SMART MATERIALS

1. Introduction

The primary characteristic of a "smart material" is that it has the ability to respond to external stimuli in a *technically useful* and *technically controlled* way. The words "technically useful" and "technically controlled" are emphasized since all materials respond to external stimuli of some sort or other (as a simple example, all materials respond to temperature by changing their volume), however, to be considered a "smart material" the response must be one that is useful in an engineering application. Thus, any discussion of smart materials must include a consideration of the application of these materials. (Animals and plants could be considered as consisting of a large number of smart materials, however, the scope of this article will be restricted to inorganic and organic materials that are used in a more traditional engineering sense.)

The term smart material often also has a historical context, only being applied to relatively new materials. For example, consider the simple bimetallic strip. Bimetallic strips have been around for centuries and consist of two metals joined so that the difference in the coefficient of thermal expansion causes the strip to bend in response to a change in temperature. This can be used, eg, to open or close a mechanical valve or electrical circuit. The stimuli may either be provided by the natural environment or engineered into a structure that the material is part of. However, bimetallic strips are often not thought of as smart materials because they have been around and used for a long time.

Smart materials are also often characterized by the fact that they transform energy from one mode to another, eg, from electrical energy to mechanical energy. Smart materials are also often incorporated in so-called Smart Structures, which are structures that, as well as being the structural support of a building or vehicle, also have a further function. For example, a load-bearing structure that also measures the load that it is carrying is an example of a smart structure.

2. Classification Schemes

How a material is considered or classified depends to some extent on the scientific or technical discipline that is considering the material. For example, a material scientist is interested in the internal structure and how this may change under the influence of an external stimulus, whereas an application engineer may be more concerned with the function of the material and what it can be used for.

2.1. Classification According to Function. Smart materials can be classified according to the intended primary function, eg, as a sensor, actuator, or energy generator. Piezoelectric material is an example of a class of smart materials that can be used in all three of these functions. When subjected to stress these materials generate an electrical voltage that can be used as a response signal and also to generate power. Alternatively, when subjected to a voltage these materials generate a mechanical stress. The interchangeable nature of stimulus and response is a common, but not universal, characteristic of

smart materials. Materials that exhibit this interchangeable nature are often good candidates for smart structures with minimal external support requirements: one smart material both sensing and generating power and also capable of providing a mechanical or other response.

Active Sensing Materials.   The primary action of these materials is to transform one form of energy to another form of energy for, in most cases, a further device or material used to then generate a response. Active sensing materials may often be used to generate energy. For example, the voltage developed by electric polarization of a material can be used to accumulate charge, and the solar cell both detects the presence of incident light and generates a significant voltage and current.

Passive Sensing Materials.   These materials have a passive response to external stimuli, ie, do not transform an energy source to another energy. Thus these devices need an external source of power to operate. They are not really "smart", but are included here for completeness since they do appear as sensors in larger smart systems. An example of a passive response is a change in electrical conductivity due to, eg, a change in pH of a solution.

Actuating Materials.   The primary function is to transform one form of energy to another form as a response to some external stimuli and to perform an action.

2.2. Classification According to Smartness.   Another possible classification is according to the degree of independence of operation that the smart material needs to operate in a smart structure. In this case, materials that require the least external support (eg, external power or processing capability) being considered smarter. A common example of a totally independent smart material is that used in photochromic sunglasses. In this case, the energy required to drive the response, darkening of the sunglasses is provided directly by the stimulus, the incident light.

2.3. Classification According to Material Properties.   A further way to look at smart materials is to consider the primary physical–chemical property of the material that is used in smart applications. This is particularly useful in studying and understanding the operation of smart materials.

Crystal Structure Modification.   A number of classes of smart materials have crystal structural properties that can be used directly for smart actuating or sensing applications. These include materials that undergo a crystallographic phase change (eg, shape memory alloys), materials that have an electrical polarization natural to the crystal structure that responds to external stress (eg, piezoelectric materials) and materials that undergo realignment of internal domains, such as electro- and magnetostrictive materials.

Energy Absorption–Emission.   This includes materials that absorb incident energy by an internal excitation process (eg, promotion of electrons, on absorption of a photon, to a higher energy band). These often have a de-excitation process that involves the emission of energy. Examples include semiconductor devices as light sensors and energy harvesting devices.

Macroscopic Ordering.   Includes (generally) mixtures of materials where the large scale ordering of the particles in the mixture induces a change in properties of the mixture. Examples include electro- and magnetorheological fluids,

where an applied field induces particles in the fluid to align resulting in a change in viscosity. The Liquid Crystal Display can also be considered in this category.

Chemical Interaction. Includes materials with sensitized surfaces that interact with target chemical or biological species. Examples include conducting polymers with functional groups that bind to chemical species and change the resistance of the polymer, and antigen coatings on microbalance mass detectors. Indicator chemicals that change color with, eg, pH, are another form of chemical sensor.

3. Smart Materials Overview

Table 1 is a summary of a number of materials that can be used in smart applications, ie, classified as to function. The following sections consider a number of these materials in more detail. Some sections deal with a particular type of smart material, whereas others deal with a class of material types. Inevitably, there are overlaps between these two, however, consideration of smart materials in this way is beneficial since, as discussed above, the view of the subject is colored by the point of view of the discussion. Smart materials include such a wide range of materials and possibilities it is worthwhile viewing the subject from a number of angles. The following is not an exhaustive list of smart materials, but serves as examples of the more common smart materials.

Many of the materials in Table 1 can be described as "responsive" rather than truly smart, ie, these materials can form one part of a smart system, either the sensor or actuator, but require another responsive material for the actuator or sensor, respectively, to make up a complete smart system. Only a few materials, eg, the photochromic sunglasses mentioned in the section classification schemes, are both sensor and actuator. Even materials that can be used as an actuator and sensor often cannot be engineered to perform both functions effectively at the same time. Thus, most smart materials are used in combinations to form smart systems. An example of a possible system is an antivibration device that uses a piezoelectric sensor to detect the vibration and a magnetorheological fluid as the damper.

The reference section includes a number of Internet web sites for further practical information and as examples of the use and current availability of some smart materials. A number of these references are to commercial web sites as useful sites regarding the application and maturity of some of the technologies, but this in no way is an implied endorsement of the particular companies.

4. Piezoelectric and Related Phenomena

Piezoelectric materials are materials that exhibit a linear relationship between electric and mechanical variables. The electric polarization is proportional to the mechanical stress. Piezoelectric materials are "two-way"; (a) they convert mechanical stress into an electric field (Fig. 1**a**), and this effect is employed in piezoelectric sensors; (b) application of an electric field produces a mechanical

stress (Fig. 1**b**, **c**), and this behavior is utilized in actuator and power generator–harvesting devices. Only materials with an electrically poled, anisotropic crystal stucture can form piezoelectrics; ie, there must be an intrinsic electric field maintained in a particular direction throughout the material. Thus the material must be pyroelectric. A feature of a pyroelectric material is the disappearance of this spontaneous electric field above the Curie point temperature. Piezoelectric devices are formed by raising the material above the Curie point temperature and then cooling in the presence of a strong electric field. The common term for this action is to say that the material is "poled" in the presence of the electric field. This results in partial or complete alignment of the spontaneous electric field within the material.

A related material property is the ferroelectric effect. All ferroelectric materials are necessarily both pyroelectric and piezoelectric. The ferroelectric effect is the electric polarization brought about by the complete or partial realignment of the spontaneous polarization resulting in a static electric field at the surfaces of the materials. (But note, a net field is not normally detected because the surface charge is rapidly neutralized by ambient charged particles.)

There are two principal types of materials that can function as piezoelectrics: the ceramics and polymers.

1. ***Ceramics***: The most widely used materials are the piezoceramics based on the lead zirconate titanate (PZT) formations, mixed sodium and potassium niobates, lithium niobate, and quartz. The advantages of these piezoceramics are that they have a high piezoelectric activity and they can be fabricated in many different shapes.

2. ***Polymers***: Poly(vinylidene fluoride), PVDF, is the most widely used polymer piezoelectric material. It has the advantages over ceramic devices of flexibility, formability and can be simply cut to shape. Polymer piezoelectric materials have lower authority (force and displacement) than ceramic devices. The PVDF structure is a good example of the spontaneous electric field seen in these types of material (Fig. 2**a**, **b**).

A limitation of piezoelectric materials is that they exhibit small dimensional changes (but with high applied force). Composite structures consisting of a length of piezoelectric bonded to a nonpiezoelectric substrate can be used to convert the lateral change in dimension of the piezoelectric to a bending force. In this way, larger actuation strokes can be achieved.

Piezoelectric materials are used in many different types of sensing and actuating devices and also for power harvesting. Examples include Sensors: vibration, sound, accelerometers, pressure, ultrasonics, strain, power generation. Actuators: print heads, vibration suppression, speakers and buzzers, spark generators, ultrasonic transducers, micropositioning and translation. Electrical components: filters and resonators.

5. Shape Memory Alloys and Polymers

Metal shape memory alloys (SMAs) exhibit the properties of pseudo-elasticity and the shape memory effect. These alloys undergo thermomechanical changes passing from a martensitic phase at low temperature to an austenitic phase at higher temperature (Fig. 3**a**).

5.1. Shape Memory Effect. In the martensite phase, the alloy is softer and easily manipulated through large strains with a little change in stress, ie, it can be easily deformed. As the temperature of the alloy is increased above the critical (transformation) temperature, it changes into the austentic phase. In the austentic phase, the alloy regains its high strength and high modulus and also reverts back to its original shape. Thus a SMA can be formed into shape above the transformation temperature, cooled below the transformation temperature, and formed into different shape. On heating, the SMA will revert to the shape that it was formed into above the transformation temperature (Fig. 3**b**).

5.2. Pseudo-Elasticity. This occurs when the alloy is completely composed of austenite (ie, the temperature is above the transformation temperature). If the temperature is kept constant and the material is loaded, then at some point there will be a transformation to the martensite phase simply due to loading. The load is absorbed by deformation of the softer martensite phase, but upon unloading the martensite starts to transform back into austenite and the materials springs back into its original shape (Fig. 3**c**).

Shape memory alloys (SMAs) can be divided into three functional groups: one-way SMAs, two-way SMAs, and magnetically controlled SMAs. The magnetically controlled SMAs show great potential as actuator materials for smart structures because they could provide rapid strokes with large amplitudes under precise control. The most extensively used conventional shape memory alloys are the nickel–titanium, copper–zinc–aluminium, and copper–aluminium–nickel alloys. Due to their low cost, iron-based shape memory alloys are becoming more popular in smart structure applications. Iron–manganese–silicon steels alloyed with chromium, nickel, and cobalt, and iron–manganese–silicon steels alloyed with nitrogen all fit into this category. As previously mentioned, the nickel–titanium alloys have been the most widely used shape memory alloys. This family of nickel–titanium alloys is known as Nitinol (*Ni*ckel *Ti*tanium *N*aval *O*rdnance *L*aboratory in honor of the place where this material behavior was first observed). Nitinol can be used in robotics actuators and micromanipulators that simulate human muscle motion. The ability of Nitinol to exert a smooth, controlled force when activated is an advantage of this material family.

SMAs have been used for military, medical, safety, and robotics applications. Specific usages include hydraulic lines, medical tweezers, anchors for attaching tendons to bones, eyeglass frames, control of hot house windows, underwire brassieres, and antiscalding valves used in water taps, and shower heads.

5.3. Shape Memory Polymers. Shape memory polymers (SMP) are polymers (polyurethane based thermoplastics) that can be heated (above the glass transition temperature), deformed, and cooled to retain the deformed

shape. Upon heating above the transition temperature, the material softens and returns to the shape that it had prior to deformation. Advantages of SMPs over metallic SMAs include light weight, high recoverable strains (up to 400%), injection moulding (to form complex shapes), low cost and SMPs have shape recovery temperatures selectable between -30 and 70°C. The SMAs, however, have superior force characteristics and can operate at higher temperatures.

6. Electrostrictive Materials

Electrostrictive materials are materials that exhibit a quadratic relationship between mechanical stress and an applied electric polarization (Fig. 4). Electrostriction can occur in any material. Whenever an electric field is applied, the induced charges in the material attract each other resulting in a compressive force. This attraction is independent of the sign of the electric field. The strain in the material lies along the axis of the induced polarization, which is preferably the direction of the applied electric field. Electrostriction is a small effect and, in contrast to piezoelectric materials, electrostrictive materials show a large effect near the Curie temperature, especially for ferroelectric substances, such as members of the perovskite family.

Typical electrostrictive materials include such compounds as lead manganese niobate:lead titanate (PMN:PT) and lead lanthanium zirconate titanate (PLZT). Electrostriction is used in actuators for accurate and fine positioning. Electrostrictive translators are less stable than piezoelectric devices with greater sensitivity to temperature. The one advantage they offer is lower hysteresis than piezoelectric materials at temperatures typically $>15^\circ$C.

7. Magnetostrictive Materials

The same type of material response as that seen in electrostrictive materials discussed above can be observed when the stimulus is a magnetic field. Shape changes are the largest in ferromagnetic and ferrimagnetic solids. The repositioning of domain walls that occur when these solids are placed in magnetic field leads to hysteresis between magnetization and an applied magnetic field. All of these effects disappear when the ferromagnetic material is heated above its Curie temperature. Ferrimagnetic materials have macroscopic properties similar to ferromagnetics; however, their microscopic properties are different. The magnetic dipoles of a ferromagnetic solid are aligned parallel to each other; whereas in a ferrimagnetic the alignment can be either parallel or in other directions.

Materials that have shown a response to a magnetic stimuli are primarily inorganic: alloys of iron, nickel, and cobalt doped with rare earths. TERFENOL-D, an alloy of terbium, dysprosium, and iron, $Tb_x Dy_{1-x} Fe_y$ with x between 0.27 and 0.30 and y between 1.90 and 1.95, is the most effective magnetostrictive material and has been described as the "200 lb" gorilla of magnetostrictive materials. The name TERFENOL is an acronym for two of the elements present in the alloy and NOL refers to the Naval Ordinance Laboratory where this type

of material behavior was developed. Magnetostriction occurs at its fullest potential in crystalline materials. Cost still appears to be one of the hindrances to magnetostrictive materials becoming commercially important.

Piezoelectric materials are generally more compact and require less energy to operate than magnetostrictive materials. Magnetostrictive materials (ie, TERFENOL-D) are useful where high force, high power, and a long stroke are required or where the high drive voltages typical of the piezoelectric materials cannot be tolerated.

8. Electro- and Magnetorheological Materials

Electrorheological and magnetorheological materials are fluids that exhibit a dramatic change in viscosity with an applied electric or magnetic field. The fluid can change from a thick oily consistency to virtually a solid substance within a millisecond. There are a wide assortment of electrorheological and magnetorheological fluids, which are usually a uniform dispersion or suspension of particles within a fluid. A typical example of an electrorheological fluid is a mixture of cornstarch in a silicone oil. The mechanism of how electrorheological fluids work is simple. When there is no electric field the particles in the fluid are distributed randomly and are free to move in the fluid. In an applied electric field the particles orient themselves in fiber-like structures (fibrils) that are much harder to move and impede the flow of the fluid, dramatically increasing the viscosity of the fluid–particle mixture (Fig. 5). Typical magnetorheological fluids consist of tiny iron particles suspended in oil and have a similar behavior to the electrorheological fluids except initiated by the application of a magnetic field.

8.1. Electrorheological Materials. Electrorheological fluids are non-Newtonian fluids, ie, the relationship between shear stress and strain rate is nonlinear. The changes in viscous properties of electrorheological fluids are only obtained at relatively high electric fields, in the order of 1 kV/mm. The practical applications of electrorheological fluids center around their abilities to transfer shear stresses and of acting as a variable damping material in an electric field. They have been demonstrated in shock absorbers, brake systems, clutches, vibration damping, control valves, and actuators. An illustrative application of electrorheological fluids is their use as a smart space material. In this application, a single-link flexible-beam was constructed in a sandwich configuration with ER fluids distributed along its length. When the beam is to be rapidly moved back and forth, the ER fluid is not energized, providing flexibility during the transient response period of the maneuver (for speed). At the end point of the maneuver the beam is made rigid (for stability).

8.2. Magnetorheological Materials. Magnetorheological fluids are the magnetic equivalent of electrorheological fluids. An advantage over the ER fluids is that high voltages are not required to actuate the MR fluids. These fluids are under development for use in shock absorbers, vibration damping, exercise equipment and surface polishing of machine parts.

9. Photoresponsive and Sensitive Materials

There are several different types of material families that exhibit different types of light transmission−absorption or other responses to a stimulus. These include electrochromism (a change in color as a function of an electrical field); thermochromism (color change with heat); photochromic materials (reversible light-sensitive materials); photographic materials (irreversible light-sensitive materials); photostrictive materials (shape changes due to light usually caused by changes in electronic structure); fluorescence (emission of light (photons) at a different wavelength to the incident light). An interesting material with both electro- and thermochromism behavior, VO_2, was evaluated for a smart window application. Materials are being developed to exhibit both photochromic and photographic behaviors and one such system is based on a substituted indolinospirobenzopyrene embedded in a polystyrene matrix. This system acts as a photochromic system at low exposure in the ultraviolet (uv) range and at high exposure it functions as a photographic system. The image can be devisualized by heat and can be restored many times with uv irradiation. Another interesting application is the use of polymers that fluoresce or change color in the presence of particular metal ions. This is being tested as a corrosion sensor with optical fibers coated with an appropriate polymer or with the polymer incorporated in a composite structure. The system is optically excited and the presence of light at the fluorescence wavelength indicates metal ions (and thus corrosion). Thermochromic materials find use in security devices and in thermal mapping applications.

All semiconductor materials exhibit an electrical response to incident light due to the electron absorption of photons, of sufficient energy, and promotion of the electrons to the conduction band (change in resistance) and across doping gradients, as in diodes (generation of current and voltage) in solar cells. Of particular interest in this area is the development of non-silicon systems, which may results in cheap, flexible, robust, and easy to transport and deploy solar energy collectors.

10. Chemical and Biochemically Sensitive Materials

The most widely known classes of chemically sensitive materials are the pH-sensitive materials that include the acids, bases, and indicators. The most interesting of these for smart applications are the indicators. These materials change colors as a function of pH and are usually totally reversible. Indicators have also been used in the development of novel chemical indicating systems. Devices based on the permeability of organic vapors through polymeric films or porous polymeric plugs, and subsequent reaction with an indicator, are used for monitoring the condition of time and/or temperature sensitive items, eg, pharmaceutics, foods and other perishables. The system is activated by crushing the vial releasing the volatile component, which then slowly permeates through the film reacting with the indicator to give a visible color change. This change is

dependent on both time and temperature. Other examples of pH-sensitive materials include the smart hydrogels and smart polymers (see below in EAPs).

There is increasing interest in the detection of other chemicals, particularly in the detection of chemical warfare agents, environmentally noxious chemicals, and the control and monitoring of (engine) emissions. Semiconductor film sensors based on metal oxides (eg, SnO_2, ZnO, TiO_2, WO_3) are used to measure the concentration of toxic and flammable gases. These devices operate at several hundreds of degrees and a chemical reaction between the gas and the metal oxide changes the electrical conductivity of the oxide. The conductivity is a function of the temperature and gas concentration. Higher temperature devices (to $\sim 1000^\circ C$) have been demonstrated using SiC and $SrTiO_3$ systems. At low temperatures, the gases interact with the metal oxide by a chemisorption mechanism. The chemically adsorbed particles receive a partial charge and the opposite charge is made available to the oxide as a free electron to increase its conductivity. Metal oxide sensors (MOS) are finding applications in the automotive industry monitoring the composition of exhaust gases.

Many actions in organic systems are governed by highly selective reactions that are in effect molecular recognition mechanisms. The molecules responsible for these processes are highly selective in the molecules that they bind to (ie, recognize) and can be used in engineered devices as sensors. An example of this is coating piezoelectric material with a selective material and then detecting the increase in mass of the coating as the target molecule binds to the coating. Being organic in nature means that a wide range of ways to modify these molecules are available, eg, light stimulated regions that change their fluorescence frequency in the presence of the target molecule.

Conducting polymers can also be tailored to respond (by a change in resistance) to different chemicals. In this case, the response is rather broad (ie, not very selective), however, systems have been developed with a number of polymers treated to react to different types of chemicals to obtain "fingerprints" that are specific to particular chemicals. These systems generally have a limited lifetime and increasing the life and stability of the conducting polymers is the main challenge facing their acceptance as sensors.

A novel proposal for chemical detection is the use of molecularly imprinted plastics (MIPs). In this case, target molecules are imbedded in a (porous) plastic matrix that is applied to some sensing–transducer device. The target molecule is then dissolved away leaving a physical imprint in the plastic matrix. On exposure to the molecule in a gas or liquid the physical imprints left in the plastic are selective for the target molecule and collect it, altering the properties (eg, mass) of the plastic.

11. Electroactive Polymers (Actuators)

An electroactive polymer (EAP) is a polymer that exhibits a response to an applied electrical stimulation and often also develops an electrical response to a mechanical stimulation. Some of these materials have been touched on in previous sections (eg, PVDF, a piezoelectric polymer), however, the general class of polymer materials is important enough to warrant more detailed consideration.

Advantages of polymer actuators include low mass, pliability and quiet operation, and the potential to be low cost materials. Polymers are adaptable, can include sensors and other components, are easily shaped for specific actuators, and can be manufactured on macro and micro scales. Polymers operate with a variety of principles allowing a wide range of design and application tradeoffs of power, extensibility, reaction time, and other qualities. A major goal of current work in EAPs is the development of artificial muscles that are essentially polymers (plastics) that change shape and size under electrical stimulation. EAP artificial muscles can be classified into two main categories according to their main means of activation being either electronic or ionic.

11.1. Electronic EAPs.   Electronic EAPs operate by the movement of electrons and have relatively fast reactions times (µS), high energy density, and can be operated in air. These materials require high electric fields to operate (typically in excess of 150V/µm), which is close to the breakdown voltage of the materials. This can be a major limitation, however, recent advances are reducing the required electric field with reports of devices operating at one tenth of this value. Efficiencies of up to 80% can be achieved for the conversion of electrical to mechanical energy. The force produced by these devices is in the form of an expansion or contraction. Passive dielectrics, piezoelectric polymers (considered above), graft elastomers, liquid-crystals, and electrostrictive polymers are all examples of this class of material.

Passive dielectric polymers consist of two conducting plates separated by a spongy polymer. Upon application of an electric field, the polymer is compressed–stretched as the plates attract–repel each other. Low force materials have been developed that expand up to 380% as well as high force materials (8 MPa) with much more limited strain.

Graft elastomers consist of long backbone molecules that have elements that respond to an electric field grafted to the backbone. High voltages are generally required to cause contraction of the polymer.

Liquid-crystal actuators operate by a temperature induced phase change from an ordered crystalline structure to a disordered "soup". Forces in excess of those for the piezoelectric polymers have been reported, however, the need to heat and cool these devices is a limitation.

11.2. Ionic EAPs.   Ionic EAPs operate by the movement of ions and are much slower than the electronic materials often taking seconds to move to a final position. They are also much less efficient (30% at best), but have two major advantages; low actuation voltages (1–3 V applied across typically 1 mm thick strips) and the ability to produce bending motion directly. Polymer gels, polymer metal composites, conducting polymers, and carbon nanotubes are examples of ionic EAPs.

Polymer gels are formed of cross-linked chain-like molecules swollen in a solvent to form a semisolid. They can be used as sensors or actuators. Movement of ions into or out off the gel due to, eg, a change in pH, can cause the material to swell or shrink. This can be used as an actuation force responding directly to a change in the environment. A possible application would be the operation of a valve to control the flow of a liquid. The swelling or contraction can also be detected electrically to form the basis of a sensor. Electrical stimulation can produce the same effect to give electrically controlled polymer gel actuators.

Polymer metal composites operate by the movement of ions from one side of a device to the other inducing contraction on one side and swelling on the other. This results in a bending motion that can be easily reversed and has seen application in steerable catheters.

Conducting polymers achieve the same type of bending motion by the use of two conductive polymer films separated by a polymer electrolyte. The films are then oppositely polarized (one positive, the other negative) with the result that ions enter one film and leave the other producing swelling and contraction and thus a bending force (Fig. 6).

Carbon Nanotubes (CNTs) have the promise of spectacular capabilities that have not yet been achieved. The CNTs are related to the buckminsterfullerene (C_{60}) molecule, a soccerball-shaped cage of 60 carbon atoms. It can be considered as the two halves of a soccerball connected by a tube consisting of graphitic sheets or ribbons wound to form the tube (see below for more detail). The CNTs have the highest tensile strength know, some 100 s as strong as the equivalent mass of steel, and survive up to temperatures of 1000°C. Electric charging causes ions to attach to the carbon cage, shortening the C−C bond lengths and creating strains of up to 1%. This is not very high, however, the potential stress (force) is high.

12. Nanotechnology

The field of nanotechnology has seen a dramatic increase in attention over the last few years. While not a material per se, nanotechnology is an enabling technology. Nano-engineered materials have unique properties compared to bulk materials due to their extremely high surface area/volume ratio, high surface energy and the ability for elements to be located together, or compounded, in ways that would not occur under "normal" chemical or physical processing routes. Nano-engineered and nano-fabricated materials promise to produce materials with unique properties to enhance smart materials, imbue a material with smart characteristics, or be a smart material in its own right.

12.1. Fullerenes and Carbon Nanotubes (CNT). Fullerenes are spherical caged molecules with carbon atoms at the corner of a polyhedral structure consisting of pentagons and hexagons. Buckminsterfullerene, which is known as the "buckyball", is the best known of this family. Fullerenes have been under commercial development for several years. One interesting application of fullerene as a smart material has been in the area of embedding fullerenes into sol−gel matrices for the purpose of enhancing optical limiting properties. A semiconducting material with a magnetic ordering at 16.1 K was produced from the reaction of buckyball with tetra(dimethylamino)ethylene. The CNTs, as described above, consists of a roll of graphite structure capped with carbon cages at each end. CNTs are produced as either single walled (SWNT), which consists of a single carbon roll layer, or multiwalled (MWNT), which consists of many concentric rolls of graphitic-like carbon. The way in which the graphitic roll connects to itself and the size of the roll affects the electrical properties of the CNT producing insulator, conductor, and semiconductor materials.

12.2. Nanoparticles and Nanowires.   These can be fabricated from a number of materials using different techniques. High surface area nanowires of Pt can be used as catalytic gas detectors: A nano Pt wire is heated and a catalytic reaction occurs in the presence of, eg, oxygen and a hydrocarbon. The heat of this reaction is then detected by the wire itself. The color of nanoparticle aggregates is very dependent on the spacing of the particles. Nanoparticles coated with suitable molecules can be used to detect chemical species. The molecule changes shape in the presence of the target chemical, and thus the spacing of the nanoparticles changes resulting in a change in color. The electrical conductivity of conductive nanoparticles is also very dependent on the spacing of the particles and thus an electrical response can also be obtained.

12.3. Nano–Microstructured Surfaces.   Nano–microstructures surfaces are not a material, but a modification to a material. However, "simply" altering the surface of a material can result in interesting properties since many material interactions with the external world are through the surface of the material. Examples include low friction surfaces, self-cleaning (which has seen application in self-cleaning windows), and properties associated with exceptionally high surface area.

13. Other Materials

Smart catalysts behave in such a way as to reduce the chance of exothermic chemical runaways. One class of smart catalysts is based on homogeneous rhodium-based poly(alkene oxide)s, in particular those with a poly(ethylene oxide) backbone. Traditionally, catalyzed chemical reactions proceed in a manner in which the catalysts becomes more soluble and active as the temperature is raised. This can lead to exothermal runaways that pose both safety and yield problems. On the other hand, as the temperature increases smart catalysts become less soluble, precipitate out of solution and become inactive. As the reaction mixture cools down the smart catalysts redissolves and becomes active again. Other smart catalysts are being developed that dissociate at high temperatures (less active) and recombine at low temperatures (more active).

Water is one of the few materials with the property that it expands as the liquid approaches the freezing point. This behavior is responsible for the freeze–thaw–freeze erosion of cracked rocks and has been used in indicator system where the expansion of the water cracks a container indicating that the temperature has dropped below the freezing point of water.

14. Considerations for the Future

Activity in the area of smart materials escalated in the closing years of the twentieth century and has continued into this century. The ability to tailor these materials to exhibit multistimuli and multiresponsive behaviors is becoming more of a key feature of smart materials. This ability has received a dramatic boost from the increased global interest in nanotechnology and the increased sophistication and understanding of polymer materials. Both of these areas

will result in materials tailored for smart applications. Some of this is moving close to mimicry of biological systems: small molecular motors have been built "from scratch" and have demonstrated response to chemicals similar to the action of flagella in single celled organisms. There appear to be few boundaries to the possibilities of smart materials. The challenge, as always, will be to harness the promise into practical applications. Materials, processes and technologies must come together to realize the full potential of the smart materials age. Finally, Table 2 gives an indication of the level of technical and scientific understanding and the commercial maturity of the materials considered above.

BIBLIOGRAPHY

"Smart Materials" in *ECT* 4th ed., Suppl. Vol., pp. 502–514, JA Harvey, Hewlett-Packard Co. and Oregon Graduate Institute of Science & Technology: "Smart Materials", in *ECT* (online), posting date: December 2, 2000, by JA Harvey, Hewlett-Packard Co. and Oregon Graduate Institute of Science & Technology.

GENERAL REFERENCES

Piezoelectric and Related Phenomena

Piezoelectric products http://www.piezo.com/index.html Use of piezoelectric transducers for Non-Destructive Testing http://www.ndt-ed.org/EducationResources/Community-College/Ultrasonics/EquipmentTrans/piezotransducers.htm

Shape Memory Alloys and Polymers

Commercially available SMAs for the hobby market? http://www.robotstore.com/shape-memoryalloys.asp?afid=home Medical applications http://www.azom.com/details.asp?ArticleID=134 Nitinol applications http://www.nitinol.com/4applications. htm

Electro- and Magnetostrictive Materials

Etrema – manufacturer of TERFENOL-D http://etrema-usa.com/products/terfenol/

Electro- and Magnetorheological Materials

A general article on these fluids http://www.aip.org/tip/INPHFA/vol-9/iss-6/p14.html Electro: http://www.smarttec.co.uk/index.htm Magneto: A couple of the few commercial suppliers http://www.lord.com/Default.aspx?tabid=718 http://www.liquidsresearch.com/products/magnet.asp

Photo Responsive and Sensitive Materials

Study of electrochromic use on windows http://windows.lbl.gov/comm_perf/electroSys. htm Thermochromic materials http://www.hwsands.com/index.html http://www. gansink.com/inks/ink_pages/security_index_eg.html

Chemical and Biochemically Sensitive Materials

A large number of sol-gel references http://www.solgel.com/Resources/biblio/sensors. htm Metal oxide gas sensors: a good summary with bibliography http://www.tms.org/ pubs/journals/JOM/0010/Cosandey/Cosandey-0010.html

Electroactive Polymers

A good starting point with links http://ndeaa.jpl.nasa.gov/nasa-nde/lommas/eap/EAP-web.htm   http://ndeaa.jpl.nasa.gov/nasa-nde/lommas/eap/WW-EAP-Newsletter.html General article "Electrically activated plastic muscles will let robots smile, arm-wrestle and maybe even fly like bugs", Yoseph Bar-Cohen:
http://www.spectrum.ieee.org/WEBONLY/publicfeature/jun04/0604art.html

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Table 1. **Nonexhaustive Summary of a Number of Types of Smart Materials with the Stimulus Required to Elicit the Response**[a]

Materials type	Stimulus	Response	Examples
piezoelectric and ferroelectric	mechanical electric	electric mechanical	lead zirconate titanate, poly(vinylidene fluoride)
pyroelectric	temperature	electric	barium strontium titanate
electrostrictor	mechanical electric	electric mechanical	lead magnesium niobate-lead titanate
magnetostrictor	mechanical magnetic	magnetic mechanical	terfenol-D
electroactive polymer	mechanical electric chemical species	electric mechanical mechanical	polyacrylonitrile, polypyrrole, sol−gel
liquid-crystal elastomer	temperature change	mechanical	
electroluminescent	electric field	light emission	gallium arsenide (GaAs), poly(alkylfluorines)
photoluminescent	incident light	light emission	copolymers with poly(p-phenylene benzobisthiazole), zinc oxide (ZnO)
electrochromic	electric	color change	tungsten oxide (WO$_3$)
other chromic photochromic, thermochromic, piezochromic, solvatochromic, carsolchromic	light temperature strain	color change	vanadium oxide (VO$_2$)
photostrictive	light	mechanical	lead lanthanum zirconium titanate (PLZT)
semiconductor	temperature incident light mechanical	charge resistance resistance	doped silicon, germanium, semiconducting polymers
piezoresistive	mechanical, temperature	resistance	doped semiconductor
metal oxide semiconductor	chemical species (chemisorption)	resistance	oxides of Tin (SnO$_2$), zinc (ZnO), titanium (TiO$_2$), tungsten W(O$_3$), silicon carbide (SiC)
conducting polymer	chemical species, temperature	resistance/ impedance	polypyrrole, polyaniline
optical fiber	strain, temperature, electric/magnetic fields	light intensity, phase, frequency, polarization	
shape memory alloy	temperature change	mechanical	Nitinol
shape memory polymer	temperature change	mechanical	thermoplastic poly(urethane)
electrorheological fluid	electric field	viscosity change	cornstarch in silicone oil
magnetorheological fluid	magnetic field	viscosity change	magnetic particles suspended in fluid
nanoparticles, carbon nanotubes	chemical light	color, resistance reactivity, resistance	coated gold nanoparticles

[a]A number of these, as indicated, are two-way systems, ie, the stimulus and response can be interchanged.

Table 2. **Somewhat Subjective Summary of the Level of Technical and Scientific Maturity and the Commercial Availability and Level of Use of the Materials Considered Above**

| Materials type	Technical/scientific understanding	Commercial maturity
piezoelectric, ferroelectric and co-workers	good	off the shelf, used in products, reasonable industry.
shape memory alloys and polymers	good (metals) fair (polymers)	material available, some products. evaluation stage.
electrostrictor and magnetostrictor	good	material available, proposed uses but not wide spread.
electro- and magnetorheological fluid	good	material available, proposed uses but not wide spread.
photoresponsive and sensitive materials	very good (inorganic semiconductors) fair, active research (polymers)	semiconductors highly developed with extensive industry. other materials are mainly in the evaluation stage with some products.
chemical and biochemical sensitive materials	good (metal oxides) fair, active research (polymers)	metal oxide sensors widely used. polymer systems are mainly in the evaluation stage.
electroactive polymers	fair, active research	low, some years away
nanotechnology	good to poor, very active and extensive (mainly fundamental) research	low. Used in a limited range of products. Some materials available. Expected to be a disruptive technology. A number of technical evaluations underway.
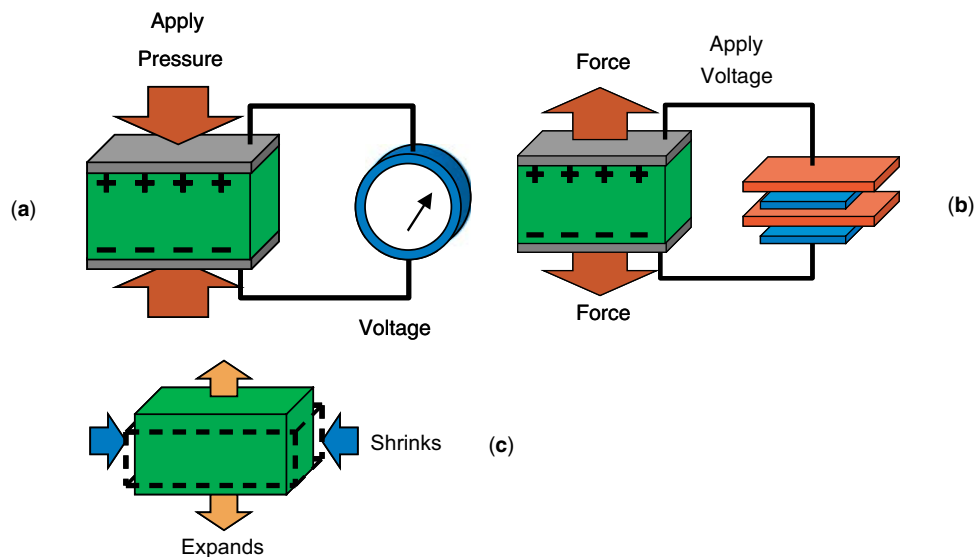
Fig. 1. (**a**) Piezoelectric materials generate a voltage when subjected to pressure. (**b**) Conversely, piezoelectric materials generate a force when a voltage is applied. Reversing the voltage results in a force in the opposite direction. (**c**) Exaggerated diagram showing the dimensional changes that a piezoelectric material undergoes when subjected to an applied voltage.
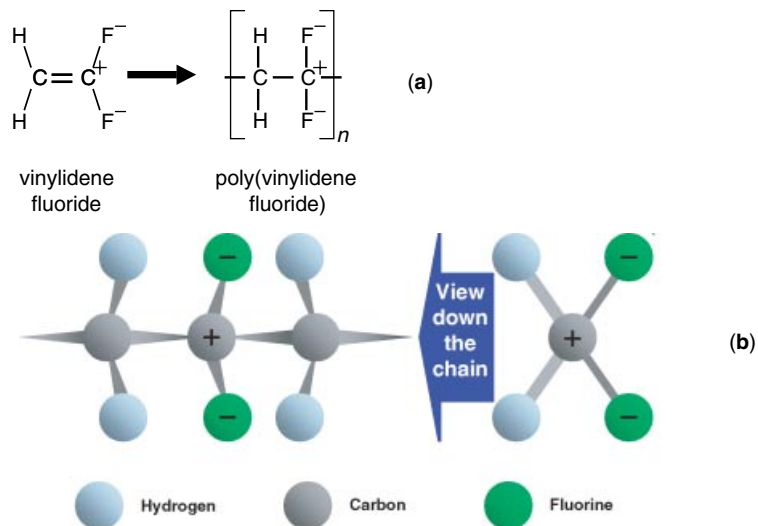

Fig. 2. (**a**) Monomer and polymer for the polymer piezoelectric material, poly(vinylidene fluoride), PVDF. (**b**) Model of PVDF looking from above the chain (left) and down the chain (right) showing the polarization due to the strongly electronegative fluorine.
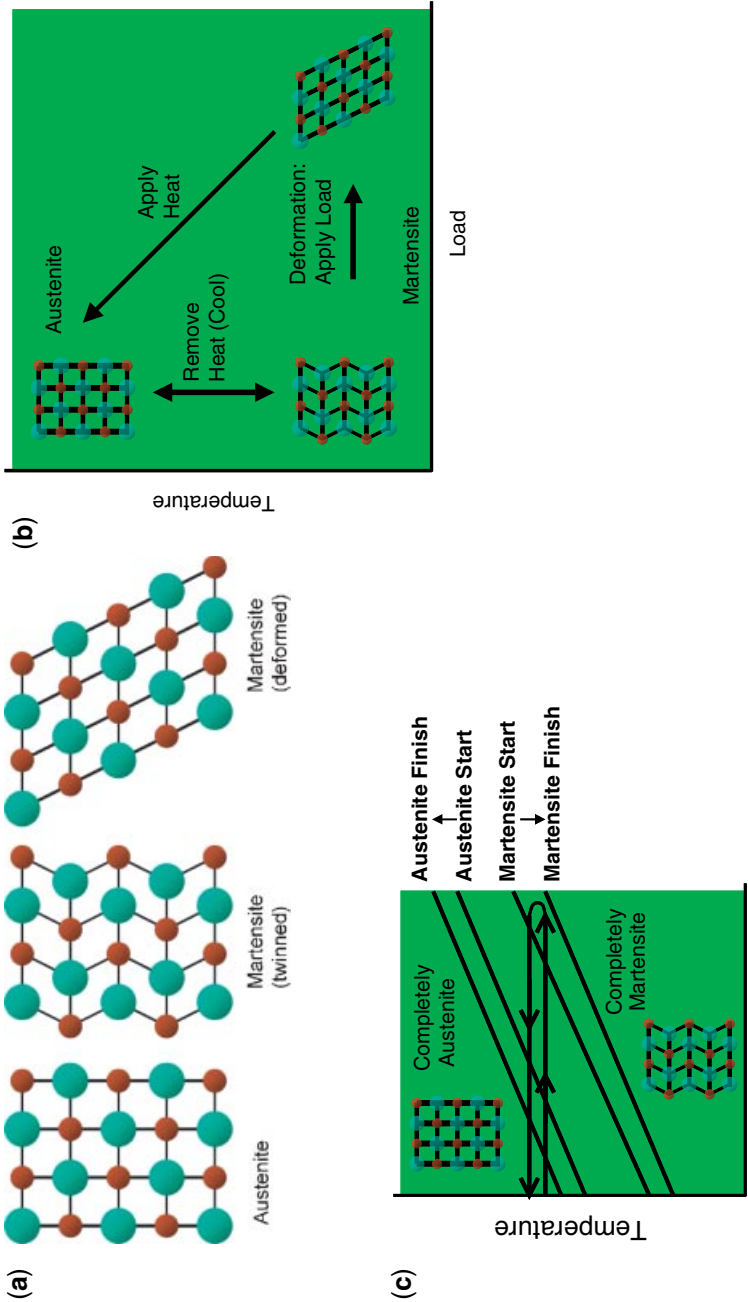
Fig. 3. (**a**) Models of austenite, martensite (twinned) and martensite (deformed) showing the different atomic configurations for shape memory alloys. (**b**) Diagram showing the temperature, load, and heating and cooling cycle for the shape memory effect in a SMA. The SMA has a particular shape at high temperature. On cooling the structure transforms to the softer martensite and can be deformed to another shape. On heating, the structure transforms back into austentite and back to the original shape. (**c**) Super elastic effect. At a constant temperature the SMA deforms as load is applied, transforming into martensite. As the load is released it transforms back to austenite and regains its original shape.
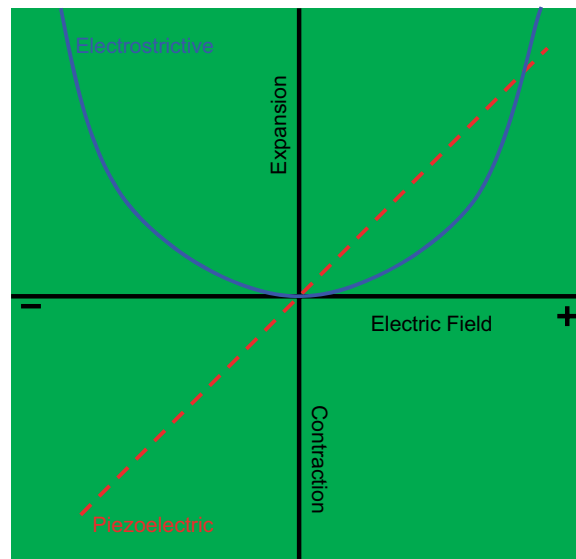
Fig. 4. The form of the dimensional changes for electrostrictive and piezoelectric materials. Electrostrictive materials expand with a quadratic relationship to the applied field, whereas piezoelectric materials are essentially linear.
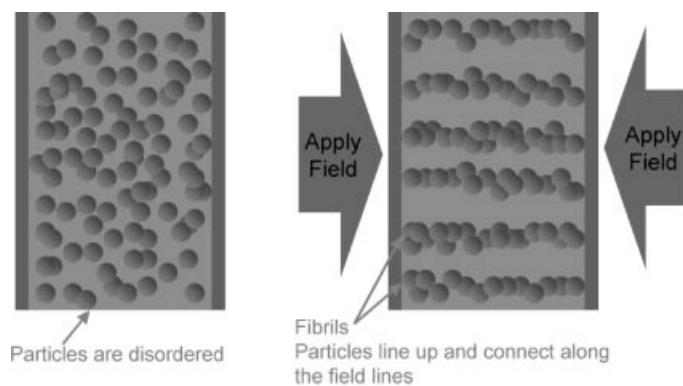

Fig. 5. Representation of how the particles in an electro- or magnetorheological fluid gather together to form fibrils under the influence of an electric or magnetic field.
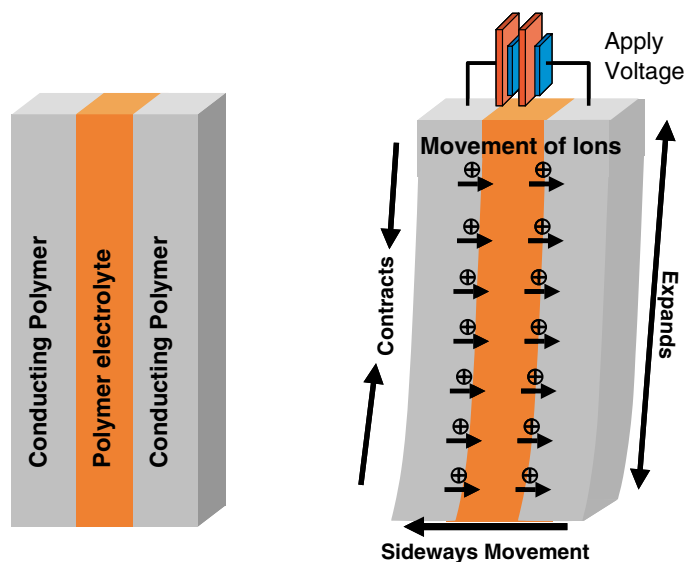
Fig. 6. Bending motion in a conducting polymer cantilever induced by the contraction and swelling of the polymer by the flow of ions out of and into the different parts of the polymer under the influence of an applied voltage.