DR. RUPA DASGUPTA
Sr. Principal Scientist, CSIR - AMPRI

Designing Shape Memory Materials for the Future

Most familiar engineering materials and structures are 'dumb'. They are at best pre-processed and/or designed to offer optimised response to external stimuli to which such a material or structure is exposed. 'Dumb' materials and structures contrast sharply with the natural world where animals and plants have the clear ability to adapt to their environment in real time which involves the capability to sense their environment, process this data, and respond. The natural world is full of examples including the ability of plants to adapt their shape in real time; for example, to allow leaf surfaces to follow the direction of sunlight; limping, which is essentially a real time change in the load path through the structure to avoid overload of a damaged region; reflex to heat and pain and the like. These have much to teach on the design of future manmade materials where engineering materials need to be made 'smart' by exploiting some of its inherit characteristics. For example, an engineering structure would be truly 'smart' or can be said to have intelligent response, if a flexible structure can be designed to adapt its form in real time to minimise the effects of an external force, thus avoiding catastrophic collapse.

'Smart materials' refer to a class of materials that are able to respond dynamically to selected external stimulus and in addition to sensing, have functions that can be used for a wide range of engineering and commercial applications. These are classified based on their response to the external stimulus and include:

- Piezoelectric materials are materials that produce a voltage when stress is applied and vice versa.
- Shape memory alloys and shape memory polymers are thermo-responsive materials where deformation can be induced and recovered through temperature changes.
- Magnetic shape memory alloys are materials that change their shape in response to a significant change in the magnetic field.
- pH-sensitive polymers are materials which swell/collapse when the pH of the surrounding media changes.
- Halochromic materials change their colour as a result of changing acidity.
- Chromogenic systems change colour in response to electrical, optical or thermal changes.
- Non-Newtonian fluid is a liquid which changes its viscosity in response to an applied shear rate.
- Ferrofluid

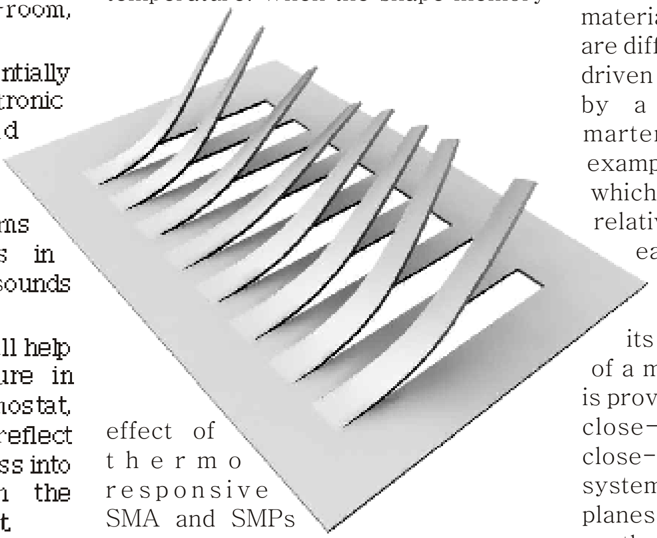
Such materials are used for making 'Sensual' devices and structures in the manmade world. There are many applications for such devices which include:

- Engineering structures could operate at the limit of performance and structural levels without fear of exceeding either while having the ability to counteract unwanted or potentially dangerous conditions and could give a full report on performance history, as well as the location of defects, etc.

- 'Sensual' devices can sense their environment and generate data for use in health and usage monitoring systems (HUMS). This would minimize the overheads associated and allow systems to be used for more time before human intervention is required.
- Monitoring of civil/aviation engineering structures to assess durability.
- Domestic applications in food packaging for monitoring safe storage.
- Adaptive materials can be made which will have the capability to move, vibrate, and exhibit a multitude of other real time responses.
- Develop smart car seats that can identify primary occupants and adapt to their preferences for height, leg-room, back support, and so forth.
- Mechatronics relating essentially to hybrid mechanical and electronic systems where sensing and actuation occurs at the atomic or molecular level.
- Sensor and actuator systems which will counteract noises in airplane cabins and dampen sounds emitted by submarines.
- Electro-chromatic glass will help maintain a constant temperature in buildings. Attached to a thermostat, this active material could either reflect solar heat or allow the heat to pass into the building, depending on the temperature needs of the moment.
- Smart fluids that can change viscosity quickly will allow development of simpler, more reliable exercise equipment.
- Shape-memory alloys will allow construction of more comfortable and lighter bullet-proof vests.
- The future of stereophonic sound will be altered with the use of smart materials. Developing ultra-high-fidelity stereo speakers using piezoelectric actuators, which expand and contract in thousandths of a second in response to applied voltage is in progress which is aimed at turning whole house walls or car interiors into speakers by imbedding them with the tiny actuators.
- Smart polymer / gels that experience reversible phase transitions to external stimuli such as temperature, solvent composition, pH, chemicals, and light have attracted special attention to develop smart textiles by grafting the copolymerization of environment-responsive polymers (ERP) onto the surface of fabrics.

Some of the above mentioned applications are in vogue but most are still in the dream of engineers and researchers. Needless to mention, with the help of the above smart materials it would be possible to incorporate features of safety, durability, and convenience that are the goals of today's researchers.

Shape memory materials (alloys or polymers) are a type of smart materials that which change their shape due to temperature. When the shape memory effect of thermo responsive SMA and SMPs is correctly harnessed, the material becomes a lightweight, solid-state alternative to conventional actuators such as hydraulic, pneumatic, and motor-based systems using the pseudo-elastic properties of the metal during the high temperature phase. Depending on the requirement, these materials are required in different forms and shapes varying from wires, rods/plates or thin films on desired substrates. The alloys that exhibit so-called "shape memory" can undergo surprisingly large amounts of strain and then, upon temperature increase or unloading, revert to their original shape thus imparting actuating properties. Shape Memory materials has been in the forefront of research worldwide since half a century now. Many applications exist for these alloys in different sectors including general engineering, automobile, aerospace, military, medical, safety and robotics applications.



Shape Memory Effect is exhibited due to reversible phase transformation when subjected to appropriate thermal procedure. The reversible transformation involves austenite - to -martensite during cooling and martensite - to - austenite transformations during heating. The phase change is associated with a shape change also giving rise to Pseudoelasticity. This leads to interesting and useful effects, such as a capacity to cycle a component between two different macroscopic shapes by cycling the temperature and are commonly known as Shape Memory effect exhibited by shape memory materials. Martensitic transformations are diffusionless shear transformations driven by mechanical deformation or by a change in temperature. A martensitic transformation is an example of a displacive transition, in which there is cooperative motion of a relatively large number of atoms, each being displaced by only a small distance (a fraction of an interatomic spacing) relative to its neighbours. A simple example of a martensitic phase transformation is provided by the transition from cubic close-packed (ccp) to hexagonal close-packed (hcp). This occurs by the systematic sliding of close-packed planes, ie {111}planes in ccp, over one another. As it happens, the same kind of sliding (in the same direction and by the same distance) can also lead to formation of a twin (ie the same ccp crystal structure, but in a different orientation). A twin is formed when every (111) plane undergoes this displacement, relative to the plane below it, whereas the hcp structure is created when every second (111) plane does this.

The same effect can be induced by loading when it is termed Superelasticity (SE), sometimes termed "pseudo-elasticity" or "pseudo-plasticity", which occurs without any change in temperature. SE takes place at temperatures above As - although usually only slightly above - where the austenitic phase is the more stable of the two thermodynamically, although marginally. When a mechanical strain is imposed, this can stimulate the transformation of austenite to martensite, sometimes termed “stress-induced martensite”. The associated shear of local regions accommodates the imposed macroscopic shape change, while the lower strain energy component ensures that the overall free energy is now lower than it would be if the austenitic phase were still predominant. Relatively large strains (up to about 8%) can be accommodated in this way. As the strain is increased, the proportion of the specimen that has transformed to martensite progressively rises.

The characteristics of SMMs can be used for a number of applications like:

❖ Free recovery applications (e.g. blood-clot filters) Shape memory element causes strains :

● One-way memory effect. The sample is deformed and unloaded at a temperature below Mf. The residual deformation is restored during heating to a temperature above Af.

● The two- way memory effect. A spontaneous shape change occurs during cooling to a temperature below Mf. This shape change is recovered during subsequent heating to a temperature above Af.

❖ Constrained recovery applications (e.g. hydraulic couplings)

● SMA element prevented from recovering, i.e. generation of shape recovery stresses.

❖ Force actuators (e.g. fire safety valves)

● There is a motion against a bias force so work can be done by SMA element

❖ Proportional control (e.g. fluid flow control valve)

❖ Superelastic applications (e.g. eyeglass frames and guidewires for steering catheters into vessels in the body)

❖ Damping applications (e.g. automobile bumpers and earth-quake resistant structures).

There are a number of advantages in using SMAS in place of conventional actuators. They are:

(a) Simplicity, compactness and safety

● Additional parts suchas reduction gears not required

● Stroke and force easily modified by using right SMAs

● Actuator can be reduced to a single SMA wire: Example: An electrically activated SMA wire

(b) Clean, silent, spark-free and zero-gravity working conditions

● Dust particle generation avoided (So no friction in SMA elements)

● Dusty environment has no effect on performance of SMA elements

● Noiseless activation since no additional vibrating parts

● Work completely spark-free (So used in inflammable environments)

● Acceleration of only a few micro 'g' generated

● Smooth movement

(c) High power / weight ratio (or power / volume ratio)

● SMA actuators offer the highest ratio at low levels of weight(< 100g)

● So extremely attractive for microactuator technology

● Production of high quality and reliable thin foils on Ni-Ti difficult

● Thin films produced by magnetron sputtering and melt spinning

(d) Excellent corrosion resistance

(e) Biocompatibility

Shape Memory phenomena is exhibited by Ni-Ti, Cu-Al and some Fe-based alloys. Ni-Ti based shape memory alloys have to date provided the best combination of properties for most commercial applications; however they are very expensive.

Ni-Ti SMAs commonly known as Nitinol due to their excellent corrosion resistance, biocompatibility and magnetic resonance visibility and opacity to X-rays find applications in

● Orthopedic implants

● Cardiovascular devices

● Surgical instruments

● Orthodontic devices

● Endodontic files

The main method of making the alloys is through liquid and powder metallurgy ; however since the advantageous properties are very sensitive to the chemical composition care needs to be taken. In an attempt to further improve the properties and widen the scope of application, attempts are being made to fabricate them using advanced techniques like High pressure torsion (HPT) and the equal-channel angular pressing (ECAP), mechanical alloying and self sustained high temperature synthesis (SHS). Also making porous SMAs is being thought of in addition to conventional plate and wire solid SMAs.

In many applications, Cu-based alloys could provide a more economical alternative to Ni-Ti. In addition to cost factors, these shape memory alloys are being paid more attention due to their good shape recovery, easy fabrication, excellent conductivity of heat and electricity. Predominant among these are the Cu-Zn, Cu-Al alloys with and without ternary additions. Again, Cu-Zn based shape memory alloys have actually been used and Cu-Al based shape memory alloys have shown promise.

In addition to the shape memory, super elastic and pseudo elastic effects, these alloys also present a temperature memory effect (TME), which appears after an incomplete reverse MT. Taking advantage of the temperature memory effect, shape memory effect and high damping applications attainable in these alloys these can find commercial use in a wide variety of applications such as biomechanics, vibration control, medicine, industry and aerospace engineering. However, their applications are still limited for the shortcomings of thermal stability, brittleness and mechanical strength; these are closely related with microstructure characteristic of Cu-based shape memory alloys, such as coarse grain sizes, high elastic anisotropies and the congregation of secondary phases or impurities along the grain boundaries. Efforts are being made to overcome these drawbacks with the proper ternary additions that can improve the SME and thermal stability and also optimising the heat treatment cycles. Also alternate processing techniques like powder metallurgy and rapid solidification techniques were developed to fabricate fine grained Cu-based shape memory alloys. The following table gives the average properties of commercially available SMAs.

Property	Ni-Ti	Cu-Zn-Al	Cu-Al-Ni
Melting Point, °C	1250	1020	1050
Density, kg.m-3	6450	7900	7150
Electrical Resistivity, Ω.m.10-6	0.5-1.1	0.07-0.12	0.1-0.14
Thermal Conductivity at RT, W.m-1.K-1	10-18	20	75
Thermal Expansion Coefficient, K.10-6	6.6-10	17	17
Specific Heat, J.Kg.-1K-1	490	390	440
Transformation Enthalpy, J.Kg.-1	28000	7000	4000
Elastic Modulus, GPa	95	70-100	80-100
UTS Martensite, MPa	800-1000	800-900	1000
Fatigue Strength, MPa (N = 106)	350	15	8
Grain Size, m.10-6	20-100	50-150	30-100
Transformation Temp. Range (0C)	-100 to 110	-200 to110	-150 to 200
Hysteresis (K)	30	15	20
Max one-way memory (%)	7	4	6
Normal two-way memory (%)	3.2	0.8	1.0
Normal working Stress (MPa)	100 – 130	40	70
Normal number of thermal cycles	100000	10000	5000
Max Overheating Temp. (0C)	400	150	300
Damping Capacity (SDC%)	20	85	20
Corrosion Resistance	Excellent	Fair	Good
Biological Compatibility	Excellent	Bad	Bad

Inspite of the ability of Cu-Al-Ni shape memory alloys to operate in sensors and actuators operating at much higher than the working temperature of the widely used Ni-Ti shape memory alloys (around 100°C), large elastic anisotropy leads to intergranular fracture of polycrystalline Cu-Al-Ni alloys and finally to poor mechanical properties, rendering the alloy system unsuitable for widespread practical applications. Conventional casting method for synthesizing Cu-Al-Ni alloys suffers from the disadvantage of coarse grained structure with grain size as large as several millimetres. Thus, brittleness is a severe problem in the cast alloys due to the large grain size coupled with large elastic anisotropy. Several attempts have been made to improve the ductility of conventionally cast through grain refining by the addition of elements like Ti, Zr, Mn, B, Y,V and rare earths. However the beneficial effect of grain refinement is lost on use which involves annealing/heating. Processing of Cu-based shape memory alloys via powder metallurgy route opens up a way to produce fine-grained material with better chemical homogeneity and improved mechanical properties. In particular, mechanical alloying has emerged as a promising method to produce a variety of nanocrystalline and ultra-fine grained powders which have shown to possess better control over composition and chemical homogeneity as compared to their conventionally produced counterparts. Attempts have also been made to consolidate mechanically alloyed and pre-alloyed Cu-Al-Ni powders by pressureless sintering under inert atmosphere, hot isostatic pressing, hot extrusion, or a combination of these processes. Consolidation of mechanically alloyed Cu-Al-Ni alloy powder by vacuum hot pressing followed by extrusion of powder compacts could provide an alternative technique. Present shape memory alloys are limited to maximal Af temperatures of 120°C, M, generally being below 100°C. New designs have however revealed the need for materials that transform at much higher temperatures (above 150°C) or where the martensite remains stable if exposed for very long term at high temperatures, generally combined with high recovery stresses. However, a major breakthrough is not reported yet mainly because of the following problems: stabilisation of martensite, decomposition of the parent or martensite phase, brittleness, price.

The main drawback of Cu-based SMAs is that it cannot be used in a corrosive environment. Fe-based mainly Fe-Mn-Si alloys provide an alternative in such cases with additions of Co, Ni, Cr. Newer categories of SMAs are being developed. The following table gives the most commonly reported SMAs alongwith their transformation temperatures, alloying additions and lucrative properties envisaged.

Other than alloys, certain polymers also exhibit shape memory properties. The polymers used as SMP include thermoplastic polyurethanes (TPUs): The hard segment was based on 4,40-diphenylmethane di-isocyanate and 1,4-butanediol, poly(ε-caprolactone) based SMP, polyesterpolyol series of

Alloy	As Temp., 0C	Alloying Element	Reasons for Alloying Additions
Fe-Mn-Si	15-200	Co, Ni, Cr	• Corrosion resistance
Cu-Al-Ni	100-200	Mn, Ti, B, Zr	• Machinability • Control transformation temperatures • Grain refinement • Ductility
(Ni-X) –Ti	150-500	X= Pt, Pd, Au, Rh, B	• Increase transformation temperatures • Reduce grain size • Strength
Ni-(Ti-X)	120-350	X=Hf, Zr	• Increase transformation temperatures
Ni-Al	100-600	Cu, Co, Ag, Fe, Co, Mn, B	• Increase transformation temperatures • Ductility
500-750	Ni-Mn	Al, Ti, Cu for Ni, Mg, Al, Si, Ti, V, Sn, Cr, Fe, Mo for Mn	• Decrease Ms • Increase SME
Zr-based intermetallics	200-900	Ti, Ni	• Ductility

polyurethane SMP, MMA crosslinked with PEGDMA, polyurethane SMP prepared from diphenylmethane-4,4_-diisocynate, adipic acid, ethylene oxide, polypropylene oxide,1,4-butanediol, and bisphenol, Styrene-based resin & cross linked Styrene. Significant work is going on SMP in the area of bio medical activities however comparatively less work is reported in International Journals for engineering applications. The low stiffness of SMP resins produces a relatively small recovery force in a temperature change process. Insulating tendency also restrict its response to temperature. Functional fillers and reinforcements like carbon black (CB), Short Carbon Fibres (SCF), Hydroxy apatite (HA), AIN hold potential to improve the conductivity of SMP and an improvement in glass transition temperature. Different compositions and dispersive methods are being employed to have a breakthrough to have recovery stress more than 3 MPa of present that has been commonly reported.

A major problem with SMMs is its degradation and fatigue since the reliability of SMA devices depends on its lifetime performance which is influenced by factors both external including like time, temperature, stress, strain, strain rate and no. of cycles and internal like alloy system, alloy composition, heat treatment and processing. The basis of selecting an SMA is maximum recovery strain and maximum recovery stress which in reality have an inverse proportion.

Shape Memory Alloys are characterized mainly by :

❖ Differential Scanning Calorimetry which is the most direct method giving the heat absorbed and given off by the sample as it is heated and cooled through the transformation range is measured. Endothermic and exothermic peaks are observed as the sample absorbs and releases heat due to the transformation indicating the transformation temperatures.

❖ Resistivity Measurement : this is also often used in which resistivity changes as the sample is heated and cooled again due to phase transformations.

❖ Strain Measurement by Standard Tension Test. This is a direct method of measuring the Pseudoelasticity wherein a constant stress is applied to the sample and cycled through the transformation range while measuring the strain that occurs during the transformation in both directions.

The worldwide smart materials market was around $8.1 billion in 2005 and was expected to rise at an average annual growth rate (AAGR) of 8.6%. Of this, the piezo-smart materials account for practically 50% of the total smart material market followed by the need for bio-mimetic.

The average annual growth rates for thermo-responsive materials is in the double digit. Currently the bio-mimetic and thermo-responsive categories account for nearly 30% and 15% of the total smart material market respectively leaving a lot of scope for further development.

❍❍❍