SYMPOSIUM LL

Issues in Solid Freeforming

November 29 - 30, 2004

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* Invited paper

SESSION LL1: Special Invited Symposium Address J. Fenn, Virginia Commonwealth University
Chair: Suwan Jayasinghe
Monday Morning, November 29, 2004
Room 203 (Hynes)

8:00 AM LL1.1
Electrospray Wings for Molecular Elephants. John B. Fenn, Department of Analytical Chemistry, Virginia Commonwealth University, Richmond, Virginia.

Small effusive leaks into vacuum systems, as in Knudsen cells and classical molecular beam machines, made many conributions to science in the twentieth century. They have continued to serve both both science and technology in the early years of the twenty first. Beginning in the 1950s, big convective leaks have turned out to be even more powerful and versatile tools. The supersonic free jets produced by these big leaks have greatly extended molecular beam methods, become a cornerstone of cluster science and technology, and rewritten the book on molecular spectroscopy. Thoss jets are now adding new dimensions to the techniques of mass spectrometry by making possible the production of intact ions from the large, complex and fragile species that play such vital roles in living systems. The path from the first crude experiments of Dunoyer into the groves of atomic and molecular physics followed along the trail blazed by Otto Stern and his disciples. That trail was then extended into the fertile fields of chemistry by the likes of Herschbach, Lee, Polanyi, Smalley, Zare and Zewail, five of whom received Nobel Prizes for their contributions. More recently that trail entered the lush gardens of biology where mass spectrometry is providing bumper crops of information and understanding. This travelogue will describe some of the landmarks along what has been a fascinating journey.

SESSION LL2: Solid Freeforming
Chairs: Gian Babini and Joseph Beaman
Monday Morning, November 29, 2004
Room 203 (Hynes)

9:00 AM *LL2.1
Jet-based Processing of Micro- and Nano-Suspensions. M. J. Edirisinghe, Department of Materials, University of London-Queen Mary, London, United Kingdom.

This paper reviews over a decade of research into the use of jet technology to process advanced materials, thus pioneering the development of novel solid freeforming methods in our laboratories. Firstly, ink-jet printing has been used to fabricate a wide variety of complex ceramic architectures. Subsequently, the size of printed relics has been reduced by over an order of magnitude by using stable cone-jet mode electrohydrodynamic atomization. The latter process has been used to fabricate structural, functional and biological microstructures from a range of concentrated suspensions containing both micro- and nano-powders.

9:30 AM LL2.2
Preceramic Polymers for Inkjet Printing: Crosslinking Mechanism and Filler-loading. Michael Scheffler[1], Franziska Scheffler[2], Celine Schneider[2], Colin F. Fyfe[2] and Rajendra K. Bordia[1]; [1]Department of Materials Science and Engineering, University of Washington, Seattle, Washington; [2]Chemistry Department, University of British Columbia, Vancouver, British Columbia, Canada.

Recently, inkjet printing has been used for ceramic slurry printing and the manufacturing of small 3D parts. Among the different systems, inks based on preceramic polymers are promising candidates for a high ceramic yield with a high potential for tailoring properties by loading with particulate fillers. A ceramic ink base system for multichannel inkjet printing was developed based on a mixture of a liquid preceramic polymer and a latent water source. The water was generated in situ by the addition of a tin based catalyst. Both, the preceramic mixture and the catalyst can be added from different inkjet channels, and crosslinking occurred at room temperature within minutes. The crosslinking mechanism was investigated by FT-IR spectroscopy and by 1H, 13C and 29Si MAS NMR spectroscopy. The first step is rapid water formation by catalyst-driven polycondensation of the hydroxyterminated polymethylsiloxane used as a latent water source. The water then associated with the methoxy groups of the poly(methoxymethylsiloxane), which was used as the preceramic polymer, and the formation of Si-O-Si bonds was observed after a reaction time of about 40 minutes at room temperature. The preceramic inks were investigated with respect to their ceramic yield after pyrolysis, and a ceramic yield of more than 50 % was measured at optimized compositions in the filler-free base system. The preceramic ink can be diluted with n-hexane for viscosity adjustment which makes it suitable for loading with particulate fillers. As a dispersant silicone resins were dissolved in monomeric silanes and added to the base system. Pyrolysis of such complex systems lead to a ceramic yield of more than 60 %. Further optimization of the ink system is expected to increase the filler content and thus, the ceramic yield after thermal conversion.

9:45 AM *LL2.3
Direct Ink Jet Printing of Structural, Functional and Biological Materials. Brian Derby, School of Materials, University of Manchester, Manchester, United Kingdom.

Ink jet printing is a highly versatile tool suitable for rapid prototyping and rapid manufacture where liquid precursors or suspensions are available. Solid objects are built up from solidified liquid drops, which must coalesce prior to solidification to provide a defect free 3-dimensional structure. The principles of drop formation and spreading will be reviewed and the key physical properties of the fluids identified. This will be illustrated with examples in structural ceramics, electronic materials and biological applications.

10:30 AM LL2.4
Fugitive Inks for Direct-Write Assembly of Complex Three-Dimensional Microvascular Networks. Daniel Therriault[1], Robert F. Shepherd[3], Scott R. White[2] and Jennifer A. Lewis[3]; [1]Mechanical Engineering, Ecole Polytechnique, Montreal, Quebec, Canada; [2]Aerospace Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois; [3]Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois.

The creation of geometrically complex fluidic devices is a subject of broad fundamental interest with a wide array of potential technological applications, including biotechnology, microelectronics, chemical reactors, sensors and autonomic materials. Several approaches have emerged for fabricating two- and three-dimensional (2D/3D) microfluidic devices such as photolithographic or soft-lithographic techniques, laser micromachining and direct-write assembly of a fugitive ink. The latter was recently demonstrated through the creation of 3D microvascular networks, consisting of 16-layer structures with interconnected microchannels (diameter of 200 microns) encapsulated in an epoxy matrix. The approach involved the robotic deposition of a fugitive nanoparticle-filled organic ink, which yields the desired cylindrical microchannel network with defined connectivity upon its subsequent removal from the matrix. Difficulties, such as deformation of this fugitive ink scaffold, were encountered during assembly which prevented fabrication of larger 3D structures. Here, we report the development and rheological characterization of a new fugitive ink that enables the direct-write assembly of 3D scaffolds with unparalleled geometric complexity that retain their shape during fabrication and subsequent matrix infiltration under ambient conditions. Using this new ink, we have built 104-layer microvascular networks comprised of 1,664 microchannels embedded in a 20 x 20 x 20 mm^3 optically clear epoxy cube with a total pore volume of 13%. These advances provide new opportunities for 3-D microfluidic systems for a broad range of technological applications including chaotic mixers based on triangular-spiral tower architecture.

10:45 AM *LL2.5
Fused Deposition of Ceramics (FDC) and Related Processing Issues. Ahmad Safari and Mehdi Allahverdi; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

Fused Deposition of Ceramics (FDC) is a free forming technique developed at Rutgers University for rapid prototyping of ceramic components. Various structural, electrical, and biomedical parts have been prototyped, showing comparable properties to conventionally made parts. In a newly developed Fused Deposition of Multi-Materials system, components with up to four materials can be built. Features such as vision control, polishing, and adaptive road width and toolpath are built into the system to produce high quality prototypes. In FDC, the feedstock is a mixture of a thermoplastic binder and ceramic particles, formed into a flexible filament. The filament functions as a feeding mechanism to drive the material into a liquefier, where it softens and is extruded through a nozzle. The thermoplastic (polyolefine-based) binder of the feedstock must possess desirable properties. During build, the thermoplastic binder must soften at relatively low temperatures and exhibit proper tackiness, plasticity, and flow behavior. This would facilitate control of material flow while building parts and provide strongly bonded layers once the thermoplastic binder cools to room temperature. Upon successful deposition, the binder has to be removed (burnt out) slowly and completely at temperatures up to 600C without affecting the integrity of the green component. Ceramic loading of the filaments is about 55 vol.%. At such a high loading, surfactants are used to uniformly disperse fine particles in the binder to obtain relatively low viscosity at deposition temperatures. If the particles are agglomerated, the viscosity would be high and the pressure required to extrude the material through a fine nozzle could be excessive, resulting in filament buckling. Since the filament works as a feeding mechanism, it is essential for the filament to exhibit high compressive strength before entering liquefier. Based on the viscosity and compressive strength of various filaments such as silicon nitride, graphite, wax, and lead zirconate titanate at deposition temperatures, a selection map was built to predict if a new filament can be used in the FDC process successfully. During filament extrusion and deposition, the materials is sheared, therefore, it is possible to obtain oriented asymmetric particles (seeds). This capability allows preparation of grain-oriented microstructures through "templated grain growth" process in net shaped prototypes. Fine (10-50 μm) asymmetric (needle and platelet) seeds of materials have been added to the fine ceramic powders (matrix) and partial orientation has been achieved in the process. It appears that needle-shaped seeds can be aligned more effectively during the FDC process as compared to the platelet particles. In addition to the shape of asymmetric particles, parameters such as size, aspect ratio, and dispersion in the fine matrix also influence the orientation.

11:15 AM LL2.6
Droplet Behaviour in Inkjet Printing. Jonathan Edward Stringer and Brian Derby; Materials Science Centre, UMIST, Manchester, United Kingdom.

Ink jet printing constructs solid objects by the coalescence of impacting drops and their solidification. The size of an individual drop after printing depends upon its impact velocity and fluid properties below some splashing threshold. Here we present results from ceramic filled waxes exploring the parameter space for printing in terms of the Reynolds and Weber numbers of the droplets. High-speed photography is used to characterise drop formation and impact. The behaviour of the drops are compared with existing models of drop spreading and splashing.

11:30 AM *LL2.7
Direct Laser Sintering of Metal Parts: Characterisation and Evaluation of Joining Mechanisms. E. Bassoli[1], A. Gatto[1], Luca Iuliano[2] and E. Atzeni[2]; [1]Department of Manufacturing Systems and Economics, Polytechnic of Turin, Turin, Italy; [2]Department of Mechanical and Civil Engineering, University of Modena and Reggio Emilia, Modena, Italy.

Rapid Prototyping and Tooling are playing a more and more important role in the achievement of compressed time to market solutions, where prototype parts and tools are produced directly from the CAD model. Even so, the diffusion of these techniques is hardly supported by scientific knowledge about the micro-mechanisms ruling the macroscopic performances of the part. In the present research, dimensional and mechanical performances of Direct Laser Sintering technique have been studied. Tensile specimens of Direct Metal and Direct Steel materials have been produced, following the specifications of standard ASTM E8. Specimens' different orientations in regard to laser path have been adopted, to investigate the effect of laser sintering strategy on the part performances. Figure 1 summarises experimental stress-strain curves obtained for Direct Steel 20. Rupture surfaces of the tensile specimens were observed at the SEM, in order to understand failure mechanisms, whereas the observation of polished sections helped investigating joining phenomena between the particles.

SESSION LL3: 3-D Fabrication and its Applications
Chairs: Brian Derby and Luca Iuliano
Monday Afternoon, November 29, 2004
Room 305 (Hynes)

1:30 PM *LL3.1
Materials Issues in Rapid Manufacturing. D. L. Bourell, Joseph J. Beaman, R. S. Evans and S. Barrows; Mechanical Engineering Department, University of Texas, Austin, Texas.

Materials flexibility in rapid manufacturing (RM), along with accuracy and surface finish, has been a critical factor in the technology from the very beginning of the technology. It is an enabling feature of RM. Just as fluidity is critical for casting and plasticity is requisite for forging, RM processes impose constraints on the range of available materials. Coupled to process constraints is product demands desired by the final user of the product. A major role of materials developers in RM is the tailoring of materials, alloys and multi-component systems to create process-able materials with acceptable end performance. An overview of materials issues in RM is given with specific attention given to silicon-infiltrated silicon carbide parts. The research was funded by a grant from the State of Texas, #TDT003658-0590-2001.

2:00 PM *LL3.2
The Direct Fabrication of Metal Parts by Three Dimensional Printing. Emanuel Sachs, Fred F. Flowers and Daniel F. Flowers; Mechanical Engineering Department, MIT, Cambridge, Massachusetts.

Three Dimensional Printing (3DP) has long been used to print ceramic molds into which metal castings are poured. More recently, the direct fabrication of metal parts by 3DP using metal powder has become an attractive option, especially for higher performance ferrous alloys. This paper reviews the development of 3D printing of metal parts and highlights some of the recent technical advances which have made this an attractive option. At first, direct metal parts were fabricated by 3DP using a stainless steel powder and a polymeric binder to 3D print a green skeleton. The skeleton was then lightly centered and infiltrated with a copper alloy to produce a fully dense part. While useful for some applications, the mechanical properties were significantly lower than conventionally fabricated parts of a homogeneous composition. Perhaps more importantly, designers would greatly prefer to use a metal part of a homogeneous and standard alloy. These preferences derive from certification issues as well as concerns such as corrosion. Accordingly, a first focus was on the direct printing of parts of homogeneous composition and where possible, standard alloys. Two routes have been demonstrated. In the first, fine ($<$25 μm) powder is used to print small fine-featured green parts which are then sintered to full density. In this way some extremely fine-featured components have been made by direct printing in stainless steel alloys. The second route returns to infiltration but creates a part of nearly homogeneous composition by using an infiltrant with a composition very similar to that of a skeleton but with a melting point depressant added. For example, a nickel skeleton can be infiltrated with a nickel silicon alloy, and a moderate range of high performance ferrous alloys can be infiltrated by using carbon to depress the melting point of the infiltrant. During and after infiltration, the melting point depressant diffuses from the infiltrant into the skeleton thereby achieving homogenization. For example in the case of D2 tool steel, mechanical properties close to those of raw alloys have been obtained using this method. Another area of concern is the dimensional stability of the skeleton during the high temperature infiltration process. Here the focus has been on increasing the size of the necks between powder particles, including the use of binders which carry inorganic material (for example as a nanoparticulate phase). Experience and theoretical modeling with a range of inorganic binders will be discussed.

2:30 PM LL3.3
Strengthing Porous Skeletons by Metal Deposition from a Nanoparticle Suspension. Nathan B. Crane[1], Emanuel Sachs[1] and Andreas Frank[1,2]; [1]Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Mechanical Engineering, RWTH, Aachen, North Rhine-Westphalia, Germany.

Solid freeform fabrication (SFF) processes such as three-dimensional printing (3DP) and selective laser sintering (SLS) produce porous bodies that must be densified. New homogenous infiltration techniques can produce dense, homogenous parts of selected standard alloys, but the increased infiltration temperature dramatically increases creep deflection under self-weight. This paper reports on a method that improves dimensional stability by reducing creep deflection rates at high temperature. This method is applicable to all metal skeletons that must be strengthened without increasing shrinkage or reducing porosity. In this method, the skeletons are reinforced by addition of nanometer sized particles dispersed in a liquid. The nanometer-sized particles are necessary for their reduced sintering temperatures, ability to pass through the pores in the skeleton, and stability with respect to settling in the dispersion. The liquid may be added as the primary binder in a three-dimensional printing process (3DP) or infiltrated into a preformed skeleton produced from 3DP, SLS, or traditional processes such as pressing. The liquid is evaporated, depositing the metal in the skeleton. The metal nanoparticles of the deposited metal are densified by sintering at moderate temperatures at which the sintering of the larger skeleton particles is negligible. The process can achieve significant improvements with small amounts of added metal, if the liquid is dried slowly so that the deposits are concentrated in particle contact regions where they reinforce skeleton bonds. This process is demonstrated using a suspension of 8-10 nm Iron particles obtained from NanoMat Inc. The drying and sintering processes are characterized using TEM images, nanoindentation, and gas adsorption pore-size analysis. Test parts of 410 SS were produced by 3DP and infiltrated with varying amounts of the nano-iron suspension. When heated with an unsupported overhang to a typical infiltration temperature, creep deflection was reduced 50% and indentation area reduced by more than 20% relative to untreated specimens. SEM images confirm that the particle bonds are larger in the specimens treated with the nano-iron suspension than in the untreated control specimens.

3:00 PM *LL3.4
Precision Extruding Deposition and Characterization of Cellular Poly-?-Caprolactone Tissue Scaffolds. L. Shor, F. Wang, A. Darling, S. Khalil, W. Sun, S. Guceri and A. Lau; Department of Mechanical Engineering and Mechanics, Drexel University, Philadelphia, Pennsylvania.

Successes in scaffold guided tissue engineering require scaffolds to have specific macroscopic geometries and internal architectures in order to provide the needed biological and biophysical functions. Freeform fabrication provides an effective process tool to manufacture many advanced scaffolds with designed properties. This paper reports our recent study on using a novel Precision Extruding Deposition (PED) process technique to directly fabricate cellular Poly-ϵ-Caprolactone (PCL) scaffolds. Scaffolds with a controlled pore size of 250 μm and designed structural orientations were fabricated. The scaffold morphology, internal micro-architecture and mechanical properties were evaluated using SEM, Micro-Computed Tomography (μ-CT) and the mechanical testing. Preliminary biological study was also conducted to investigate the cell responses to the as-fabricated tissue scaffolds. The results and the characterizations demonstrate the viability of the PED process to the scaffold fabrication as well as a good mechanical property, structural integrity, controlled pore size, pore interconnectivity, and the anticipated biological compatibility of the as-fabricated PCL scaffolds.

3:30 PM *LL3.5
Structure and Properties of Nanotube-Containing Nanofibers. Yury G. Gogotsi, H. Ye, H. Lam, N. Titchenal and Frank Ko; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Nanocomposite fibers containing carbon nanotubes (CNT) can be manufactured using electrospinning. A number of organic polymers such as polyacrylonitrile (PAN), polylactic acid (PLA) and silk used as a matrix, while single-wall CNT or multi-wall CNT were used for reinforcement. The typical diameters of the composite fibers are in the range 20-200 nm with the indiscrete lengths up to a few centimeters. Continuous fibers can also be produced by this method. This paper presents a review of the studies of structure of the nanotube-containing nanofibers. The structure, composition and reinforcement mechanisms of the nanocomposite fibers have been thoroughly investigated using high resolution transmission electron microscopy (TEM), electron energy loss spectroscopy (EELS) and Raman microspectroscopy. It is found that the presence of CNT may significantly modify the structure and improve the mechanical properties of the nanocomposite fibers. Alignment of CNT in the polymer matrix and interfacial adhesion between CNT and matrix are two major factors to determine the reinforcement effect. Further treatment of the polymer nanocomposite fibers was conducted to produce nanometer-sized carbon fibers or single crystalline SiC whiskers. CNT may serve as seeds to accelerate crystallization and graphitization during the synthesis of carbon fibers or SiC whiskers.

4:00 PM LL3.6
Optical Components with SFF. Joseph J. Beaman, K. L. Wood and R. Ruizpalacios; Mechanical Engineering Department, University of Texas, Austin, Texas.

Research in manufacturing techniques for novel and cost effective optical components has focused on factors such as versatile new materials and low temperature processing. The combination of sol-gel materials with freeform direct-write techniques has the potential of successfully addressing these factors, for the fabrication of photonic components for rapid prototyping purposes. Our research over the past two years has focused on the use of hybrid organic/inorganic sol-gel materials in combination with laser photophysical processing to create simple optical structures. This talk presents an overview of the proposed manufacturing process, along with results from our investigation, which includes preliminary results that demonstrate light propagation through a simple waveguide made by our process. In general, the process consists of five basic steps. First is the preparation of standard silicate sol-gels, synthesized with doping materials to increase the refractive index. The second step consists of depositing a thin film by spin coating on silicon or quartz wafers. Subsequently, the third step includes the thermal treatment mainly to drive off solvents and reduce the porosity of the nanostructured optical film. The fourth step of the process consists of exposing the sample to a laser beam, and tracing the desired computer generated geometry by moving the sample in a 3D space with translating stages. Finally, the last step includes any post-processing thermal or chemical operations. Sol-gel processing allows the deposition of high optical-quality films through the strict control of processing parameters (concentration, pH, temperature, humidity) in combination with high-purity sol-gel precursors. Some additional advantages include the possibility of processing at low temperatures and standard atmospheric conditions, together with the ability to integrate organic and inorganic matrices that impact physicochemical factors such as shrinkage or refractive index from a chemical standpoint. Likewise, laser photophysical processing has the ability to selectively achieve high-density levels of sol-gels comparable to vapor deposition and melting. A direct relation exists between a sol-gel's density and index of refraction; hence the ability to control the index of refraction through density changes based on laser power control is an area of keen interest. Finally, a freeform fabrication approach that integrates CAD/CAM design and manufacturing concepts, offers the possibility of a fast and flexible process that helps reduce the concept-to-market time for a product.

4:15 PM LL3.7
Nanotube Reinforced Composites Processed by Extrusion Freeform Fabrication. Meisha L. Shofner[1], Ranji Vaidyanathan[2] and Enrique V. Barrera[3]; [1]Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]Advanced Ceramics Research, Tucson, Arizona; [3]Department of Mechanical Engineering and Materials Science, Rice University, Houston, Texas.

The inherent high strength, thermal conductivity, and electrical conductivity make carbon nanotubes attractive reinforcements for polymer matrix composites. However, maximum property increases in composites are obtained when the nanotubes are aligned, requiring additional processing consideration to the anisotropic structure. The combination of extrusion-based solid freeform fabrication (SFF) techniques and nanotube reinforced composites creates an opportunity for simultaneous processing and material enhancements. The multifunctional reinforcement provided by nanotubes extends the application range of the SFF process, and extrusion-based SFF is a novel technique for processing nanotube reinforced composites because it allows for the direct fabrication of parts with prescribed fiber orientation. This research demonstrates ability of extrusion freeform fabrication (EFF) to orient single wall carbon nanotubes (SWNTs) and vapor grown carbon fibers (VGCFs) in a poly(acrylonitrile-co-butadiene-co-styrene) matrix. The capability of EFF to manipulate SWNTs and VGCFs is evaluated through observing the degree of alignment and mechanical property testing. The results show that VGCFs align to a higher degree than SWNTs but that the greater mechanical property improvements are achieved with SWNT reinforcement. In addition, both the VGCF and SWNT reinforced materials processed by EFF displayed improved tensile modulus compared to similarly processed ABS and corresponding composite materials with isotropic fiber orientation. This research represents an initial step in creating multifunctional composites by evaluating the compatibility of SFF and nanotubes.

4:30 PM LL3.8
Ink-Jet Deposition of YBa2Cu3O7- via Sol-Gel Processing for Coated Conductor Technology. Tarek Mouganie[1,2] and Bartek A. Glowacki[1,2]; [1]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; [2]IRC in Superconductivity, University of Cambridge, Cambridge, United Kingdom.

Development of computer controlled deposition techniques for YBa2Cu3O7-? (YBCO) coated conductors is discussed in detail and presented. These deposition processes are for drop-on-demand ink-jet coating and the ink-jet printing allowing non-vacuum formation of multi-layer superconducting patterns on metal substrates (with and without the aid of buffer layers). The advantage of ink-jet coating includes the ability to mimic the popular dip-coating process often found in the deposition of sol-gels. This process also allows the coating to form on just one side of the substrate hence avoiding the use of cleaning steps in the reel-to-reel deposition process. Ink-jet printing is the ultimate direction in computer controlled deposition processing for YBCO conductors. Here, complex patterns may be created by the multi-layer formation of superconductors and superconducting devices thus allowing the possibility to create efficient and low ac-loss conductors. Printing and substrate parameters that alter solid-liquid interface properties were investigated and the sol-inks synthesised were aqueous and non-aqueous based therefore allowing variable chemical properties depending on what was required from the deposition process. The formation and the stability of the sol-inks has been studied and discussed, with the various synthesis steps and additives yielding the different properties required to produce the different coatings. Characterisation of the inks was by Differential Thermal Analysis and Thermal Gravitometry whilst characterisation of the coatings was by X-Ray Diffraction, Atomic Force Microscopy and Scanning Electron Microscopy. AC susceptibility and Hall-Probe analysis was used to assess the superconductivity of the printed samples. Initial results have shown that the project is successful and as a result has been chosen to be part of the COCON project.

4:45 PM LL3.9
Magnetic Properties of Amorphous Fe-Based Alloys Prepared by Mechanical Alloying. Hui He[1], Xiao-Hua Zhang[2], Rui-Jun

Wang[3] and Wei Yang[3]; [1]College of Machinery and Electronic Engineering, University of Petroleum, Dongying, Shandong, China; [2]Department of Electronic Engineering, Shandong Shengli Vocational College, Dongying, Shandong, China; [3]College of Physics Science and Technology, University of Petroleum, Dongying, Shandong, China.

The Fe-based amorphous alloy has been prepared by mechanical alloying. The Fe-based mixed powders with different milling-time of mechanical alloying have been studied by X-ray diffraction. The influences of milling conditions on the magnetic properties of Fe-based amorphous powders have been investigated by VSM. It is found the addition of C into Fe-Ni or Fe-Co accelerated the transformation of Fe-Ni or Fe-Co crystal alloy to amorphous. Fe40Ni40C20, Fe60Ni20C20, Fe40Co40C20 and Fe60Co20C20 amorphous alloys were prepared by mechanical alloying. The conditions of ball-milling were as follows: for Fe40Ni40C20 and Fe40Co40C20, the weight ratio of ball to powder was 40:1, the revolving velocity was 300r/min, it shows lower milling energy; for Fe60Ni20C20 and Fe60Co20C20, the weight ratio of ball to powder was 80:1, the revolving velocity was 300r/min, it shows that higher milling energy. The results show that the amorphization reaction is faster under the condition of higher milling energy, the Fe-Co-C mixed powders are prone to amorphous with the same time and the same ball milling energy as the Fe-Ni-C mixed powders. With the increase of the milling-time, the grain size decreases and the lattice distortion increases. At the initial stage of ball milling, their coercivity values Hc increase. During the amorphization reaction, their coercivity values Hc decrease constantly by prolonging milling-time. When Fe-based crystal alloy transformed into amorphous alloy, minimum Mr and Hc were obtained. Meanwhile, the above mentioned result has been discussed.

SESSION LL4: Processing and Fabrication of Advanced Materials

Chairs: Mohan Edirisinghe and Emanuel Sachs
Tuesday Morning, November 30, 2004
Room 305 (Hynes)

8:30 AM *LL4.1

State of the Art on the Applications of SFF Techniques to Ceramic Materials. G. N. Babini[1], A. Fedele[1] and L. Settineri[2]; [1]Instuto di Scienza e Tecnologia dei Materiali Ceramici, Consiglio Nazionale delle Richerche, Faenza, Italy; [2]Politecnico di Torino, Torino, Italy.

The overwhelming development of the Solid Freeform Fabrication (SFF) techniques from the date of their introduction on the market, more than 20 years ago, has caused their diffusion in the mechanical sector to the point that they are today an indispensable component of the process of designing, engineering and producing a mechanical parts. At the same time, these techniques found application in different and even distant sectors, like the biomedicine or architecture. This lead to the necessity of developing SFF processes suitable for materials different from those originally involved. Such techniques, taken from the original ones or entirely developed $ex-novo$, allowed for a surprising differentiation of the applications. A relatively new field is the application of SFF to ceramic materials, which are playing an increasingly important role in sectors not traditionally covered. The present paper reports a state of the art of the techniques that appear more effective for the production of goods in ceramic materials, or in ceramic composites, with representative or even functional properties.

9:00 AM LL4.2

Use of Computational Thermodynamics in Rapid Prototyping and Infiltrating Steel Parts. Brian D. Kernan[1], Emanuel M. Sachs[1], Samuel Allen[2] and Christoph Sachs[3,2]; [1]Laboratory for Manufacturing Productivity, Massachusetts Institute of Technology, Cambridge, Massachusetts; [2]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; [3]Institute of Ferrous Metallurgy, RWTH Aachen, Aachen.

The direct manufacture of metal parts by rapid prototyping often involves building a porous skeleton from a metal powder. Densification of the skeleton can be done either by sintering or infiltration. Infiltration avoids the shrinkage and distortion that typically accompanies sintering. However, in steels, the use of copper or bronze infiltrants limits the usefulness of finished parts because of the non-homogeneous structure and properties. In this work, a method termed Homogeneous Steel Infiltration has been developed for infiltrating steels to make conventional tool steel alloys. The method uses a gated infiltration route that uses as the infiltrant a steel alloy with a lower melting point than the base powder. The infiltrant liquid may use carbon and/or silicon as a melting point depressant. Premature freeze-off of the steel infiltrant is avoided by operating at a temperature where some liquid is stable at chemical equilibrium. The compositions of the skeleton and infiltrant and the infiltration temperature are selected by using computational thermodynamics. Examples of successful infiltrations using D2 and A3 tool steels as target compositions are shown. Mechanical properties (hardness and impact strength) following various heat treatments of the infiltrated D2 are compared with conventional wrought D2 tool steel and found to be very similar. The thermodynamic design method enables suitable parameters to make other tool steels, some stainless steels and manganese steels. Further, the process is applicable to the post processing of any suitable steel skeleton made by rapid prototyping, as well as traditional powder metallurgy processes such as metal injection molding and die-pressing.

9:15 AM LL4.3

Jet-Based Photonic Crystals for Terahertz Technology - A Need for Higher Resolution. Jin Li[1], Thomas Horgan[2], Andrew Gatesman[2] and William D. Goodhue[1]; [1]Photonics Center, University of Massachusetts Lowell, Lowell, Massachusetts; [2]Submillimeter-Wave Technology Laboratory, University of Massachusetts Lowell, Lowell, Massachusetts.

Two-dimensional hexagonal photonic crystals of air columns in a wax substrate were fabricated by jet-based methods. By modifying the structure of the photonic crystals, electromagnetic waves can be controlled, enabling the design of novel devices for waveguides, filters, and couplers. The jet-based processing is a solid freeforming method that can fabricate complex 2D or 3D photonic structures quickly and easily as compared to micro-machining and lithographic methods. It "prints" physical models from 3D CAD data files by spraying layers of tiny droplets of wax onto a platform surface using a solid object printer. The model is built up layer by layer until it is complete. The resolution of our ThermoJet® printer is 300 x 400 x 600 dpi (XYZ) with the layer thickness of 0.042 mm. The wax used is a thermopolymer build material, similar to production investment casting wax material. The periodicity of the lattice of our 2D photonic crystals was designed to form bandstop filters in the 0.1 – 0.3 THz range. The transmission spectra of the structures were measured with Bruker IFS 66v FT-IR interferometer. The photonic band gaps were observed at 0.18 THz (bandwidth 35 GHz) and 0.23 THz (bandwidth 50 GHz) along M-K direction for both TM and TE polarized incident beam for the PC structures with lattice constant of 0.787 mm and 0.586 mm, respectively. The location and width of the bandgaps agree with theoretical calculation based on a block-iterative frequency-domain method for Maxwell's equations in a planewave basis. To the best of our knowledge, this is the first time a jet-based process has been used successfully to fabricate photonic crystals at these high frequencies. However, the ThermoJet® printer as well as other current available solid freeforming technologies lack the resolution to produce crystals operating in the terahertz regime. To extend this technology to terahertz applications, such as terahertz lasers, waveguides and imaging system, a 10-fold increse in machine resolution is required to produce finer structures. Engineering materials with lower electromagnetic absorption and higher dielectric constants at terahertz frequencies are also critical to developing THz photonic bandgap technology.

9:30 AM LL4.4

Study on deposition resolution in localized electrochemical deposition. Seung Kwon Seol[1], Aram Pyun[1], Jin Xiao[1], Jung Ho Je[1], Yung Chin Yang[2], Yeukuang Hwu[2] and Giorgio Margaritondo[3]; [1]Materials Sciences, Pohang University of Science and Technology, Pohang City, South Korea; [2]Physics, Academia Sinica, Taipei, Taiwan; [3]Physics, EPFL, Lausanne, Switzerland.

Three dimensional (3D) high aspect ratio objects attract interest for a broad range of applications. Localized electrochemical deposition (LECD) is one of technologies for inexpensive and effective fabrication of high-aspect-ratio microstructure of diverse materials. One of the issues in LECD is deposition resolution problem which is due to undesirable wide deposition in the initial stage. This problem can lead to malfunction of integrated structures because of electric shorts between adjacent objects used in electrostatic or high-frequency applications. We observe that the width of undesirable deposition in initial stage increases with the distance between microelectrode and substrate. For instance, the width can increase up to 3 times for the distance of 25 micron. On the other hand, when the distance is small as below 10 micron, the structure becomes porous in spite of high resolution. We attribute the distance dependence of the width to the electric field effect from microelectrode to substrate.

10:15 AM LL4.5

Freeform Fabrication of Meso- and Micro-structured Devices by Direct-Write Deposition and Laser Processing of Dry Fine Powders. Pranav Kumar and Suman Das; Mechanical Engineering, University of Michigan, Ann Arbor, Michigan.

We present a multi-material rapid prototyping technique for producing 2D and layered 3D meso- and micro-structured multi-functional devices with spatially varying heterogeneous material compositions. This technique involves direct-write deposition of multiple, patterned powder materials followed by laser sintering. The direct-write deposition system features miniature hopper-nozzles for depositing dry powdered materials by gravity or by high frequency vibration-assisted flow on to a movable substrate. Deposition of 10-125 micron powder particles via 100 micron-2mm hopper-nozzles orifices has yielded a 100 micron minimum attainable feature size for device footprints ranging from sub-millimeter to a few centimeters. The feasibility of this direct-write concept was proved by patterning single and multiple materials onto substrates to demonstrate various prototype devices envisaged by this technique. These include micro-battery, interdigitated capacitor, fractal antenna, Swiss-roll microcombustor, and functionally graded polymeric bioimplants.

10:30 AM LL4.6
Advanced Thick Films by Direct-Write Technology.
Mehdi Allahverdi, Enver Koray Akdogan, Muharrem Kunduraci, Jingjing Sun and Ahmad Safari; Ceramic and Materials Engineering, Rutgers University, Piscataway, New Jersey.

We have utilized Direct-Write Technology by MicroPen^{TM} to make thick film patterns for a variety of applications. Films with thickness in the range of a few microns to several tens of microns can be written by MicroPen^{TM}. Piezoelectric (lead zirconate titanate, PZT), electrostrictive (lead magnesium niobate-lead titanate, PMN-PT), and paraelectric (barium strontium titanate, BST) films as well as optical waveguides (erbium-doped aluminosilicate) have been made on different substrates. To make PZT, PMN-PT, and BST thick film pastes, ceramic powders were first coated with suitable surfactants (such as stearic acid) and then added to a solution of "terpineol-ethyl cellulose". The mixtures were homogenized using a three-roll mill. The solid loading was in the range of 30-50 vol.%. After writing, the patterns were allowed to level, followed by drying, binder removal (600°C), and sintering at elevated temperature. For the fabrication of optical waveguides, only low temperature treatment (curing) was performed. PZT thick films were prepared for piezoelectric applications such as micro-valves and pumps among others. Due to small thickness of the films, the lead evaporation could be severe during sintering at elevated temperatures. Additives such as lithium bismuth silicate, lead oxide and borosilicate in the range of 1-3 wt% were examined to lower the sintering temperature and therefore, the lead loss. The microstructure and dielectric properties of the PZT films sintered at temperatures 1000° to 1150°C will be reviewed. Thick films of paraelectric BST (60/40) were also made by MicroPen^{TM}. The BST films are to be used as phase shifter in microwave circuits. The BST films, deposited on alumina substrates, were sintered at 1100° to 1400°C. It was found that a sintering temperature of 1300°C would result in a dense film with virtually no second phase formed at the interface with the alumina substrate. The XRD techniques were utilized to study phase analysis of the BST films and its residual stresses using $\mathrm{Sin}^2\Psi$ technique. The effects of film thickness and residual stress on dielectric/microwave properties are being investigated. In another work, optical waveguides have been made using optical polymers and nanocomposites. Nanopowders of erbium-supersaturated aluminosilicates, made by chemical vapor condensation and sol-gel techniques, were thoroughly mixed with optical polymers such as perfluorocyclobutyl and the resulting nanocomposite were deposited on glass and alumina substrates. In a similar fashion, hybrid organic/inorganic nanocomposites were also synthesized via sol-gel approach to obtain intimate mixing of the constituents. The deposition issues and optical properties (fluorescence spectra) of these waveguides and films will be presented.

10:45 AM LL4.7
Characterisation of Innovative Materials for Direct Laser Sintering. E. Bassoli[1], A. Gatto[1], Luca Iuliano[2] and E. Atzeni[2]; [1]Department of Manufacturing Systems and Economics, Poltechnic of Turin, Turin, Italy; [2]Department of Mechanical and Civil Engineering, University of Modena and Reggio Emilia, Modena, Italy.

The performances achieved by Rapid Prototyping techniques, also through the innovation in the field of materials, are progressively leading towards Rapid Manufacturing, that is the capability to produce end products, directly from the CAD model. Even so, the diffusion of these techniques is hardly supported by scientific knowledge about the micro-mechanisms ruling the macroscopic performances of the part. In the present research, dimensional and mechanical performances of new materials produced by Direct Laser Sintering technique have been studied. Tensile specimens have been produced, using a Polyamide and an innovative Polyamide-Aluminium composite (Alumide). The specimens have been realised following the specifications of standard ASTM E8, with different orientations in regard to powder deposition plane and laser path. Thus, it was possible to investigate how the manufacturing anisotropy, both in terms of additive construction and laser sintering strategy, affects the part performances. Rupture surfaces of the tensile specimens were observed at the SEM, in order to understand failure mechanisms, whereas the observation of polished sections helped investigating joining phenomena between the particles.

SESSION LL5: Electrohydrodynamic Atomization and its Applications
Chairs: Michael Brenner and Juan F. De la Mora
Tuesday Afternoon, November 30, 2004
Room 305 (Hynes)

1:30 PM *LL5.1
Electrosprays of Ionic Liquids in Vacuo.
Juan Fernandez de la Mora, Mechanical Engineering Department, Yale University, New Haven, Connecticut.

In the cone-jet mode, electrified Taylor cones form a steady jet at the tip of a conical meniscus, which may break up into drops [1], or remain in filament form [2]. Increase in liquid conductivity K or reduction of its flow rate (within a finite range of stability) yields decreasing jet diameters, down to about 10 nm (K $\sim$ 1 S/m). At K > 1 S/m, the increasing electric fields arising on the meniscus lead to ion evaporation from its surface, a phenomenon well studied for concentrated solutions of NaI in glycerol held in a vacuum [3] (electrical discharge would arise in a gas). The identification of relatively involatile and inviscid solvents such as formamide first enabled the study of single Taylor cones ejecting most of their current ($\sim$90%) in the form of ions [4]. Vacuum electrosprays of room temperature molten salts (ionic liquids) have proven to be good sources of nanodrops and ions, as well as ions alone [5]! The materials science potential of this phenomenon is best understood in relation to the better known field of liquid metal ion sources (LMIS) [6], where Taylor cones of liquid metals form ion beams at several microAmpere, and with narrowly defined energies, which can as a result be focused on submicrometer spots for direct writing or etching. The main advantages (presently purely hypothetical) of ion beams from electrosprays of ionic liquids are: (i) wide range of ionic chemical compositions for chemically-assisted etching; (ii) ion masses up to at least 1000 amu [7]; (iii) both positive and negative ion beams may be formed. This potential hinges partly on how sharply these beams can be focused, governed by the width of the ion energy distribution and its initial angular spread. Studies on such properties indicate high beam quality [8], but this and other basic features of these electrosprays remain relatively unknown. The presentation will review what is known on the subject, including which ionic liquids are most promising and why. References [1] Cloupeau M, Prunet-Foch B., J. Electrostatics, **22**, 135-159, 1989 [2] Larsen G, Velarde-Ortiz R, Minchow K, Barrero A, Loscertales IG, J. Am. Chem. Soc. **125**, 1154, 2003 [3] K. D. Cook, Mass Spectrometry Reviews, **5**, 467-519, 1986. [4] Gamero-Castaño, M. & J. Fernández de la Mora, J. Chem. Phys., **113**, 815-832, 2000. [5] I. Romero, R. Bocanegra, J. Fernández de la Mora and M. Gamero-Castaño, J. Appl. Phys., **94**, 3599, 3605, 2003. [6] P. D. Prewett and G. L. R. Mair, *FocusedionbeamsfromLMIS* (Wiley, New York; 1991). [7] I. Romero-Sanz, I. Aguirre-de-Carcer and J. Fernández de la Mora, Ionic propulsion based on heated Taylor cones of ionic liquids, paper presented at the 39th AIAA/ASME/SAE/ASEE Joint Propulsion Conference, Huntsville, Alabama. Under review in J. Prop. & Power, 2004 [8] I. Romero-Sanz and J. Fernández de la Mora, J. Applied Phys., 95 (4): 2123-2129, 2004

2:00 PM LL5.2
Electrohydrodynamic Atomization: A Novel Method for the Synthesis, Processing and Forming of Advanced Materials.
Suwan Jayasinghe and M. J. Edirsinghe; Materials Department, University of London, London, United Kingdom.

The development of novel methods for the synthesis, processing and forming of advanced materials is a key aspect in the utilisation of these materials for human benefit and wealth generation. In this paper we show how research into electrohydrodynamic atomization has heralded procedures for: (a) the synthesis of nano- and micro-powders of advanced functional and structural materials such as PZT and SiC (b) the processing of a variety of different biological materials of polymeric and ceramic origin (c) the forming of porous structures including graded ceramic foams and ceramic micro-channels (d) solid freeforming of structural features

2:15 PM *LL5.3
3-D Ceramic Parts Fabricated by Laser Assisted-ESAVD Method. Kwang-Leong Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, University Park, United Kingdom.

A novel hybrid technique has been developed to fabricate three-dimensional ceramics based on selective laser deposition and electrostatic spray-assisted vapour deposition methods. This hybrid technique involves electrospraying of liquid precursor onto a substrate heated by a focused laser beam. The laser beam is also used to induce the decomposition and chemical reaction of precursor to produce a solid object. Dense or porous ceramic can be deposited $in-situ$ on the substrate by optimizing the processing parameters (e.g. laser energy density, field strength, precursor flow rate, concentration of precursors etc). A desired three-dimensional ceramic object can be formed layer-by-layer onto a computer-controlled object forming table. This paper reports the 3D fabrication of ceramic parts using sol precursor solutions. Scanning electron microscope (SEM) and X-ray diffraction (XRD) have been used to characterize the phase and structure of the deposited ceramic parts. The fundamental aspects of this novel solid freeform fabrication method, including process principle and deposition mechanism will be presented. The processing/ microstructure /property relationships of the fabricated parts will be discussed. The results have demonstrated that the novel hybrid technique is potentially a simple, versatile and cost-effective method to fabricate three-dimensional ceramic objects with well controlled dimension, structure and composition.

3:15 PM *LL5.4
The Physical Mechanisms of Electrospinning. Michael Brenner, Division of Engineering and Applied Science, Harvard University, Cambridge, Massachusetts.

Electrospinning is a process in which a millimeter sized polymeric jet of liquid is transformed into a fabric made of 100nm fibers, through the interaction of an external electric field with the jet. I will describe our recent work aimed at identifying the physical mechanisms of this process, in particular focusing on (a) what controls the parameter regime of electrospinning, and (b) which parameters and physical processes control the diameter of the jet. Theory and experiment will be presented and compared.

3:45 PM LL5.5
Controlled Deposition of Nanostructured Materials using Electrostatic Aerosol Assisted Jet Deposition.
Kwang-Leong Choy, School of Mechanical, Materials, Manufacturing Engineering and Management, University of Nottingham, University Park, United Kingdom.

This contribution gives an overview of an emerging and cost-effective deposition process based on Electrostatic Aerosol Assisted Jet Deposition (EAAJD) method for the fabrication of nanostructured materials with well controlled structure and composition. EAAJD is a variant of the Electrostatic Spray Assisted Vapour Deposition process. EAAJD involves the generation of aerosol precursor, and the aerosol is subsequently charged. The charged aerosol is directed towards a heated substrate. Nanocrystalline dense films can be deposited by tailoring heterogeneous chemical reactions in the gas phase. A combination of heterogeneous and homogeneous chemical reactions will result in the deposition of porous films with well controlled nanopore size and particle size. Nanosized powders could be deposited by tailoring the homogeneous gas phase reaction. EAAJD is a versatile process. It can produce a wide range of simple, doped and multicomponent oxides, as well as sulphide and selenide materials for various structural and functional applications. This paper will describe the control deposition of nanostructured materials using the EAAJD method. The deposition mechanism and relationship of the process/structure/property will be presented. The scientific and technological significant of the ESAVD methods will be discussed and compared with other vapour processing techniques such as ESAVD, Chemical Vapour Deposition and Physical Vapour Deposition.

4:00 PM LL5.6
Controlled Electrospray for Tissue Engineering Applications.
J. Stark, M. Paine, K. Smith and M. Alexander; Department of Engineering, Queen Mary, University of London, London, United Kingdom.

The development and status of a novel electrospray system, capable of a variety of applications, including the fabrication of tissue engineered structures is described. The system requirements dictate the following key components: a micro-fabricated silicon electrospray emitter, a mass spectrometer capable of selecting molecules having a charge to mass ratio up to 32,000 with a resolution of 10,000, and an integrated ion optics system permitting depositing the selected molecules 'softly' onto a target with a spatial resolution of 0.1μm. One critical feature of the system is the overall efficiency of transferring biomolecules from a buffer solution, typically comprising water, acetonitrile and ammonium acetate, into an ion flux. Commercial ES/MS systems are generally designed with simplicity of operation as a design driver, together with the low probability of transmitting spray droplets directly into the quadrupole mass selection system. This has focused attention onto the detailed design and characterization of the electrospray emitter and the environment into which the spray is launched. This has highlighted the need to evaluate in detail, an electrospray operating into a low pressure environment and to improve our understanding of the interaction between voltage and flow rate in the transition from nano-electrospray mode, wherein no positive pressure is applied to the fluid and normal electrospray mode, close to minimum flow rate. Early results of this investigation will be presented. There is evidence that at reduced ambient pressure there is a small reduction in spray current, however this is offset by improved transmission of the beam into the first quadrupole stage. Other results we have obtained further demonstrate that at low positive pressure fed flow rates, nominally operating at some prescribed flow rate, that variation of the voltage applied can have a significant influence on the actual flow rate achieved. This then has a consequential effect on the spray itself.

4:15 PM LL5.7
Co-axial Electrohydrodynamic Atomization of Ceramic Suspensions. K. Balasubramanian, S. N. Jayasinghe and M. J. Edirisinghe; Department of Materials, University of London-Queen Mary, London, United Kingdom.

In this paper we use a co-axial nozzle set-up to subject different types of ceramic suspensions to electrohydrodynamic atomization. The ensuing sprays have been deposited and thus we show that different types of composite ceramic microstructures can be prepared using this method. Examples of several zirconia-alumina microstructures prepared using this method are characterised using advanced analytical techniques.

4:30 PM LL5.8
Electrostatic Atomization Printing. D. Wang, S. N. Jayasinghe and M. J. Edirisinghe; Department of Materials, University of London-Queen Mary, London, United Kingdom.

In this paper we elucidate how a concentrated particulate suspension is subjected to electrohydrodynamic atomization and the resulting droplets are deposited according to a pre-determined architecture using a point-like ground electrode. We show that by optimising the applied voltage, flow rate and nozzle-ground electrode and substrate-ground electrode distances tracks of about $<10\mu$m in width can be printed with remarkable accuracy.

4:45 PM LL5.9
Production of complex nano-structures by electro-hydro-dynamics. Ignacio Gonzalez Loscertales, Dep. Ingenieria Mecanica y Mecanica de Fluidos, Universidad de Malaga, Malaga, Spain.

Abstract Not Available.