New Horizons in Coatings and Thin Films
Room Royal Palm 1-3 - Session F5

Additive-manufacturing-based Methods and Surface Engineering

Moderators: Ramana Chintalapalle, University of Texas at El Paso, Sven Ulrich, Karlsruhe Institute of Technology (KIT)

3:30pm **F5-7 3D-Painted Metals and Alloys: A New Approach to Metal and Alloy Advanced Manufacturing**, *A Jakus, S Taylor,* ***Nicholas Geisendorfer****, D Dunand, R Shah,* Northwestern University, USA

We present a alternative technology to traditional laser and e-beam based metal and alloy additive manufacturing (AM) approaches that utilizes room-temperature extrusion of particle-based liquid inks comprised of metal oxide powder(s), elastomeric binder, and graded volatility solvents to create self-supporting, complex constructs that can be thermochemically reduced and sintered, resulting in metallic constructs. This particular ink formulation results in 3D-printed green bodies that, although comprised of up to 90 vol.% metal, alloy, and/or metal compound particles, can be bent, rolled, folded, cut, and even fused with other similar materials using the ink as an adhesive. The inks may also be used to rapidly create flexible, conformal films via dip-coating and other non-3D-printing methods. We demonstrate that this process can be applied to a variety of ferrous and non-ferrous primary metal and alloy systems to create objects as small as a single cubic millimeter and as large as many cubic centimeters, comprised of structural features as small as 100 µm. In this manner, nano- and micron-scale oxide powders, which are generally far more economical than their metallic or pre-alloyed powder counterparts, can be utilized to rapidly create large scale, user-defined architectures. Mechanical testing of 3D-printed oxide green bodies reveals that tensile and compressive strengths and moduli depend heavily on the concentration of particles within the construct, as well as the size of the comprising particles. None of the green bodies tested, including those comprised of 90 vol.% particles, catastrophically fail under compressive loads, but rather, plastically deform. Inks comprised of a variety of metals - including but not limited to those of iron, nickel, copper, tungsten - are presented along with inks comprised of mixed oxides corresponding to desired final binary and ternary alloy compositions. Oxide green bodies are thermochemically reduced in pure H_2 atmosphere at elevated temperatures to metals and alloys, which then continue to be sintered in H_2 or inert atmosphere. The resulting metallic constructs, although volumetrically reduced due to sintering and to oxide-to-metal density changes, retain their originally shapes without warping, cracking, or sagging. Metallographic and electron microscopic analyses of the resulting metal and alloy structures reveal near fully dense metallic constructs can be achieved with the majority of the systems tested. Finally, we show how this process can be extended towards creating complex, multi-metal/alloy constructs through co-3D-printing of multiple liquid oxide inks.

3:50pm **F5-8 3D Printing of 2D Materials**, *A Juhl,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; A Stroud,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; W Lai,* University of Dayton/Sensors Directorate, Air Force Research Laboratory, USA*; S Kim,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; N Glavin, R Berry, G Leuty,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; R Naik,* Human Effectiveness Directorate, Air Force Research Laboratory, USA*; M Durstock,* Materials and Manufacturing Directorate, Air Force Research Laboratory, USA*; P DeRosa,* Institute for Micromanufacturing/Physics Program, Louisiana Tech University, USA*; E Heckman,* Sensors Directorate, Air Force Research Laboratory, USA*;* ***Christopher Muratore****,* University of Dayton, USA

Alternative materials and fabrication techniques are necessary to revolutionize the performance of large scale flexible electronics. Direct printing of electro-optical devices is a promising new fabrication approach, especially for integration of emerging two dimensional (2D) materials which have uncommon and useful combinations of properties, such as tunable band gaps, mechanical flexibility and optical transparency. However, challenges in conventional printing of suspended 2D particles and low performance of printed circuits remain. Here we describe a printing technique based on a novel a selective molecular attachment (SMA) approach for integration of 2D and other materials into printed circuits or devices. Peptide molecules have been identified via phage display techniques that adhere selectively to semiconducting few-layer MoS_2 flakes and graphene. These peptides are dissolved in 'ink' and printed on insulating surfaces to print transistors and other devices. The printed substrates are then dipped in suspensions of graphene and MoS_2 and the particles stick only to the peptide printed surfaces. Simulations of the peptide surface interactions reveal the specific amino acids that bind to substrate and particle. For example we observe that for the HLL peptide adsorbed on MoS_2, the phenylalanine ring had the closest binding position of any amino acid. The other ring residue structures, histidine and the two prolines, were also shown to very close to the surface. The n-term, c-term, and arginine residues were seen to migrate away from the surface. This knowledge enables design of peptides for enhanced adhesion and also for sensing of target molecules in vapor or solution phase. It is anticipated that the exotic combinations of properties found in 2D materials will add unique functionality to devices over standard printed materials and architectures. Here we demonstrate the technique and explore the peptide-surface interactions in SMA processes.

4:10pm **F5-9 Direct Laser Deposition of High Entropy Alloy Coatings on High Temperature Alloys**, ***Daniel Fabijanic****, Q Chao,* Deakin University, Australia*; T Jarvis, X Wu,* Monash University, Australia*; P Hodgson,* Deakin University, Australia

High entropy alloys (HEAs) are relatively a new alloy system comprising of a minimum of 5 principle alloy elements at a concentration between 5-35 atomic percent. Contrary to phase rule prediction many HEA compositions form simple solid solutions. HEAs have attractive properties as bulk or coating materials in elevated temperature applications: high resistance to thermal softening, thermally stable microstructure, low inter-diffusion, and high oxidation resistance. Limited studies have explored the formation of HEA coatings on steel substrates by laser surface melting a static layer of pre-alloyed powders. This technique is restricted to horizontal surfaces, limiting practical implementation. To clad complex shapes an appropriate technique is "blown powder" additive manufacturing (Direct laser deposition, DLD) where powder is delivered to a focused laser on a controllable head. The formation of HEA coatings by this technique is unreported in the literature. This work addresses two main research questions; *Can chemically homogenous coatings be manufactured by the DLD of a blend of 5 elemental powders?* and *Can the DLD process parameters be controlled to eliminate the dilution effect of the substrate?*.

$Al_xCoCrFeNi$ (x=0.3, 0.6 and 0.9) HEA coatings of were produced by single-pass DLD on 253MA austenitic steel and Inconel 600 superalloy using a mixture of blended elemental powders. A three-level parametric study was performed on key variables: laser power, scan speed, spot size, powder feed rate, focal offset and hatch distance. Through thickness elemental composition (GDOES) and phase analysis (XRD) was determined. The coating microstructure (SEM, AsB detector), local homogeneity (EDS) and properties (microhardness) were obtained in cross-section. Increasing Al mole fraction from 0.3 to 0.6 and 0.85 resulted in a change in HEA coating crystal structures from FCC, FCC/BCC and BCC. The compositional mixing between the deposited layer and the substrate was quantified using a proposed mixing factor, which was significantly influenced by the deposition variables, chiefly powder feed rate. Homogenous HEA coating compositions were obtained at a relatively higher powder feed rate.

4:30pm **F5-10 In-situ Impedance Spectroscopy Evaluation of Electrolytic Plasma Polishing Process for Stainless Steels**, *V Mukaeva, E Parfenov, R Nevyantseva,* Ufa State Aviation Technical University, Russian Federation*; A Matthews,* ***Aleksey Yerokhin****,* University of Manchester, UK

Electrolytic Plasma Polishing (EPPo) is currently attracting increasing attention due its ability to provide excellent surface finish to components manufactured by various methods, including 3D printing parts of stainless steels, Ti, Cu and Ni alloys. The method is based on anodic dissolution of metals combined with sputtering by glow discharge which is developed in the Vapour Gaseous Envelope (VGE) formed at the surface of the working electrode under the conditions of high-voltage electrolysis. However, how these two different material removal mechanisms coexist and interact with each other remains unclear. To elucidate these relationships in-situ impedance spectroscopy studies of the EPPo process of AISI 420 stainless steel have performed. The impedance spectra have been acquired for the treatments carried out at voltages and temperatures ranging from 250 to 350 V and 70 to 90 ^oC respectively. Based on the analysis of impedance spectra, an equivalent circuit was developed, including three kinetic processes with different time constants representing charge transport through the VGE by normal conduction and plasma discharge mechanisms followed by charge transfer across the interface with the metal anode.

Physical meanings of the circuit elements have been discussed and dependencies on processing parameters established. These dependencies have been correlated with kinetic characteristics of material removal and quality of surface finish achieved. As a result, optimum conditions for EPPo treatment of AISI 420 stainless steel have been established.

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