SYMPOSIUM W
Mechanically Active Materials

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* Invited paper
Symmetry breaking at the Curie temperature results in multiple spontaneously electrically polarized and mechanically distorted states in a ferroelectric perovskite. These states coexist in characteristic domain patterns which switch from one state to another depending on the applied electrical and mechanical boundary conditions. Interestingly, domain switching can form the basis of interesting nonlinear properties. This talk will describe an effort that explicitly exploits domain switching in ferroelectric perovskites to create materials capable of large electrostriction against significant forces. This work is motivated by the technological need to develop high energy density microactuators. We will describe the theoretical background and the experimental validation in bulk materials. We will then describe how this approach can be adapted to thin films in geometries that can be obtained by standard micromachining tools, issues related to materials integration and the experimental validation.

The role of oxygen vacancy in dielectric breakdown and fatigue has been a topic of intense research in ferroelectric perovskites like BaTiO$_3$. This paper presents a comprehensive model that treats the ferroelectrics as polarizable wide gap semiconductors where the oxygen vacancies act as dopants. First, a fully coupled and nonlinear model is developed with space charges, polarization, electric potential and elastic displacements as variables without making any prior assumptions on the space charge distribution and the polarization profile. Both analytical and numerical results show that polarization profiles and space charge distributions change dramatically when the film thickness and doping level are varied. Particularly, an donor-doped Pt/BaTiO$_3$/Pt structure is considered in this paper in view of the fact oxygen vacancies are acting as donors in ferroelectric perovskite. A 2-D FEM simulation show the interactions of oxygen vacancies with 180 and 90 degree domain walls. Numerical results show that 90 degree domain wall may play a significant role in the fatigue process. Finally the forced diffusion of oxygen vacancies under local electric fields due to nonuniform polarization and space charge generation is considered. The switching process and fatigue are then studied by examining the stability of the system. The probability of fatigue as intrinsic property of the system under different circumstances (film thickness, doping level, defects level etc.) are investigated. Comparison with experimental results and implications for device design are discussed. 

Recent advances in the geometric nonlinear theory of martensites have explained the cause of large thermal/stress hysteresis commonly exhibited by known shape memory alloys (SMAs) and prescribed a set of conditions that an ideal SMA must satisfy. An ideal SMA is defined as having a hysteresis width approaching zero. These conditions are a set of constraints on the lattice parameters that might be satisfied by fine-tuning the compositions of the materials. The combinatorial thin film synthesis technique can be used to prepare hundreds of samples with different compositions within a short period of time, and thus, it is the ideal method to search for the composition of the ideal SMA. Here, we report on preliminary results of our search using the combinatorial technique. The work involves synchrotron x-ray analysis on hundreds of free-standing thin film specimens prepared by combinatorial thin film synthesis. We have demonstrated that x-ray analysis can be used to precisely determine the lattice constants of predominantly textured SMA thin films. Systematic change in the lattice parameters are traced on ternary composition spread samples fabricated in a combinatorial co-sputtering system.

**9:45 AM W1.5**

**Superelastic Thin Film TiNi-Polymer-Composites.**

Eckhard Quandt$^1$, Holger Rumpf$^2$, Christiane Zamponi$^3$, Christoph Bourru$^4$ and Dieter Drechsel$^5$

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Superelastic shape memory materials are of special interest in medical applications due to the large obtainable strains, the constant stress level and their biocompatibility. Superelastic TiNi-polymer-composites have the potential to be used for novel applications in orthodontics and medical instrumentation as well as in certain areas of mechanical engineering. Especially, using TiNi thin films these composites have the potential to substantially reduce those forces compared to conventional TiNi wires and tubes. In orthodontic applications lowering the forces during arch wire treatment is of significant importance due to tooth root resorption, which can be caused by the application of oversized forces during arch wire treatment [1]. Furthermore, the use of superelastic materials or composites enables the application of constant forces independent of diminutive tooth movements during the therapy due to the superelastic plateau. Superelastic TiNi thin films have been fabricated by magnetron sputtering using extremely pure cast melted targets [2]. Special heat treatment were performed for the adjustment of the superelastic properties and the transformation temperatures. A superelastic strain of up to 4.5% at 37°C was obtained. In this paper the fabrication of superelastic thin film TiNi-polymer-composites is presented and their characteristics are compared to wires and tubes in view of orthodontic applications. [1] D. Drechsel et al. (2003). [2] E. Quandt, C. Zamponi, H. Rumpf, B. Wehner, J. Frenzel, E. Quandt, Mat. Sci. and Eng. Techn. 2004; 35 No.5, 355-364.
crystal thin films with excellent control of crystallographic and domain microstructure relative to other thin film fabrication methods. Details of the procedure are shared in these proceedings. In this study, Ni at.% 50.5 and Ni at.% 50.9 were tested with various mechanical properties. The results confirm that NiTi thin films are an appropriate medium for thermomechanical data storage. This study examines the effect of repeated thermomechanical cycling of indentations as well as the effect of the primary martensitic transformation. Models were developed with a high degree of complexity and precision to simulate the behavior of the cast NiTi material. The results confirm that Ti3Ni4 precipitates can be used to elicit a desired transformation behavior during indentation with traditional stress-strain properties. Although, such a link was difficult to establish. However, using Atomic Force Microscopy to characterize NiTi precipitates, it is shown that the resistance to dislocation motion and the ease of the martensite transformation cannot be simultaneously maximized, although an optimal combination should exist.

The objective of this study is to examine the effect of heat treatment on polycrystalline Ti 50.9 at.% Ni in hot-rolled and cold-drawn states. In particular, we examine microstructure, transformation temperatures, as well as, mechanical behavior in terms of both uniaxial monotonic testing and instrumented Vickers micro-indentation. The results constitute a comprehensive understanding of the effect of heat treatment on thermal stress induced martensite and resistance to plastic flow in NiTi, all of which are critical for optimizing the mechanical properties. The high temperature of the hot-rolling process causes recrystallization, recovery and hindered precipitate formation, essentially problematizing the NiTi. The subsequent cold-drawing induced a high density of dislocations and martensite. Heat treatments were carried out on hot-rolled, as well as, hot-rolled then cold-drawn materials at various temperatures for a duration of 1.5 hours, inducing Ti3Ni4 precipitates. Based on transmission electron microscopy (TEM) observations, these precipitates progressively increased in size from coherent to incoherent, as a function of increased heat treatment temperature. Texture and coherency were observed to systematically shift the transformation temperatures, bringing out the R-phase and multiple-stage transformations. Room temperature stress-strain tests illustrated a variety of mechanical responses for the various heat treatments from pseudoelastic to shape memory, which were related to the shift in the primary martensite transformation temperatures, rather than the nature of the precipitate formation. The results confirm that Ti3Ni4 precipitates can be used to elicit a desired transformation behavior in polycrystalline NiTi. In addition, instrumented micro-indentation tests were performed, and no significant correlation of the Vickers force-displacement behavior during indentation with traditional stress-strain properties, although, such a link was difficult to establish. However, using Atomic Force Microscopy (AFM) to measure indentation depth before and after heating more distinctly confirmed shape memory behavior as observed in pseudoelastic behavior. The Martens (Universal) Hardness revealed that Ti3Ni4 precipitates were more effective at blocking plastic flow than coherent or even larger coherent precipitates. Although, previous dislocation density in NiTi was shown to be more influential than Ti3Ni4 precipitates at inhibiting plasticity and hence increasing hardness. Based on comparison of hardness and the stress required to induce martensite, it is shown that the resistance to dislocation motion and the ease of the martensite transformation cannot be simultaneously maximized, although an optimal combination should exist.

The dependence of a solid's elastic properties on temperature in the vicinity of a structural transformation provides insight into the nature of the transition. Therefore, the temperature dependences of the elastic constants of both martensitic and austenitic Ni50.5Mn28.4Ga21.4, Mn53.8K, and Ni50Mn28.4Ga21.4 were studied in the wide range of 50K-333K. The results confirm that Ti3Ni4 precipitates can be used to elicit a desired transformation behavior during indentation with traditional stress-strain properties, although, such a link was difficult to establish. However, using Atomic Force Microscopy (AFM) to measure indentation depth before and after heating more distinctly confirmed shape memory behavior as observed in pseudoelastic behavior. The Martens (Universal) Hardness revealed that Ti3Ni4 precipitates were more effective at blocking plastic flow than coherent or even larger coherent precipitates. Although, previous dislocation density in NiTi was shown to be more influential than Ti3Ni4 precipitates at inhibiting plasticity and hence increasing hardness. Based on comparison of hardness and the stress required to induce martensite, it is shown that the resistance to dislocation motion and the ease of the martensite transformation cannot be simultaneously maximized, although an optimal combination should exist.
Ni-Mn-Ga magnetic shape memory alloys appeared on the scene of active materials in 1996 with a 0.2% field-induced strain and 6% field-induced strain at room temperature. Since then, the advantages and challenges of this material have been discovered. It remains a promising candidate for many high-strain, moderate stiffness applications, an area not well served by piezoelectric and magnetostrictive materials. Current and pulse-field induced strain show 6% field induced strain with bandwidths up to 2 kHz. More recently, promising results have been realized with Ni-Mn-Ga used in combination with other piezoelectric stack actuators or as fillers in polymer composites. The 4% to 5% field induced strain to fully actuate Ni-Mn-Ga crystals can be significantly reduced by application of a modest acoustic signal (50 V, 1 kHz). Ni-Mn-Ga particles aligned into chains in a polymer matrix show superior vibration energy absorption compared to visco-elastic materials or Terfenol-filled polymers. The data will be interpreted in terms of phenomenological and microscopic models of field-induced and stress induced twin-boundary motion.

2:00 PM W2.2 Magnetostriction of Stress-Induced Martensite. Jun Cui1, Tom Shield2 and Manfred Wittig1, 2
1 Materials Science & Engineering, University of Minnesota, Minneapolis, Minnesota
2 Aerospace Engineering and Mechanics, University of Minnesota, Minneapolis, Minnesota

The magnetostriction of stress induced Fe7Pd3 martensite has been investigated. The strain reaches a value 1980 ppm if this martensite is induced by a compressive stress of -12 MPa in the temperature interval Ms<Ms<10°C. It is proposed that the effect is associated with the adaptive phase and that the interplay of stress and magnetic fields results in non-monotonous magnetostrictive behavior in the temperature range where it and the tetragonal phases can be stabilized.

2:15 PM W2.3 Temperature Dependence of Magneto-Mechanical Response in Ni-Mn-Ga Magnetic Shape Memory Alloys. Leon Cheng, Garrett Landry, Shannon Farrell and Calvin Hyatt, Emerging Materials Section, Defence R&D Canada - Atlantic, Dartmouth, Nova Scotia, Canada

Ferromagnetic shape memory alloys have received much attention since a large reversible, magnetic-field-induced strain was observed in Ni-Mn-Ga alloys in 1996. So far, up to 10% reversible magnetic field induced strains have been observed in Ni-Mn-Ga alloys with an orthorhombic lattice. Unlike the martensitic shape memory effect in which the reversible strain is related to the diffusionless structural phase transition from a high-temperature high-symmetry phase to a low-temperature low-symmetry martensitic phase; it is generally accepted that the magnetic shape memory (MSM) effect is due to the rearrangement of twin variants in the martensite by an applied magnetic field leading to an overall change of shape. The main thermodynamic driving force for twin boundary motion in the presence of a magnetic field is the high magnetoelastic anisotropy of the low-symmetry martensitic phase. High twin boundary mobility, low twin boundary energy and high magnetoelastic anisotropy energy are the key factors for large magnetic field induced strain. In this work, a systematic investigation is being carried out on single crystals of varying composition near the stoichiometric Ni2MnGa Heusler alloy to determine the effect of temperature on the magneto-mechanical behaviour of the Ni-Mn-Ga alloys. Repeated mechanical and magnetic forces have been applied to Ni-Mn-Ga samples at various temperatures below the martensite finish temperature. Twin boundary motions and evolution of martensite variant structure during mechanical and magnetic loading were observed by means of an optical microscope capable of applying longitudinal stress and transverse magnetic field simultaneously. In addition, influence of additional alloying elements (such as Fe) on the magneto-mechanical response of Ni-Mn-Ga alloys are also being investigated.

2:30 PM W2.4 Ferromagnetic Resonance Enhancement of Magnetostrictive Coupling in Magnetostrictive Materials. J. R. Petrie1, N. C. Woo2,3, J. A. Lieberman1 and R. B. van Dover1
1 Materials Science and Engineering, Cornell University, Ithaca, New York
2 Chemistry and Chemical Biology, Cornell University, Ithaca, New York
3 Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota

Magnetostriiction is an induced strain in ferromagnetic materials caused by the reorientation of their spins due to an applied field. An AC magnetic field results in an oscillating magnetostrictive strain. We have studied the feasibility of enhancing the magnetostatic coupling by applying an AC field at the ferromagnetic resonance (FMR) frequency. The magnons produced at this frequency should transfer their energy to phonons at the same frequency, thus increasing the amplitude of the strain oscillations. To explore this effect, we examined a YIG platelet with low magnetic anisotropy using a custom-built single-turn permeameter. The dissipative component of the UHF permeability (p*) was found to exhibit distinct peaks when the FMR frequency corresponds to an integral number of acoustic wavelengths in the sample, consistent with acoustic resonance (AR). We are currently studying the coincident AR/FMR effect in a variety of metallic and rare-earth materials, such as Ni and (Tb,Dy)Fe thin films. This effect could be particularly useful for improving insertion loss in magnetically-transduced SAW (MTSAW) devices, which employ magnetostriuctive transducers to generate surface acoustic waves of arbitrary frequency. These devices have been proposed for a number of applications, notably including 'electronic nose' sensor technology on silicon integrated circuits.


Giant magnetostrictive thin films deposited on nonmagnetic substrates can constitute effective sensors and actuators for microdevices. In this work, we investigated the effects of a stress-induced anisotropy on the magnetoelastic properties of Mn-based multilayers deposited on Si substrates. The magnetostrictive thin films were fabricated by means of RF sputtering and were subjected to a post-deposition annealing treatment. The uniaxial magnetocrystalline anisotropy induced by annealing the substrate before deposition and then allowing it to resume its original flat shape after depositing the film. Different levels of tensile and compressive stresses induced by this method were considered. The heat treatment was performed either in a furnace in which there was forming gas flowing through at a rate of 1 ml/min or in a vacuum system whose pressure is maintained at 10⁻⁶ Torr. The magnetic properties of the specimens fabricated were measured using a SQUID. SEM and XRD analyses were performed to ensure that the thermal treatment would relax the internal stresses induced during...
the deposition process without crystallizing the film. The thickness of the single layer thin films studied was between 400 and 1000 nm. Typical multilayered systems consisted of 40-200 layers, whose thickness ranged from about 10 to 50 nm. Typical multilayer sample results exhibited saturation magnetization of about 0.24T with coercive field of 100 Gauss. Three main factors which influence the properties of the deposited films were thickness, time and intensity of external stress applied and post-deposition annealing. The sputtering and heat treatment parameters were optimized aiming at improving the low field magnetostriiction and the magnetoresistive susceptibility of the films.

4:15 PM W2.8

Magnetic Properties of Submicron Ni-Mn-Ga Martensitic Thin Films. Manfred Kohl1, Volodymyr A. Chernenko2,3,4, Makoto Ohtsuka5, Heike Reuter6 and Toshiyuki Tabata6, 1IMT, Forschungszentrum Karlsruhe, Karlsruhe, Germany; 2Institute of Magnetism, University of Kiev, Kiev, Ukraine; 3IMRAM, Tokue University, Sodegaura, Japan; 4IMF III, Forschungszentrum Karlsruhe, Karlsruhe, Germany; 5IFS, Tokue University, Sendai, Japan.

Ferroelastic properties in the middle of the spread. In order to create tunable multiferroic properties and the magnetoelectric composition spread technique. We have used the layout of the spread distribution of the in-plane components of the magnetic moments and the out-of-plane components. The deposition was performed at 200 W on alumina ceramic substrates using targets of Ni43:5Mn28:6Ga25:5 for thin films A and Ni52:3Mn24:Ga24:2 for thin films B. All films were vacuum annealed at 1073 K for 20 h. The temperature dependence of the electrical resistivity in all films is typical for the ferromagnetic Heusler alloys transforming martensitically. X-ray diffraction patterns reveal a 10M and 14M crystal structure for films A and B, respectively. The magnetic properties of the thin films have been characterized by the in-plane and out-of-plane field dependences of magnetization, M(H), at 300 K and the temperature dependences of saturation magnetization, Ms(T), upon heating in the temperature range 250-400 K at the field H=5000 Oe, using a SQUID magnetometer. In thin films A, the ferromagnetic transition at the Curie temperature, TC, occurs in the austenitic state while in thin films B, TC occurs in the martensitic state. We find that the magnetic properties of the thin films exhibit a considerable thickness variation in the submicron range, which is not present in the range of 1-5 m. For thin films of type A, TC increases as a function of thickness by about 18 K, while it decreases non-monotonously by about 20K for thin films of type B. Up to the maximum field of 5 Tesla, no saturation is observed. Therefore, it can be assumed that the magnetic moments are inclined to the film plane at certain angles. This conclusion is supported by magnetic force microscopy measurements showing a pronounced magnetic contrast, which is stronger in the presence of a perpendicular magnetic field. The magnetic susceptibility at high fields shows a sharp nonlinear decrease with increasing thickness, similar to the susceptibility at low fields. The opposite dependence is observed for the critical magnetic fields, which indicate the starting points of perfect linear behavior of the M(H) curves at high fields, reflecting the change of magnetic anisotropy of the thin films. Magnetic results can be interpreted by assuming a more uniform distribution of the in-plane components of the magnetic moments and a less uniform distribution of their out-of-plane components showing larger inclination angles in the thinner films.

The magnetoelectric effect can be achieved in composite systems as a product property arising from the elastic coupling of piezomagnetic and piezoelectric components. In order to systematically explore the multiferroic properties and the magnetoelectric effect in thin film structures, we have fabricated nanocomposite structures using a composition spread technique. We have used the layout of the spread where two end compositions are pure PbTiO3 (PTO) and CoFe2O4 (CFO) and they are intermixed on the single phase. The deposited heterostructure results in a rich variety of nanocomposite configurations. They include single layer structures as well as layered structures where one of the components is formed as nanopillars or nanoplatelets. X-ray microdiffraction is used to map the structural change of the components. We have found that the transformer behavior of the PTO component in the composite can be continuously tuned all the way from 500 °C down to below the room temperature. We have observed the magnetoelectric effect using the microwave microscopy at 1 GHz in a range of composition on the spread. 100 Oe ac magnetic field was used, and the change in the dielectric properties of the nanocomposite is detected. This work was performed in collaboration with M. Murakami, K.-S. Chang, C. Guo, C.-L. Lin, L. A. Bendersky, M. A. Aronov, S. E. Lofland, and M. Wuttig.

The piezoelectric performance of relaxor single crystals provides excellent opportunities for improvements in medical ultrasonic imaging, sonar applications, active damping, and high strain actuation, if the costs can be reduced. PMN(PZN)-PT single crystals exhibit unique electromechanical properties when poled along the non-polar c100 direction. This is related to the fact that single crystal domains easily oriente during poling so that the maximum response is obtained. A longitudinal coupling coefficient k33 of 90% and an exceptional piezoelectric coefficient dB3 > 2000 pC/N can be obtained (1-2). The key to the improved properties observed in single crystals is the ease with which the crystal and poling directions can be aligned. While expensive crystal growth techniques are advancing, it is of great practical importance to develop an alternative low-cost production method based on strongly oriented or textured ceramics. We present the thermal expansion and Raman spectroscopy study of Pb(Mg1/3Nb2/3)O3-PbTiO3 solid solution (PMN-(1-x)-PT) ceramics prepared by homo-epitaxial templated grain growth (HTGG) using cubic PMN-PT single crystal seeds as templates and nanocomposites as ceramic matrix. Relationships between Raman parameters such as peak intensity and peak position with composition are proposed. The piezoelectric property is observed to be a function of composition, while the Curie temperature remains constant. The high quality of the textured ceramics is revealed by the high quality Raman bands and the high quality Raman peaks. The high quality of the textured ceramics is revealed by the high quality Raman bands and the high quality Raman peaks.
be a mechanical displacement that can be used to accomplish mechanical work. Despite several benefits (low operating voltages, conducting nature, high temperature performance, and unusual electro-mechanical coupling), some open questions concerning the actuation principle/mechanism remain. They stretch if they are electrically charged and stretching is due to the elongation of C–C bond (i.e., the original displacement mode) if bonding states are depopulated or if anti-bonding states are populated. This study addresses these issues and aims to comprehend the various contributing factors by investigating the charge transfer dynamics on the surface of single-wall carbon nanotubes using in situ resonance Raman spectroscopy (RRS) and to determine the associated parameters. The contributions by investigating the charge transfer dynamics on the surface of single-wall carbon nanotubes using in situ resonance Raman spectroscopy will be discussed briefly which help to demonstrate well-developed capacitive behavior of single-wall carbon nanotubes sheet and to estimate the gravimetric/specific capacitances as well. [1] S. Gupta, M. Hughes, A. H. Windle, and J. Robertson, J. Appl. Phys. 95, 2038 (2004) and references therein.

W3.3 Crystallization and Phase Transformations in Amorphous NiTi Thin Films on Micromachined Membranes. Hai Ni,
Hoo-Keung Lee and Alimaa G. Ramirez; Mechanical Engineering, Yale University, New Haven, Connecticut.

Amorphous sputtered nickel-titanium thin films were deposited onto micromachined silicon-nitride membranes and subjected to heating and cooling conditions. Their associated microstructure was monitored directly and simultaneously with a situ transmission electron microscopy. These electron-transparent micromachined membranes constrained the NiTi films and rendered it possible for observation of the martensitic transformation cycle, which results in the crystallization of the amorphous phase to austenite phase (cubic B2 structure) with heating; and the conversion of austenite (B2) to martensite (monoclinic B19') structure with cooling. Electron micrographs show the nucleation and growth of grains occurs at temperature of 470°C and at a rate that indicates a polynucleated transformation. The onset of martensitic transformation occurs between 25 and 35°C. Calorimetric measurements are consistent with the observed crystallization. Actuation properties were also measured by wafer curvature methods.

W3.4 Enhanced Strain and Force in Electrochemical Deformation of Conducting Polymers, Polyaniion and Polypyrrolole

Kenchir Kaneto, Life Science and Systems Engineering, Kyushu Institute of Technology, Kitakyushu, Japan.

Strain and force of conducting polymers generated by electrochemical oxidation and reduction have been increased greatly, since the beginning of the research started approximately 15 years. The largest strain has been obtained from polyaniyon film deposited electrolyslyically in methyl benzoate solution of tetra-n-butylammonium bis(trifluoromethanesufonyl)imide. The strain is closing to that of natural muscle. The force has been found to be 6.7 MPa, being 6 times larger than that of the natural muscle. The strain in polyaniyon film has been found to exhibit more than 7% at pH2 in concentrated NaCl solution.

W3.5 Advanced Experimental Approach for Probing Superalensility in Ni-Mn-Ga Shape Memory Ferrromagnets. Uwe Gaitzsch1, Stefani Roth1, Norbert Mattern2, Bernd F. Rellinghaus1 and Ludwig Schultz2; 1Institute for Metallic Materials, IFW Dresden, Dresden, Germany. 2Institute of Solid State Analysis and Structural Research, IFW Dresden, Dresden, Germany.

Intermetallic compounds in a wide concentration range around the Ni-MnGa composition are known to exhibit a large magnetic field induced strain (MFIS), the size of which is owed to field driven movement of twin boundaries in the ferromagnetic tetragonal (martensite) low temperature phase of these Heusler alloys. Samples of Ni(100-x-y)Mn(x)Ga(y) with (x,y) = (26,20) and (x,y) = (20,20) were prepared by arc melting the pure elements in Argon. The martensitic start temperatures, M_S, and Curie temperatures, T_C, of the samples were measured by means of differential scanning calorimetry (DSC) and Faraday magnetometry, respectively. Annealing at and below the B2 - L2 ordering temperature (T_0 \approx 750°C) followed by water quenching was found to affect the structure of the low temperature martensite phase. XRD investigations revealed the expected martensite structure to be tetragonal with some monoclinic distortion of the unit cell for the sample with (x,y) = (30,20), thereby indicating the seven-layered type of martensite (7M). Compression tests at pressures of up to 50 MPa resulted in permanent deformations of the samples. Thermal annealing at temperatures of about 20 K above the martensitic transformation temperature, M_S, and below the thermodynamic L2 ordering temperature, T_0, allowed to fully recover the original shape of the sample, thereby providing evidence for the occurrence of the shape memory effect (SME) in these alloys. The application of the magnetic fields of up to 2 T did not result in any permanent shape change of the deformed sample. From measurements of the magnetic anisotropy field by means of singular point detection (SPD) technique the magnetic anisotropy constant was determined to be roughly 1.5×10^5 J/m^3 for samples which were annealed at 800°C for 6 hours and subsequently cooled to room temperature at a rate of 2 K/min. Magneto-mechanical tests with and without a magnetic field
applied perpendicular to the force direction revealed a significant influence of the field on the stress-strain-curves.


Biosensors for detecting and quantifying the presence of a small amount of biological threat agents in a real-time manner are urgently needed due to the wide range of applications. In this paper, a novel type of micro-biosensor platform - magnetostrictive microcantilever (MMC) - is reported. Compare to the silicon and piezoelectric-based microcantilevers, the MMC has following advantages: 1) remote/electrical measurement and sensing. 2) easy fabrication. The resonance behavior and the sensitivity of MMC as sensor platform are characterized and compared to the theoretical calculation. It is found that the sensitivity of MMC is about 50% higher than that of piezoelectric-based microcantilevers. More importantly, it is found experimentally that the quality merit factor (Q value) of MMC can reach more 250, which is much higher than other cantilevers. Therefore, the development of MMC-based biosensors will significantly advance the capability to identify the biological threatening agents. The detection of yeast cells and Salmonella typhimurium cells using the biosensor made of MMC was carried out. The specifications of the biosensor is reported and compared to other biosensors.

W3.10 Abstract Withdrawn

W3.11 Classical Contractile Mechanism of Muscle Cell versus Contraction as a Phase Transition. Vaclav Bouda1, Lea Boudova2 and Denisa Haluzikova1; 1Mechanics and Material Science, Czech Technical University, Prague, Czech Republic. 2Institute of Sports Medicine, Charles University, Prague, Czech Republic.

Despite numerous modification, biological skeletal muscle has maintained a uniform construction. Skeletal muscle are built of micron-sized contractile units called sarcomere, which contain two main filaments: thin, and thick. Swinging of the myosine heads drives the thin filaments toward the centre of the sarcomere in this classical mechanism, thereby shortening the sarcomere and the muscle. Myosine heads convert the higher energy of ATP (adenosin triphosphate) to mechanical energy. The ATP breakdown then proceeds through a series of intermediates which result in the ADP (adenosin diphosphate) and P-I, during their swinging. There are many reasons for considering this classical mechanism inadequate. We believe in the paradigm of the significant role of the phase transition of the system of the myosin heads. The sarcomere contraction is interpreted as a calcium induced mechanical rearrangement and swing of myosin heads, which result in a relative actin-myosin sliding. The proposed mechanism can be applied both for the actuators in mechanical systems and for the biomechanical implants.

W3.12 Measurement of Tumor Stiffness and Mobility Using Piezoelectric Fingers. Hakki Orhan Yegulalp, Yan Wang Shih and Wei-Heng Shih; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

It is known that tumors or cancerous cells have higher stiffness than their surroundings. Measurement of tissue stiffness could aid early detection of tumor/cancer location. The goal of this study is to use piezoelectric fingers (PEFS) of various design to measure tumor stiffness both under compression and under shear for potential early cancer detection. A PEFS is a piezoelectric cantilever consisting of a highly piezoelectric layer, e.g., lead zirconate titanate (PZT) bonded to nonpiezoelectric layer, e.g., stainless steel. Using a unique dual-electrode design, a PEFS can both apply a force and detect the resultant displacement with one single device. We show that a PEFS is capable of accurately measuring the Young's modulus and shear modulus of tissues in both regular and indentation experiments. Furthermore, we show that a PEFS can measure the Young's modulus and shear modulus variations in model tumor tissues with less than one-millimeter spatial resolution to a depth of up to several centimeters. Results on experiments with PEFS on real breast tissues and prostate that have tumors inside will also be carried out. The ability of a PEFS to measure the stiffness of tumors under both compression and under shear offers great potential to aid tumor malignancy test accuracy.


A piezoelectric microcantilever biosensor is consisted of a piezoelectric layer bonded to a nonpiezoelectric layer. Receptors of a target species, e.g., molecules, or cells, are immobilized at the cantilever tip. Detection of the target species is achieved by monitoring the cantilever resonance frequency shift due to the binding of the target species to the immobilized receptors at the cantilever tip. Compared to piezoelectric microcantilevers, a piezoelectric microcantilever has two advantages of real-time, in-situ detection using simple electrical means. Piezoelectric lead magnesium niobate-lead titanate solisolution (PMN-PT)/copper (Cu) microcantilevers were made from 20 micron thick freestanding PMN-PT films bonded by 1 micron thick Cu by electric plating and immersion. Previous humidity monitoring studies using a 500 micron long, 500 micron wide PMN-PT/Cu microcantilever suggested that the cantilever exhibited a better than picogram per Hz detection sensitivity. In this study, PMN-PT microcantilever of various sizes will be used to detect yeast and salmonella T and their mass detection sensitivities will be determined. Piezoelectric cantilevers consisted of a lead zirconate titanate (PZT) layer 125 nm thick, 500 nm wide bonded to a glass layer 150 m thick with 2 mm long glass tip of a know mass detection sensitivity, 10-10g/Hz will be used for comparison and calibration.

W3.14 Microfabrication of miniaturized highly piezoelectric microcantilevers for rapid, direct, and multiple biosensing. Zuyan Shen, Huidong Li, Wan Y. Shih and Wei-Heng Shih; Department of Materials Science and Engineering, Drexel University, Philadelphia, Pennsylvania.

Miniaturized highly piezoelectric cantilevers offer the advantages of simple electrical detection and better capabilities to detect biologically active agents or microbes. These layers increase the cantilever mass and reduces its resonance frequency, which is detected by monitoring the resonance frequency shift. Our earlier work, both theoretical and experimental, revealed that piezoelectric microcantilevers less than 100 microns in length will provide femtogram/Hz mass detection sensitivities (the mass of a single virus). In this work, we focused on the development and incorporation of micro-thick highly piezoelectric lead zirconate titanate (PZT) thin films by a sol-gel method and their subsequent patterning using ICP etching. Integrated with the microelectronic fabrication technology, freestanding PZT piezoelectric microcantilevers less than 100 microns long were made to realize such sensitivities. A nonpiezoelectric tip of an optimal length included at the free end of cantilever will further enhance the mass detection sensitivity. Results of the PZT microcantilever development and the theoretical calculations that helped optimize the sensing sensitivity will be presented.

W3.15 The Effects of Materials used during Synthesis on the Material and Actuation Properties on Polypropylene. S. Nguyen Davidson, Patrick A. Anquetil and Ian W. Hunter; Mechanical Engineering, MIT, Cambridge, Massachusetts.

Use of Polypropylene based conducting polymer actuators is commonly limited by low strain rates during actuation (1%/s for strain amplitudes of 2% at 0.25 Hz was a typical average value for actuators tested). In this paper we show how synthesis conditions, namely the choice of the deposition electrode, affects this property. Polypropylene films were synthesized on a range of electrode materials such as stainless steel, gold, nickel, and glassy carbon. The resulting actuators were then characterized for mechanical and electrical properties. We show that variation of the deposition electrode material can increase the strain rate performance by as much as 93%. Possible sources for these effects were investigated by measuring differences in surface roughness, porosity, conductivity. A comparison of the actuators is presented and design choices based on the selection of deposition materials are discussed.

W3.16 Micro-fluidics applications of telephone cord delamination blisters. Alex A. Volinsky and Patrick Waters; Mechanical Engineering, University of South Florida, Tampa, Florida.

Telephone cord buckling delamination blisters are commonly observed in compressed thin films. These mechanically active features form by a loss of adhesion between the film and the substrate due to residual stress relief, and exhibit directional growth under certain conditions. This paper considers telephone cord delamination channels for micro-fluidics applications.

W3.17 Fracture Behavior of the Dielectric Ceramics Containing a Conductive Crack. Xiaosheng Gao and Tianhong Wang; Mechanical Engineering, University of South Florida, Tampa, Florida.

Micro-fluidics applications of telephone cord delamination blisters. Alex A. Volinsky and Patrick Waters; Mechanical Engineering, University of South Florida, Tampa, Florida.

Telephone cord buckling delamination blisters are commonly observed in compressed thin films. These mechanically active features form by a loss of adhesion between the film and the substrate due to residual stress relief, and exhibit directional growth under certain conditions. This paper considers telephone cord delamination channels for micro-fluidics applications.
Internal electrodes are widely adopted in electronic and electromechanical devices made from dielectric ceramics. These internal electrodes may be regarded as pre-conductive cracks or notches. Our previous fracture tests on poled and deposed lead zirconate titanate (PZT) ceramics imply that purely electric fields are able to propagate conductive cracks (notches) and fracture the samples. To understand the fracture behavior of conducting cracks in dielectric ceramics, a polarization saturation-free zone (SFZ) model was proposed to establish a failure criterion for the conductive cracks under electric and/or mechanical loads. The SFZ model treats the dielectric ceramics as mechanically brittle and electrically ductile materials and allows the local intensity factors of the electric field strength and electric displacement as well as the local stress and strain intensity factors to have finite nonzero values. Failure occurs when the local energy release rate exceeds the critical value. The predictions of the SFZ model are in good agreement with the experimental results.

To establish a failure criterion for conductive cracks in piezoelectric ceramics under combined mechanical and electrical loads, we use a discrete electric dipole to represent the local spontaneous polarization and the force couples to represent the local strains respectively, and consequently a domain structure is simulated. Using a sputtering system, magnetostriction of these films measured by a polarization on various poled samples. To understand the fracture behavior of conducting cracks in dielectric ceramics under combined mechanical and electrical loads. The giant magnetostrictive films exhibit promising applicability to devices for micro-machines, sensor systems due to high response velocity and huge stress created by the magnetostriction. The authors have showed that rapid-solidified melt-spun Fe-29.6 at% Pd and Fe-17 at% Ga films have large magnetostriction of 1000 and 270 ppm, respectively. The magnetic field distributions of these films measured by a hysteresis curve and butterfly loading for a finite medium with a single edge conductive crack. With the critical local energy release rate adopted as the fracture criterion, the domain-switching model can explain the experimental results that the critical fracture loads for fracture decrease with the increase of the applied electric field and the critical electric field for fracture decreases with the increase of the applied mechanical load. The results of the domain-switching simulation also facilitate us to establish a failure criterion for conductive cracks in piezoelectric ceramics under combined mechanical and electrical loads.


The height and shape of the meniscus formed by a non-magnetic fluid wetting a vertical wall is governed by fluid weight, interfacial surface tension and the contact angle for a particular fluid and wall material combination. The height and shape of a ferrofluid meniscus, however, can be changed by an applied magnetic field. The study of the effects of uniform and non-uniform magnetic fields on ferrofluid surface deformation is the first step in determining the contribution of magnetic fluid surface flows in rotating magnetic fields. Meniscus shape measurements were performed for different configurations of applied magnetic field. These measurements were compared to the predictions of a simple analytical model that extends Biot-Savart’s equation to non-uniform fields. Preliminary results show that the effects of an applied uniform magnetic field are more complicated than the predictions of the simple analytical model because of the non-uniform demagnetizing fields at the interface of the ferrofluid. Measurements show that horizontal applied magnetic fields tend to lower the meniscus, whereas vertical fields tend to raise the meniscus.

W3.21 Stimulus-Responsive Polymer Brushes for the Control of the Interfacial and Nanomechanical Properties. Miao Ye, Dong Zhang and Christine Ortiz; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Surfaces with chemically end-grafted stimulus-responsive polymers have great potential for a variety of applications, e.g. transport, separation, and detection of biomolecules, controlled adhesion, friction, and lubrication in microfluidic systems, and force or displacement generation in micro- and nanoscale devices. In this study, we have investigated one particular class of stimulus-responsive polymers: pH-sensitive comb-type graft copolymers with ionizable main chain segments. Mono-functional, high terminated poly(methacrylic acid-g-ethylene glycol) (SH-PMAA-g-EG) with varying molecular weights (M_w=7,000-17,000 g/mol as measured by gel permeation chromatography), PEG graft densities (1.9-8.4% as measured by 1H nuclear magnetic resonance), and a PEG molecular weight of 1,100 g/mol, was synthesized via atom transfer radical polymerization. Well-defined polymer brushes were then prepared on Au substrates via a “grafting to” chemosorption technique. Advancing contact angle (θ_a) measurements showed that an equilibrium density was achieved after 72 hours with a final θ_a of 19.3±3.8°. Chemically specific high resolution force spectroscopy (HFRFS) with an atomic resolution probe tip coupled with functionalized with 11-mercapto-1-undecanol, HS(CH2)11 OH, or 11-mercapto undecanoic acid, HS(CH2)11COOH, were employed to measure the normal nanoscale interaction forces, F, as a function of probe-tip sample separation distance, D, in a series of aqueous buffer solutions of varied pH (pH=4-9) and a constant ionic strength of 0.005 M. As the pH was reduced, the polymer brushes were observed to undergo a dramatic conformational change from a negatively charged, hydrophilic expanded state to neutral, hydrophobic, and collapsed state in the pH range of 5.0-6.0, due to the H-bonding and hydrophobic complexion interactions between MAA segments on the main chain and the PEG side chains as the MAA groups become protonated. Ongoing theoretical modeling using the dumbbell model based polyelectrolyte electrostatic double layer theory is yielding fundamental structure- nanomechanical property relationships of these stimulus-responsive polymer brushes, such as the conformation and surface charge density per unit area.


Polymeric magnetic composite nanoparticles were produced via an
electrospinning technique from colloidally-stable suspensions of magnetite nanoparticles (Fe₃O₄) in polymer solutions. Magnetite nanoparticles have average diameters ranging from 5 to 20 nm and were formed by an aqueous co-precipitation technique in the presence of a polymer that attaches to the particle surfaces and confers steric stabilization to the nanoparticle dispersion in the polymer solutions. Uniform fibers of poly(vinyl alcohol) with an average diameter of 140 nm, each containing magnetite nanoparticles, were electrospun from a aqueous poly(methylmethacrylate) (PMMA) solution. The specific binding between the two proteins was confirmed through force spectroscopy measurements. Our results encourage the use of micro-cantilevers decorated with stimulus-responsive polymer (SRP) brushes that are reversibly deflected by induced conformational changes in the polymer brush. This conformational change induces a change in the surface stress on the cantilever, ultimately causing cantilever bending. SRP brushes were synthesized on one side of the cantilever using surface-initiated atom transfer radical polymerization (ATRP). Cantilevers decorated with poly(N-isopropylacrylamide) (pNIPAAm) brushes responded to changes in temperature and solvent type, whereas cantilevers decorated with a copolymer composed of 70% pNIPAAm and 30% vinylimidazole (VI) responded sensitively to changes in solution pH. This use of SRPs for cantilever actuation is exciting because commonly available micro-fabricated cantilever sensors offer a simple and non-invasive way to sense changes in solvent type, temperature, and pH, promising great potential for sensing applications in micro-fluidic devices.

W3.25
The Use of Micro-Cantilevers for Actuation and Sensing Applications in Aqueous Environments,
Nehad Ibrahim Albalali1,2, Marwan Khabeeb3, Yue Lam4, Bruce LaMattina3, Robert Clark1,2, and Stefan Zauscher1,2; 1Mechanical Engineering and Materials Science, Duke University, Durham, North Carolina; 2Center for Biologically Inspired Materials and Material Systems, Duke University, Durham, North Carolina; 3Army Research Office, Research Triangle Park, Durham, North Carolina.

We show that mechanically active micro-cantilevers can be used in aqueous environments to detect conformational changes of polymer brushes or specific molecular recognition events between proteins. In the first respect, micro-cantilevers decorated with stimulus-responsive polymer (SRP) brushes can be reversibly deflected by induced conformational changes in the polymer brush. This conformational change induces a change in the surface stress on the cantilever, ultimately causing cantilever bending. SRP brushes were synthesized on one side of the cantilever using surface-initiated atom transfer radical polymerization (ATRP). Cantilevers decorated with poly(N-isopropylacrylamide) (pNIPAAm) brushes responded to changes in temperature and solvent type, whereas cantilevers decorated with a copolymer composed of 70% pNIPAAm and 30% vinylimidazole (VI) responded sensitively to changes in solution pH.

W3.26
Electroactive Polymer Based MEMS as Biosensor Platform.
Zhiqin Li, Suining Li and Z.-Y. Cheng; Materials Engineering, Auburn University, Auburn, Alabama.

There is an urgent need for real-time biodetectors with high performance, such as high sensitivity, reliability, and low cost. Sensor platforms based on MEMS, such as micro-cantilevers (including piezoelectric and silicon-based cantilevers), have been studied. Using of micro-electromechanical diaphragm (MEMD) as micro-sensor platform is induced in this article. The principle and the simulation results are presented. It is found that the sensitivity of MEMD is about 100 times higher than that of microcantilever. The method used to characterize the device is discussed. The high sensitivity of MEMD is demonstrated by MEMD made of electroactive polymer - P(VDF-TrFE). Additionally, it is found experimentally that the quality merit factor (Q value) of MEMD is higher than that of microcantilever. More importantly, the damping effect of liquid media on MEMD is much smaller than that of cantilever, which makes MEMD a strong candidate for developing high performance biosensor used in liquid medium.

W3.27
Shape Memory Polymers for Biomedical Applications.
Christopher M. Yakacki1, Ken Gall2, Alcin Ortega3, Alan Greenberg4, Robin Shandas1,2,7, Kristi Anseth2,4 and Nick James Willett1,7; 1Mechanical Engineering, University of Colorado, Boulder, Colorado; 2Chemical and Biological Engineering, University of Colorado, Boulder, Colorado; 3Division of Cardiology, The Children’s Hospital, Denver, Colorado; 4Howard Hughes Medical Institute, Boulder, Colorado.

We examine the shape memory effect in polymer networks intended for biomedical applications. The polymers were synthesized by photo-polymerization from a tert-butyl acrylate monomer with a dihydroxyethylene-dimethacrylate crosslinker. We first examine the
fundamental link between the polymer structure (fraction and type of crosslinker) and the resulting shape memory recovery properties. Ideal shape memory was obtained for a moderate crosslinking density and the optimized material was used for subsequent testing. The glass transition temperature, $T_g$, of the optimized polymer system was tailored to the necessary levels by changing the length of the crosslinking agent. We systematically investigated the thermomechanics of shape storage (predeformation) and shape recovery in the polymer using three-point bending. The polymers show a sigmoidal free strain recovery response as a function of increasing temperature at a constant heating rate. Free strain recovery was determined to depend on the temperature during predeformation; lower predeformation temperatures ($T < T_g$) decreased the temperature required for free strain recovery. Constrained stress recovery shows a complex evolution as a function of temperature, and also depends on the temperature during predeformation. Stress recovery after low temperature predeformation ($T < T_g$) shows a peak in the generated recovery stress, while stress recovery after high temperature predeformation ($T > T_g$) is sigmoidal. The isothermal free strain recovery rate was found to increase with increasing temperature or decreasing predeformation temperature. We also examine basic photo-polymerization issues in the polymer for the patterning of complex biomedical devices. Finally, the thermomechanical results are discussed in light of potential biomedical applications, and several prototype devices are presented.

### W3.28


Piezoelectric fingers (PEFs) are piezoelectric cantilevers consisting of a highly piezoelectric layer, e.g., lead magnesium niobate lead titanate solid solutions (PMN-PT) bonded to nonpiezoelectric layer, e.g., copper with various tip designs. With a dual electrode design, a PEF can simultaneously generate force (from the driving electrode) and measure the corresponding displacement (from the sensing electrode), making it ideal for in-vivo palpation for early disease detection. PEFs have been shown to accurately measure both tissue stiffness under compression and tissue mobility under shear and stand to greatly improve tumor malignancy test accuracy. The goal of this study is to construct miniaturized PEFs made of 20 microns thick PMN-PT films developed in our lab for cellular elasticity measurements and examine the piezoelectric response of the PEFs both theoretically and experimentally for optimal performance. We include PEFs a bottom sensing PMN-PT layer. The effective spring constant, the axial displacement generated by the applied voltage, and the induced voltage in the sensing PMN-PT layer were examined in terms of the ratio of the length of the sensing PMN-PT layer to the length of the driving PMN-PT layer and the thickness of the non-piezoelectric layer. We showed that the spring constant to decrease with an increasing cantilever length and the induced voltage to increase with a decreasing thickness of the nonpiezoelectric layer, which was quantitatively confirmed with the experiments. Results of cellular elasticity measurements using miniaturized PEFs will be discussed.

### W3.29

**High Dielectric Constant Nano-Polymer Composites as Actuator Materials**, Cheng Huang1, Qing Wang2, and Q.M. Zhang1, 2 Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; 2Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

For many electronic and electromechanical applications, flexible polymeric material with high dielectric constant is highly desirable. Although the dielectric constant of intrinsic dipolar response polymers is far below that of inorganic materials ($\varepsilon \approx 100$), recently, we demonstrated that by using nano-composite approach in which organic fillers with high dielectric response are incorporated into insulating polymer matrix, high dielectric nano-composites with their mechanical properties very similar to the polymer matrix can be developed. Furthermore, these high dielectric nano-organic composites exhibit high electromechanical response under low applied field. For example, in a fully functionalized dielectric-percolative polymer in which the high dielectric fillers (such as copper phthalocyanine and conductive polyaniline) are grafted to a polyurethane backbone, a dielectric constant of 1,000 can be achieved. The fully functionalized polymer exhibits an electromechanical strain of 1.3% with an elastic density near 1J/m$^3$, which is induced by a field of 25MV/m. Composites with conductive polymer nano-spheres as filler are also investigated and results will be presented.

### W3.30

**Improved Magnetostriectically Transduced SAW Devices.**
Field-Responsive Fluids such as magneto-rheological (MR), electrorheological (ER) and shear-thickening (ST) fluids offer numerous applications, such as controllable and self-closing energy dissipation. However, there are also numerous difficulties associated with controlling the magnitude of the response, and in fluid deployment and longevity. Many of these issues can be overcome by the use of new nanoparticle systems, microfluidic assembly and novel macroscopic deployment mechanisms. New magnetorheological fluids employing carbonyl iron particles from 200nm - 10 µm and viscoplastic carrier fluids have been prepared and the dependence of the yield-stress on fluids, these materials do not require imposition of an external field. For each type of fluid, a controllable stiffening of the cellular foam edges. In the case of MR fluids this can give rise to mechanical deformations. We present the results of experiments probing light induced stresses and shape changes in nematic elastomers and momentum exchange between particles from 50 nm - 1 µm in diameter enables the magnitude and onset point of shear thickening response to be customized and systematically varied. For each type of fluid, a controllable energy-absorbing material can be constructed consisting of an open-cell elastomeric foam impregnated with the field-responsive fluid. The mechanical properties of the resulting fluid-solid composites are investigated under various loading conditions. The viscoplastic flow of the particles inside the pores of the reticulated foam alters the mechanical properties of the composite. The energy absorbing capacity of the fluid increases by up to 30 times that of the 'dry' foam due to viscous dissipation in the pores and stiffening of the cellular foam edges. In the case of MR fluids this can be user-controlled by changing the magnetic field to vary the yield-stress of the MR fluid; for ST fluids, the material exhibits a strongly nonlinear response to the rate of loading. These new responsive composite materials thus have tremendous potential as adaptive energy absorbers. By using peptide molecules in the materials self-assembly design process, one can take advantage of inherent biomolecular attributes, intramolecular folding events and conformation to more traditional self-assembling molecular attributes such as amphiphility, to define hierarchical material structure and consequent properties. Intramolecular folding events impart a molecular-level mechanism for environmental responsiveness at the material level (e.g. infinite change in viscosity of a solution to a gel with changes in pH, ionic strength, temperature). Importantly, since the networks are physically associated, they readily shear thin for ease of processing but immediately reassemble into rigid networks after the cessation of shear. The utility in responsive material design with two classes of peptideic molecules will be discussed. First, small, 20 amino acid beta-hairpin peptides will be discussed. The self-assembly construction process is initiated on the peptides first intramolecularly folding into the beta-hairpin conformation from a random coil conformation. Importantly, the scaffold assembly is completely reversible with pH or temperature by reversibly folding and unfolding the constituent peptides that, in turn, assemble or disassemble the scaffold, respectively. In addition, the rigidity of the gel scaffold can be tuned via the magnitude of the environmental stimuli, e.g. gels triggered with temperature form a more rigid network when assembled at higher temperatures due to faster folding and self-assembly kinetics. The molecular design and self-assembly principles, including a model to explain the inherent tunability of the final gel networks that underlie the observed morphological and rheological material, will be presented. Second, the self-assembly of block copolyptides with desired secondary structure will be presented. The ultimate rigidity of the resultant hydrogel networks is directly dependent on the secondary structure of the block copolypeptides. Comparisons will be drawn with the analogous magnetorheological materials that are activated with a magnetic field.

11:00 AM W4.6
Prospects for ER Gels as Mechanically Active and Reactive Materials. Montgomery T. Shaw; Polymer Program and Dept. of Chemical Engineering, University of Connecticut, Storrs, Connecticut.

Electrorheological materials have been known for some time as substances that undergo large changes in stiffness on application of an electric field. In spite of their relatively high actuation speed and simplicity, they are used commercially in very few applications. Best known as fluids that turn into solids, they also can be formulated as soft solids that stiffen considerably, e.g., by a factor of 3 or more. Less known are ER materials that are configured to change shape, leading to bending, shrinking or shearing deformations. Not surprisingly, they can also act in reverse as transducers. This talk will describe how such materials can be made, their achieved performance, and the physical limitations on ultimate performance. Comparisons will be drawn with the analogous magnetorheological materials that are activated with a magnetic field.

11:15 AM W4.7
A Shape Memory Polymer with Improved Shape Recovery. Changdong Liu and Patrick T. Mather; Polymer Graduate Program and Chemical Engineering Department, University of Connecticut, Storrs, Connecticut.

Thermally actuated shape memory polymers have aroused great interest, both academically and industrially, due to their ability to memorize a permanent shape that is set during processing and a temporary shape that is later programmed by manipulation above a critical temperature, usually T_g or T_m. However, the thermal triggering process is usually retarded compared to cousin materials, shape memory alloys, due to the comparatively low thermal conductivity for polymers that is usually less than 0.30 W/m K. In this work, we incorporated an inorganic filler featuring high thermal conductivity into a shape memory polymer, crosslinked polycyclooctene, to increase its thermal conductivity and therefore shorten the heat transfer time. A simple mathematical model was developed that quantitatively correlated the material thermal conductivity and heat transfer time, r, that translates in shape recovery to an induction time. We analyzed experimental data that showed near doubling of thermal conductivity and an associated reduction in induction time. As an additional benefit, mechanical reinforcement was observed with the addition of this rigid thermal conducting filler.

11:30 AM W4.8
Mechanical Coupling in Endothelial Cell Development. M. Todd Thompson; Michael C. Berg, Krystyn J. Van Vliet; Materials Science & Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Health Sciences and Technology, Massachusetts Institute of Technology, Cambridge, Massachusetts.
Living biological cells are complex, mechanically active material systems that demonstrate coupling between chemical and mechanical fields. Through chemical stimuli, independently direct cell behavior is not well understood, nor is the degree to which both operate in concert to induce cellular processes. Here, we present the mechanical characterization of polymeric electrolyte membranes for which chemical composition is maintained constant and mechanical compliance is varied as a function of pH during multilayer formation. We then correlate the effects of this mechanical compliance with the capacity for vascular endothelial cells to attach, spread, and express functional molecules.

Under controlled chemical environment, we find that there exist critical levels of substrate compliance and surface roughness beyond which vascular endothelial cells do not maintain typical phenotypic presentations. Our identification of mechanical determinants of cellular behavior in a chemically decoupled environment has direct applications for tissue engineering, as well as research on inflammation and wound healing.

**SESSION W5: Modeling of Mechanically Active Materials**

Chair: Wendy Cron

Wednesday Afternoon, December 1, 2004

**1:30 PM **

**W5.1 Thermomechanical Constitutive Modeling of Shape-Memory Alloys.** Dimitris C. Lagoudas and Peter Popov; Aerospace Engineering, Texas A&M University, College Station, Texas.

A comprehensive thermomechanical constitutive model for Shape Memory Alloys (SMAs) is presented. The model is a result of a systematic effort to develop a three-dimensional constitutive model for SMAs with special features, dictated by new experimental observations. The model accounts in a unified manner for the different effects of the martensitic transformation observed during non-proportional loading, such as detraining and reorientation of the martensitic variants, as well as tension/compression asymmetry. The simultaneous reverse transformation of self-accommodated and stress induced martensite into austenite is also addressed. Different hardening functions are used to better capture the material response in pseudoelastic and detraining regimes. A numerical implementation of the model, using return-mapping algorithms, is also discussed. The model is tested on a wide range of thermomechanical paths in order to attain robust numerical implementation. Numerical simulations of different SMA actuated devices are finally presented.

**2:00 PM W5.2**

A Thermodynamically-Based Model for Martensitic Phase Transformations with an Application to Shape-Memory Alloys. Carl Jannetti1, John L. Bassani1 and Sergio Turteltaub1; 1Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania; 2Aerospace Engineering, Delft University of Technology, Delft, Netherlands.

As an important class of active materials, shape-memory alloys (SMAs) derive unique properties from martensitic phase transformations and are used in a wide variety of applications including sensors, shape-memory properties, such as pseudoelasticity, are a result of a solid-to-solid phase transformation, which occurs on the level of the crystal lattice. Although the underlying mechanism for the phase transformation is microscopic, a continuum-level description is the ideal choice to model SMAs for use in applications on the size scale of devices such as stents, sensors and actuators. Therefore a link between the microscopic phenomena and its influence on the macroscopic response is required. A continuum-mechanical framework for the thermodynamic description of martensitic phase transformations in single crystals is developed in the framework of irreversible thermodynamics with internal variables. The finite-strain kinematical representation adopted is appropriate for a multi-phase composite microstructure comprising several phases of martensite as well as austenite. Central to the model is the notion that the rate of progression of microscale structural rearrangements depends on the stress state through the thermodynamic forces conjugate to the rearrangements. These thermodynamic forces, which are taken to be the driving forces for the phase transitions, are shown to have a significant contribution from changes in the effective elastic properties that occur during transformations. Finite-element simulations for single crystal illustrate the microstructural effects of phase transformations and demonstrate important implications of the thermodynamic theory. In particular, we consider the tension-compression asymmetry associated with the pseudoelastic stress-strain path dependence on the orientation of the loading axis relative to various crystallographic axes.

**2:15 PM **

**W5.3 Kinematic and Topological Models of Martensitic Interfaces.** R. P. Bhat1, X. Ma1; 1Department of Engineering, The University of Liverpool, Liverpool, United Kingdom; 2Ramsey Canyon Rd, Hereford, Arizona.

According to the classical theory of martensitic crystallography, the interface between parent and daughter is a geometrically invariant plane of the shape transformation. Moreover, the displacements occurring as a result of transformation are homogeneous, increasing linearly with distance from the interface. This property varies with experimental observations using transmission electron microscopy which show such interfaces to be terraced at the atomic level with short-range inhomogeneous displacement fields. A model of martensitic interfaces has been developed recently which is consistent with experimental observations, and also demonstrates explicitly that the mechanism of interface motion proposed in diffusionless. The habit planes predicted by this model deviate in a systematic manner from the classical ones. The observation of the process explains the physical origin of the discrepancies between the two approaches and consider the implications in martensitic transformations.

**2:45 PM W5.4**

**Modelling of Fatigue in Ferroelectrics.** Santiago A. Serebrinsky, Irene Arias and Michael Ortiz; Graduate Aeronautical Laboratories, California Institute of Technology, Pasadena, California.

Ferroelectrics are attractive electro-mechanically active materials due to their large strain actuation and applications in non-volatile memories. Nevertheless, the fatigue of their material properties at relatively low number of cycles N hinders a more widespread use of ferroelectrics. Two forms of fatigue, which may be related, are typically encountered: (i) polarization fatigue, whereby the remanent polarization decreases with N; (ii) mechanical fatigue, i.e., the nucleation and propagation of cracks. Understanding the underlying mechanism for the phase transformation is microscopic, a multi-phase constitutive model for ferroelectric fatigue crack nucleation and growth, based on cohesive theories of fracture. The central feature of the model is a hysteretic cohesive law which couples the mechanical and electrical fields. The model is also suitable for polarization damage due to the electromechanical coupling at the cohesive level. The cohesive law is used in conjunction with general constitutive relations of bulk behavior, including domain switching, in order to predict fatigue cracking and damage under arbitrary electro-mechanical loading conditions. A particularly appealing feature of the model is its ability to deal with both crack nucleation and propagation. We apply the model to both types of fatigue, irrespective of their possible relation. Under the assumption that for smooth samples the number of cycles N required to nucleate a fatigue crack is a sizable part of the total fatigue life, we compare our calculations with experimental results. Despite the scarcity and uncertainty of the experimental data, comparisons with PZT fatigue-life data are encouraging. In particular, the model is able to predict the loss of remanent polarization under repeated electro-mechanical cycles observed in experiment.

**3:30 PM W5.5**

**First Principles-Based Modeling of Ferroelectric Polymers: Computational Design of a PVDF-Based Nano-Actuator.** Alejandro Strachan1, Habib Saaid2 and William A. Goddard, III2; 1Los Alamos National Laboratory, Los Alamos, New Mexico; 2Materials and Process Simulation Center, Caltech, Pasadena, California.

We use first principles methods to study the static and dynamical mechanical properties of the ferroelectric polymer Poly(vinylidene fluoride) (PVDF) and its copolymer with trifluoro ethylene (TrFE).

We use density functional theory [within the generalized gradient approximation (DFT-GGA)] to calculate structures and energetics for various crystalline phases for PVDF and P(VDF-TrFE). We find that the lowest energy phase for PVDF is a non-polar phase with a combination of trans (T) and gauche (G) bonds; in the case of the copolymer the role of the extra (bulkier) F atoms is to stabilize T bonds. Using the MSXX first principles-based force field (FF) with molecular dynamics (MD) we calculate that the energy necessary to nucleate a G bond in an all-T crystal is much lower (14.9 kcal/mol) in P(VDF-TrFE) copolymer than in PVDF (24.8 kcal/mol). This correlates with the observation that the polar state of the copolymer exhibits a solid-solid transition to non-polar phase under heating with MSXX DFT directly melts. We also find that the interfacial between polar and non-polar phases has a smaller threshold stress and a higher mobility in the copolymer as compared with PVDF. We then use molecular modeling to design and test a PVDF nano-actuator. Our simulations predict that large hysteresis occurs only at extremely high frequencies (over 100 Hz) can be obtained in a PVDF nano-actuator if the inter-chain packing density is appropriately chosen. We control the packing density by assembling the polymer chains on a Si <111> surface with 1/2 coverage. Under these...
conditions the equilibrium conformation of the polymer contains a combination of gauche and trans bonds which can be easily transformed to non-equi-

4:45 PM W5.6 Quantum-mechanical design of molecular actuators based on π-stacking. Damian Scherlis1,4, Timothy Swager3,4, Ian Hunter5,6, and Nicola Marzari1,4, 2Materials Science and Engineering, MIT, Cambridge, Massachusetts; 3Mechanical Engineering, MIT, Cambridge, Massachusetts; 4Institute for Soldier Nanotechnologies, Cambridge, Massachusetts.

The π-stacking between aromatic compounds has been intensely studied by experimental and theoretical groups for over three decades. Nevertheless, exploiting this phenomenon as the driving force in molecular actuators is a novel concept. In the present work we explore how thiophene oligomers can be linked to calixarene crowns to design molecular actuators with the ability for expansion and contraction as a function of the electrochemical potential. In such systems, oligomers constitute the electroactive component, while calixarenes perform the role of hinges between oligomer segments. We use first-principles quantum mechanics at the density-functional theory level to screen a variety of calixarene molecules in different conformations and to optimize the overall design. Moreover, correlated quantum-chemistry approaches are applied to describe the stacking interactions between the thiophene oligomers and to show how these can be switched on and off by the electrochemical potential to achieve molecular actuation. The effects of solution and of oligomer length are explored, and the proposed architectures tested with first-principles molecular dynamics simulations.

4:00 PM W5.7 Modeling and Analysis of Conducting Polymer-Based, Trimorph Bending Actuators in Air. Bryan D. Schmid1, Peter Madden1, John Madden2, and Ian Hunter2, 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada.

Ionic electroactive polymers, particularly polypyrrole (PPy), were analytically modeled and experimentally characterized in a non-aqueous, bending actuation configuration. The PPy trimorph design is composed of two mechnanactive polypyrrole electrodes sandwiching an ion-permeable layer impregnated with a BF4 gel electrolyte. The developed analytical models introduce a moment equilibrium analysis of the PPy trimorph and its geometrical constraints as the PPy films undergo a linear strain previously described by J. Madden. The analytical models predict both the trimorph's force and curvature as a function of the applied charge density. Non-aqueous experimental characterization of fabricated trimorph films using a dynamic mechanical analyzer verifies the analytical model within the error bounds of the trimorph's physical properties. Such PPy trimorphs were typically composed 25μm thick PPy films embedded in the trimorph and produced forces up to 0.2N and curvatures of 133m−1.

4:15 PM W5.8 Thermomechanics of the Shape Memory Effect in Polymers. Yiping Liu, Ken Gall, Martin L. Dunn and Alan R. Greenberg, Department of Mechanical Engineering, University of Colorado, Boulder, Colorado.

Shape memory polymers (SMPs) have the capacity to store and recover relatively large strains when subjected to a unique thermomechanical cycle. Owing to their ability to provide reliable low-cost actuation, shape memory polymers have potential biomedical, aerospace, and microsystem applications. Although shape memory properties exist in various polymer systems, and novel applications are emerging, little work has been done to understand or predict thermomechanical couplings in SMPs. In this study, the thermomechanics of shape storage and recovery are systematically investigated in a SMP deformed under tension and compression. During heated recovery, three cases of constraint are examined: unconstrained strain recovery, stress recovery at full strain constraint, and stress recovery at reduced strain constraint. The unconstrained strain recovery implies the absence of the external stress and the free recovery of the induced strain. The stress recovery at full strain constraint implies the fixing of the pre-deformation strain and the gradual recovery of the pre-deformation stress. The reduced strain constraint level equals the pre-deformation strain minus the strain caused by glassy state unloading. Based on the experimental results, a one-dimensional constitutive model is developed using a thermomechanical approach. The model is motivated by the shape memory mechanism of the polymer network and thermodynamics (changes in entropy and internal energy). The foundation of the model is that the entropy change is gradually stored during cooling and released during reheating as free recovery strain or constrained recovery stress. When fit to free strain recovery data, the model can predict the trends of the stress evolution during shape fixation and constrained stress recovery with/without low temperature unloading.

This paper addresses the development of a unified framework for quantifying hysteresis and constitutive nonlinearities inherent to ferroelectric, ferromagnetic and ferroelastic compounds. Because the mechanisms which produce hysteresis vary substantially at the microscopic level, it is more natural to initiate model development at the mesoscopic, or lattice, level where the materials share common energy properties along with analogous domain structures. In the first step of the model development, Helmholtz and Gibbs energy relations are combined with Boltzmann theory to construct mesoscopic models which quantify the local average polarization, magnetization and strains in ferroelectric, ferromagnetic and ferroelastic materials. In the second step of the development, stochastic homogenization techniques are invoked to construct unified macroscopic models for non-homogeneous, polycrystalline compounds exhibiting nonuniform effective fields. The combination of energy analysis and homogenization techniques produces low-order models in which a number of parameters can be correlated with physical attributes of measured data. Furthermore, the development of a unified modeling framework applicable to a broad range of ferroic compounds facilitates material characterization, transducer development, and model-based control design. Attributes of the models are illustrated through comparison with piezoceramic, magnetostrictive and shape memory alloy data and prediction of material behavior.