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Overview of Multi Functional Materials

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1. Introduction

Until relatively recent times, most periods of technological development have been linked to changes in the use of materials (eg the stone, bronze and iron ages). In more recent years the driving force for technological change in many respects has shifted towards information technology. This is amply illustrated by the way the humble microprocessor has built intelligence into everyday domestic appliances. However, it is important to note that the IT age has not left engineered materials untouched, and that the fusion between designer materials and the power of information storage and processing has led to a new family of engineered materials and structures.

The development of materials science has lead to the introduction of a new kind of material- "smart" material. Smart materials not only have the traditional structural material functions. But also have functions such as actuation, sensibility and microprocessing capability. in the materials family , we find three major materials : metals .ceramic and polymer and among those polymers being the youngest members find wide application in comparison to metals and ceramics In every sectors of our society . the recent progress in smart materials has taken the new momentum in the materials science and technology .the board spectrum of applications of smart materials cover the biomedical , environmental , communication defence , space , nanotechnolgical fields of research with tremendous progress . The present report describes the application of smart materials in terms of opportunity and future challenges.

Smart materials referred to materials that will undergo controlled transformations through physical interactions. Smart Materials are materials that respond to environmental stimuli, such as temperature, moisture, pH, or electric and magnetic fields. For example- photochromic materials that change colour in response to light; shape memory alloys and polymers which change/recover their shape in response to heat and electro- and magneto-rheological fluids that change viscosity in response to electric or magnetic stimuli. Smart Materials can be used directly to make smart systems or structures or embedded in structures whose inherent properties can be changed to meet high value-added performance needs. The different types of smart materials include piezoelectric, shape-memory alloys, electro-active conductive polymers, electrochromic materials, biomaterials,

1.1 Needs of smart materials

To achieve a specific objective for a particular function or application, a new material or alloy has to satisfy specific qualifications related to the following properties:-

- a. Technical properties, including mechanical characteristics such as plastic flow, fatigue and yield strength and behavioural characteristics such as damage tolerance and electrical, heat and fire resistance.
- b. Technological properties, encompassing manufacturing, forming, welding abilities, thermal processing, waste level, workability, automation and repair capacities.
- c. Economic criteria, related to raw material and production costs, supply expenses and availability.
- d. Environmental characteristics, including features such as toxicity and pollution.
- e. Sustainable development criteria, implying reuse and recycling capacities. If the functions of sensing and actuation are added to the list, then the new material/alloy is considered a smart material.

2. Classification of smart materials

Types of materials

- a. Piezoelectric Materials
- b. Shape memory alloy (SMA)
- c. Electro-active conductive polymers
- d. Biomaterials,
- e. Electro-rheological fluids

Piezoelectric materials, shape-memory alloys, electrostrictive materials, magnetostrictive materials, electro-rheological fluids, etc. are currently available smart materials.

2.1 Piezoelectric materials

Piezoelectric materials were first discovered by Jacques and Pierre Curie in the 19th century. The literal meaning of piezoelectric is “pressure electricity”, and this meaning aptly describes these materials, as a deformation caused by pressure on the substance will create an electric current within the material. The mechanical pressure is therefore converted to voltage. Natural piezoelectric materials are crystalline materials that exhibit the piezoelectric effect. Often they are strong physically and chemically inert. The piezoelectric effect can also be found in synthetic polycrystalline ceramics which can be designed to have other specific properties that make individual ceramics useful in many different applications. Piezoelectric materials are often linked to pyroelectric effects. Often a material can undergo both effects - one converting mechanical stress energy into electrical energy and the other converting from heat energy. A piezoelectric material does not, however, always show the pyroelectric effect as well as the piezo.

Piezoelectric materials have two unique properties which are interrelated. When a piezoelectric material is deformed, it gives off a small but measurable electrical discharge. Alternately, when an electrical current is passed through a piezoelectric material it experiences a significant increase in size (up to a 4% change in volume). Piezoelectric materials are most widely used as sensors in different environments. They are often used to measure fluid compositions, fluid density, fluid viscosity, or the force of an impact. An example of a piezoelectric material in everyday life is the airbag sensor in your car. The material senses the force of an impact on the car and sends an electric charge deploying the airbag.

2.2 How do it works

Piezoelectric materials have two crystalline configurations. One structure is organized, while the other is not. Organization of the structure has to do with polarization of the molecules that make up the material. Hence, a non-polarized material has a non-organized structure, while the polarized material is organized. To polarize the material, voltage or electricity must be conducted through it. As a result of this electrical force, the molecules of the material reorient themselves, thus changing the shape of the material; this is called electrostriction. The picture below shows this process at a microscopic level. Change in shape can produce mechanical force, as well as changes in physical characteristics (like density, shown below).

Non-polarized material:

Electricity is produced with
Input of electricity

Polarized material:

shape change is produced with
input of shape change.

Fig. 1.

Similarly, if mechanical force is exerted on the material to change its shape, an electrical field is produced; this is called piezoelectric effect. Electrostriction and piezoelectric effect are opposite phenomena. In the graphic below, a thin piezoelectric material within a plastic sheath is being bent, and electricity is being generated and passed through the red wires at the PZT is the most popular piezoelectric material in use.

Fig. 2.

Its physical properties can be optimized for certain applications by controlling the chemistry and processing of this material. Therefore, it can have a variety of compositions, geometries, and applications. Limitations in its use are related to high excitation voltages needed, mechanical durability, and stability in coupling the material to the control system and/or structure.

Some piezoelectric materials are:

- Quartz
- Barium titanate
- Cadmium sulfide
- Lead zirconium titanate (PZT)
- Piezoelectric polymers (PVDF, PVC)

Piezoelectric effects. Electric charge is created when the material is mechanical stressed.

2.3 The piezoelectric effect

A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied (the substance is squeezed or stretched). Conversely, a mechanical deformation (the substance shrinks or expands) is produced when an electric field is applied. This effect is formed in crystals that have no center of symmetry. To explain this, we have to look at the individual molecules that make up the crystal. Each molecule has a polarization, one end is more negatively charged and the other end is positively charged, and is called a dipole. This is a result of the atoms that make up the molecule and the way the molecules are shaped. The polar axis is an imaginary line that runs through the center of both charges on the molecule. In a monocrystal the polar axes of all of the dipoles lie in one direction. The crystal is said to be symmetrical because if you were to cut the crystal at any point, the resultant polar axes of the two pieces would lie in the same direction as the original. In a polycrystal, there are different regions within the material that have a different polar axis. It is asymmetrical because there is no point at which the crystal could be cut that would leave the two remaining pieces with the same resultant polar axis. Figure 3 illustrates this concept.

Fig. 3. Mono vs. Crystals

In order to produce the piezoelectric effect, the polycrystal is heated under the application of a strong electric field. The heat allows the molecules to move more freely and the electric field forces all of the dipoles in the crystal to line up and face in nearly the same direction (Figure 4).

Fig. 4. Polarization of Ceramic Material to Generate Piezoelectric Effect

The piezoelectric effect can now be observed in the crystal. Figure 5 illustrates the piezoelectric effect. Figure 5a shows the piezoelectric material without a stress or charge. If the material is compressed, then a voltage of the same polarity as the poling voltage will appear between the electrodes (b). If stretched, a voltage of opposite polarity will appear (c). Conversely, if a voltage is applied the material will deform. A voltage with the opposite polarity as the poling voltage will cause the material to expand, (d), and a voltage with the same polarity will cause the material to compress (e). If an AC signal is applied then the material will vibrate at the same frequency as the signal (f).

Fig. 5. Example of Piezoelectric Effect

Using the Piezoelectric Effect -The piezoelectric crystal bends in different ways at different frequencies. This bending is called the vibration mode. The crystal can be made into various shapes to achieve different vibration modes. To realize small, cost effective, and high performance products, several modes have been developed to operate over several frequency ranges. These modes allow us to make products working in the low kHz range up to the MHz range. Figure 6 shows the vibration modes and the frequencies over which they can work. An important group of piezoelectric materials are ceramics. Murata utilizes these various vibration modes and ceramics to make many useful products, such as ceramic resonators, ceramic bandpass filters, ceramic discriminators, ceramic traps, SAW filters, and buzzers.

2.4 Application of piezoelectric materials

Piezoelectric materials may be used passively as sensors, or actively as actuators. The piezoelectric sensors that will be used on this bridge include the PZT (lead-zirconate-titanate), a ceramic sensor, and PVDF (polyvinylidene fluoride), a polymeric sensor. The PZT's are extremely sensitive and very accurate, but due to their brittle nature, PZT's are restricted to being point sensors. Likewise, PVDF's are also very sensitive and accurate. However, PVDF's are not as brittle and may be integrated to perform distributed measurements. Therefore, PZT's will be located primarily in critical areas, whereas the PVDF's will be located along side the strain gauges.

2.5 Shape memory alloy (SMA)

Shape memory alloys were discovered in 1932, however it was not until 1961 when the most common form was discovered - nickel-titanium (NiTi). Several NiTi products can be seen in the picture to the right. A shape memory alloy (SMA) is a material that has the ability to

return to its previous shape after being deformed (bent) by applying heat or in some cases just releasing the stress. Shape Memory Alloys (SMA's) are novel materials which have the ability to return to a predetermined shape when heated. When an SMA is cold, or below its transformation temperature, it has a very low yield strength and can be deformed quite easily into any new shape--which it will retain. However, when the material is heated above its transformation temperature it undergoes a change in crystal structure which causes it to return to its original shape. If the SMA encounters any resistance during this transformation, it can generate extremely large forces. This phenomenon provides a unique mechanism for remote actuation.

The most common shape memory material is an alloy of nickel and titanium called Nitinol. This particular alloy has very good electrical and mechanical properties, long fatigue life, and high corrosion resistance. As an actuator, it is capable of up to 5% strain recovery and 50,000 psi restoration stress with many cycles. By example, a Nitinol wire 0.020 inches in diameter can lift as much as 16 pounds. Nitinol also has the resistance properties which enable it to be actuated electrically by joule heating. When an electric current is passed directly through the wire, it can generate enough heat to cause the phase transformation. In most cases, the transition temperature of the SMA is chosen such that room temperature is well below the transformation point of the material. Only with the intentional addition of heat can the SMA exhibit actuation. In essence, Nitinol is an actuator, sensor, and heater all in one material. Shape memory alloys, however, are not for all applications. One must take into account the forces, displacements, temperature conditions, and cycle rates required of a particular actuator. The advantages of Nitinol become more pronounced as the size of the application decreases. Large mechanisms may find solenoids, motors, and electromagnets more appropriate. But in applications where such actuators can not be used, shape memory alloys provide an excellent alternative. There are few actuating mechanisms which produce more useful work per unit volume than Nitinol. Nitinol is available in the form of wire, rod and bar stock, and thin film. Examples of SMA products developed by TiNi Alloy Company include silicon micro-machined gas flow microvalves, non-explosive release devices, tactile feedback device (skin stimulators), and aerospace latching mechanisms. If you are considering an application for shape memory alloys, TiNi Alloy Company can assist you in the design, prototyping, and manufacture of actuators and devices.

Physical Properties of Nitinol

- Density: 6.45gms/cc
- Melting Temperature: 1240-1310° C
- Resistivity (hi-temp state): 82 uohm-cm
- Resistivity (lo-temp state): 76 uohm-cm
- Thermal Conductivity: 0.1 W/cm-° C
- Heat Capacity: 0.077 cal/gm-° C
- Latent Heat: 5.78 cal/gm; 24.2 J/gm
- Magnetic Susceptibility (hi-temp): 3.8 uemu/gm
- Magnetic Susceptibility (lo-temp): 2.5 uemu/gm

Mechanical Properties of Nitinol

- Ultimate Tensile Strength: 754 - 960 MPa or 110 - 140 ksi
- Typical Elongation to Fracture: 15.5 percent
- Typical Yield Strength (hi-temp): 560 MPa, 80 ksi

- Typical Yield Strength (lo-temp): 100 MPa, 15 ksi
- Approximate Elastic Modulus (hi-tem): 75 GPa, 11 Mpsi
- Approximate Elastic Modulus (lo-temp): 28 GPa, 4 Mpsi
- Approximate Poisson's Ratio: 0.3

Actuation

- Energy Conversion Efficiency: 5%
- Work Output: ~1 Joule/gram
- Available Transformation Temperatures: -100 to +100° C

Stress-Strain Characteristics of Nitinol at Various Temperatures

Fig. 6.

2.6 How do shape memory alloys works

In order to understand the way in which the shape memory effect occurs it is useful to understand the crystal structure of a SMA. All shape memory alloys exhibit two very distinct crystal structures. Which phase is present depends on the temperature and the amount of stress being applied to the SMA. These phases are known as martensite which exists at lower temperatures and austenite for higher temperatures. The properties of an SMA depend on which the amount of each crystal phase is present.

The two unique properties described above are made possible through a solid state phase change that is a molecular rearrangement, which occurs in the shape memory alloy. Typically when one thinks of a phase change a solid to liquid or liquid to gas change is the first idea that comes to mind. A solid state phase change is similar in that a molecular rearrangement is occurring, but the molecules remain closely packed so that the substance remains a solid. In most shape memory alloys, a temperature change of only about 10°C is necessary to initiate this phase change. The two phases, which occur in shape memory alloys are Martensite, Austenite. Martensite is the relatively soft and easily deformed phase of shape memory alloys, which exists at lower temperatures. The molecular structure in this phase is twinned which the configuration is shown in the middle of Figure 4. Upon deformation this phase takes on the second form shown in Figure 4, on the right. Austenite,

the stronger phase of shape memory alloys, occurs at higher temperatures. The shape of the Austenite structure is cubic, the structure shown on the right side of Figure 4. The undeformed Martensite phase is the same size and shape as the cubic Austenite phase on a macroscopic scale, so that no change in size or shape is visible in shape memory alloys until the Martensite is deformed.

Fig. 7. The Martensite and Austenite phases

Fig. 8. Microscopic and Macroscopic Views of the Two Phases of Shape Memory Alloys

The temperatures at which each of these phases begin and finish forming are represented by the following variables: M_s , M_f , A_s , A_f . The amount of loading placed on a piece of shape memory alloy increases the values of these four variables as shown in Figure 9. The initial values of these four variables are also dramatically affected by the composition of the wire (i.e. what amounts of each element are present).

Fig. 9. The Dependency of Phase Change Temperature on Loading

Fig. 10. Microscopic Diagram of the Shape Memory Effect

2.7 Shape memory effect

The shape memory effect is observed when the temperature of a piece of shape memory alloy is cooled to below the temperature M_f . At this stage the alloy is completely composed of Martensite which can be easily deformed. After distorting the SMA the original shape can be recovered simply by heating the wire above the temperature A_f . The heat transferred to the

wire is the power driving the molecular rearrangement of the alloy, similar to heat melting ice into water, but the alloy remains solid. The deformed Martensite is now transformed to the cubic Austenite phase, which is configured in the original shape of the wire.

The Shape memory effect is currently being implemented in:

- Coffepots
- The space shuttle
- Thermostats
- Vascular Stents
- Hydraulic Fittings (for Airplanes)

Shape Memory Effect (SME) is a unique property of certain alloys exhibiting martensitic transformation. Even though the alloy is deformed in the low temperature phase, it recovers its original shape upon heating to a critical temperature known as the Reverse Transformation Temperature (RTT). They are most commonly Nitinol, or nickel and titanium combined. Less popular but still possessing the shape memory effect are gold cadmium, silver cadmium, copper-aluminum-nickel, copper tin, copper zinc, and copper-zinc-aluminum. The same alloys have another unique property called superelasticity (SE) at a higher temperature. It is a large (0-18%) nonlinear recoverable strain upon loading (stretching) and unloading (unstretchiung).

The basic one-way shape memory effect-The actual mechanism of the shape memory effect can be described simply as a reversible, thermoelastic, phase transformation between a parent austenitic phase and a martensitic phase. The phase transformation occurs when a material in the austenitic phase is cooled below the martensite start temperature (M_s), where the two phases coexist. The material must then accommodate the two phases without changing shape through a mechanism called twinning. This is where mirror-image lattices form adjacent to the parent lattices. The phase transformation is completed upon reaching the martensite finish temperature (M_f). The material can then be plastically deformed into another shape. During this deformation the twinned martensite is converted to a deformed martensite. The material remains deformed until it is heated to the austenite start temperature (A_s), and at this point the martensite begins to transform back into austenite. Heating above the austenite finish temperature (A_f) allows the material to regain its original shape. (The extent to which the shape is regained usually depends on the type of SMA, amount of deformation, and the material's thermomechanical history.) When cooled again the material does not automatically revert to the deformed shape. This is called the oneway shape memory effect. The entire shape memory process can be repeated.

2.8 Advantages and disadvantages of shape memory alloys

Some of the main advantages of shape memory alloys include:

- Bio-compatibility
- Diverse Fields of Application
- Good Mechanical Properties (strong, corrosion resistant)

There are still some difficulties with shape memory alloys that must be overcome before they can live up to their full potential. These alloys are still relatively expensive to manufacture and machine compared to other materials such as steel and aluminum. Most SMA's have poor fatigue properties; this means that while under the same loading conditions (i.e. twisting, bending, compressing) a steel component may survive for more than one hundred times more cycles than an SMA element.

2.9 Applications for shape memory alloys

Bioengineering:

Bones: Broken bones can be mended with shape memory alloys. The alloy plate has a memory transfer temperature that is close to body temperature, and is attached to both ends of the broken bone. From body heat, the plate wants to contract and retain its original shape, therefore exerting a compression force on the broken bone at the place of fracture. After the bone has healed, the plate continues exerting the compressive force, and aids in strengthening during rehabilitation. Memory metals also apply to hip replacements, considering the high level of super-elasticity. The photo above shows a hip replacement.

Reinforcement for Arteries and Veins: For clogged blood vessels, an alloy tube is crushed and inserted into the clogged veins. The memory metal has a memory transfer temperature close to body heat, so the memory metal expands to open the clogged arteries.

Fig. 11.

Dental wires: used for braces and dental arch wires, memory alloys maintain their shape since they are at a constant temperature, and because of the super elasticity of the memory metal, the wires retain their original shape after stress has been applied and removed.

Fire security and Protection systems: Lines that carry highly flammable and toxic fluids and gases must have a great amount of control to prevent catastrophic events. Systems can be programmed with memory metals to immediately shut down in the presence of increased heat. This can greatly decrease devastating problems in industries that involve petrochemicals, semiconductors, pharmaceuticals, and large oil and gas boilers.

Fig. 12.

Tubes, Wires, and Ribbons: For many applications that deal with a heated fluid flowing through tubes, or wire and ribbon applications where it is crucial for the alloys to maintain their shape in the midst of a heated environment, memory metals are ideal.

3. Applications of smart materials

- Piezoelectric materials - These ceramics or polymers are characterized by a swift, linear shape change in response to an electric field. The electricity makes the material expand or contract almost instantly. The materials have potential uses in actuators that control chatter in precision machine tools, improved robotic parts that move faster and with greater accuracy, smaller microelectronic circuits in machines ranging from computers to photolithography printers, and health-monitoring fibers for bridges, buildings, and wood utility poles.
- Electrostrictive and magnetostrictive materials - This refers to the material quality of changing size in response to either an electric or magnetic field, and conversely, producing a voltage when stretched. These materials show promise in applications ranging from pumps and valves, to aerospace wind tunnel and shock tube instrumentation and landing gear hydraulics, to biomechanics force measurement for ortho-pedic gait and posturography, sports, ergonomics, neurology, cardiology, and rehabilitation.
- Rheological materials - Smart materials encompass not only solids but also fluids, electrorheological and magnetorheological fluids that can change state instantly through the application of an electric or magnetic charge. These fluids show promise in shock absorbers, dampers for vehicle seats and exercise equipment, and optical finishing.
- Thermoresponsive materials - Shape memory alloys, the dominant smart material, change shape in response to heat or cold. They are most commonly Nitinol, or nickel and titanium combined. Less popular but still possessing the shape memory effect are gold cadmium, silver cadmium, copper-aluminum-nickel, copper tin, copper zinc, and copper zinc aluminum. They are useful in couplers, thermostats, automobile, plane and helicopter parts.
- pH-sensitive materials - The most interesting of these are indicators that change colors as a function of pH, and show promise in paints that change color when the metal beneath begins to corrode.
- Electrochromic materials - Electrochromism is defined as the ability of a material to change its optical properties when a voltage is applied across it. These materials are used as antistatic layers, electrochrome layers in LCDs (liquid crystal displays), and cathodes in lithium batteries.
- Fullerenes - Spherically caged molecules with carbon atoms at the corner of a polyhedral structure consisting of pentagons and hexagons. In one application of fullerenes as a smart material, they are embedded into sol-gel matrices to enhance optical limiting properties.
- Smart gels - Engineered response gels that shrink or swell by a factor of 1000, and that can be programmed to absorb or release fluids in response to almost any chemical or physical stimulus. These gels are used in many applications in agriculture, food, drug delivery, prostheses, cosmetics, and chemical processing.

4. The future for smart materials-

The development of true smart materials at the atomic scale is still some way off, although the enabling technologies are under development. These require novel aspects of nanotechnology (technologies associated with materials and processes at the nanometre scale, 10^{-9}m) and the newly developing science of shape chemistry.

Worldwide, considerable effort is being deployed to develop smart materials and structures. The technological benefits of such systems have begun to be identified and, demonstrators are under construction for a wide range of applications from space and aerospace, to civil engineering and domestic products. In many of these applications, the cost benefit analyses of such systems have yet to be fully demonstrated.

The Office of Science and Technology's Foresight Programme has recognised these systems as a strategic technology for the future, having considerable potential for wealth creation through the development of hitherto unknown products, and performance enhancement of existing products in a broad range of industrial sectors.

The core of Yanagida's philosophy of ken materials is such a concept. This is 'techno-democracy' where the general public understand and 'own' the technology. Techno-democracy can come about only through education and exposure of the general public to these technologies. However, such general acceptance of smart materials and structures may in fact be more difficult than some of the technological hurdles associated with their development.

5. Conclusion

Smart materials are poised to emerge from the laboratory of medical, defence and industrial applications. Understanding and using these advanced materials in new product development efforts may make the difference between success and failure in today's intensely competitive markets.

It's the profile job of the technocrats and management personnel to find out the promising materials for specific applications-when the use of smart memory alloys is to be replaced by a smart polymer, the primary laboratories and companies who are developing these materials, to identify the key researchers and engineers in those fields. With smart materials research taking place in hundreds of public and private sector labs across the globe, to get them available at once is difficult – yet they are vital for the advancement of technology and to profit from new developments in this fast moving field.

The concept of engineering materials and structures which respond to their environment, including their human owners, is a somewhat alien concept. It is therefore not only important that the technological and financial implications of these materials and structures are addressed, but also issues associated with public understanding and acceptance.

There are many possibilities for such materials and structures in the man made world. Engineering structures could operate at the very limit of their performance envelopes and to their structural limits without fear of exceeding either. These structures could also give maintenance engineers a full report on performance history, as well as the location of defects, whilst having the ability to counteract unwanted or potentially dangerous conditions such as excessive vibration, and effect self repair. The Office of Science and Technology Foresight Programme has stated that 'Smart materials will have an increasing range of applications (and) the underlying sciences in this area must be maintained at a

standard which helps achieve technological objectives', which means that smart materials and structures must solve engineering problems with hitherto unachievable efficiency, and provide an opportunity for new wealth creating products.

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