:20am **MA3-1-TuM-8 Self-Organized Metal Carbide Coatings: Structural Evolution and Functional Performance in Catalytic and Protective Applications***, Ewa Dobruchowska* ***[ewa.dobruchowska@tu.koszalin.pl]**,*

Tomasz Suszko, Witold Gulbiński, Koszalin University of Technology, Poland*; Grzegorz Greczynski,* Linköping University, IFM, Sweden*; Jerzy Morgiel,* Institute of Metallurgy and Materials Sciences, Polish Academy of Science, Poland **INVITED**

Nanostructured thin films continue to draw considerable attention owing to their unique and tunable properties, governed by composition, structure, and morphology. Precise control of synthesis parameters enables tailoring of film architecture and optimization of functional performance. Previous studies have shown that binary metal/carbon (Me/C) nanocomposites (Me = Ni, Co) can form amorphous, self-organized films via magnetron sputtering, characterized by high-aspect-ratio nanocolumns that may induce anisotropic behavior. These findings have inspired the development of multicomponent coatings with precisely engineered compositions and structures to further enhance performance in targeted applications.

An investigated approach employed NiMo-C coatings, synthesized with reactive magnetron sputtering of a $Ni_{80}Mo_{20}$ alloy in an acetylene atmosphere, as catalysts for the hydrogen evolution reaction (HER) in an acidic medium. The structural, chemical, and phase evolution of the coatings with increasing carbon content (5-75 at.%) was examined using X-ray diffraction, X-ray photoelectron spectroscopy, and transmission/scanning electron microscopy. Electrical conductivity measurements, performed with a conductive atomic force microscope, complemented the structural and compositional studies. It was found that progressive carbon incorporation (20-75 at.%) induced a transition from nanocrystalline to amorphous and ultimately to a quasi-amorphous nanocolumnar architecture composed of metallic columns perpendicular to the surface and encapsulated by an amorphous carbon shell. This morphology is expected to enhance charge transport along the columnar pathways. Moreover, the coatings surface exhibited nickel-enriched conductive regions (approx. 20 nm in diameter) that act as active catalytic centers for HER, while the surrounding carbon matrix improves corrosion resistance and interfacial stability.

The pronounced chemical stability of self-organized, carbon-enriched coatings validates their suitability for both catalytic and biomedical applications. This has been demonstrated in our studies of FeNiMo-C and CoCrMo-C systems derived from the medical alloys 316L and F-1537-08. Cyclic potentiodynamic testing in simulated body fluid showed that both coating systems were highly resistant to localized corrosion, including pitting. Tribocorrosion tests on CoCrMo-C further indicated that increasing the carbon content reduced the friction coefficient to approx. 0.1. The coatings containing 40 at.% carbon exhibited the most favorable tribological performance, demonstrating the lowest friction coefficient and a low wear rate irrespective of the measurement conditions.

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