Research Potential in Thermo Responsive Shape Memory Materials : CSIR-AMPRI's Initiatives

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Thermo responsive shape memory materials (SMMs) are novel materials falling under the category of Smart Materials having the ability to return to its original shape in response to temperature. These can be either Shape Memory Alloys (SMAs) or Shape Memory Polymers (SMPs). The key characteristic responsible for this behaviour of all SMAs is the occurrence of a martensitic phase transformation which is a shear-dominant diffusion less solid-state phase transformation occurring by nucleation and growth of the martensitic phase from a parent austenitic phase. When an SMA undergoes a martensitic phase transformation, it transforms from its high-symmetry, usually cubic, austenitic phase to a low-symmetry martensitic phase. Parent and product phases coexist during the phase transformation. Since the crystal lattice of the martensitic phase has lower symmetry than that of the parent austenitic phase, several variants of martensite can be formed from the same parent phase crystal.

The martensitic transformation occurs when the free energy of martensite becomes less than the free energy of austenite at a temperature below a critical temperature T_0 at which the free energies of the two phases are equal. However, the transformation does not begin exactly at T_0 but, in the absence of stress, at a temperature M_s(martensite start), which is less than T_0. The transformation continues to evolve as the temperature is lowered until a temperature denoted M_f(martensite finish) is reached. Similarly, during the heating cycle, the reverse transformation (martensite-to-austenite) begins at the temperature A_s (austenite start), and ends at A_f (austenite finish) when the material is fully austenite.

Due to the displacive character of the martensitic transformation, applied stress plays a very important role. During cooling of the SMA material below temperature M_s in absence of applied stresses, the variants of the martensitic phases arrange themselves in a self-accommodating manner through twinning, resulting in no observable macroscopic shape change; but applying mechanical loading to force martensitic variants to reorient (detwin) into a single variant, large macroscopic inelastic strain is obtained. After heating to a higher temperature, the low-symmetry martensitic phase returns to its high-symmetry austenitic phase, and the inelastic strain is thus recovered. Again, martensitic phase transformation can also be induced by pure mechanical loading while the material is in the austenitic phase, in which case detwinned martensite is directly produced from austenite by the applied stress (Stress Induced Martensite) at temperatures above M_s.

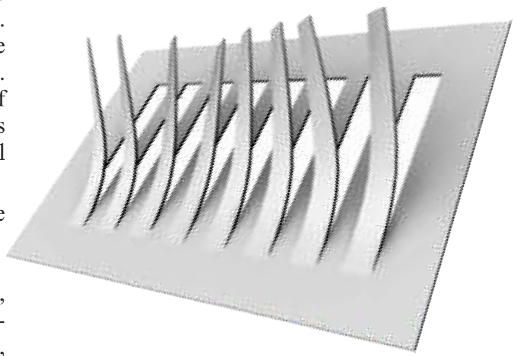
The key effects of SMAs associated with the martensitic transformation induced by temperature or stress, which are observed according to the loading path and the thermo-mechanical history of the material are: pseudoelasticity, one-way shape memory effect and two-way shape memory effect.

The transformation temperatures exhibited by shape memory alloys are highly dependent on their composition. Little change in their composition will result in large changes in their transformation temperatures. The advantage of being able to change the transformation temperature by changing the composition is that the material can be tailored to attain the desired phase at the application temperature. There are several means of measuring the transformation temperatures of SMA alloys. The two most common methods of measuring the transformation temperatures are by electrical resistivity and differential scanning calorimetry (DSC) measurements.

There are about twenty elements in the central part of the periodic table whose alloys exhibit shape memory like Ag-Cd, Au-Cd, Cu-Al-Ni, Cu-Al-Mn, Cu-Au-Zn, Cu-Sn, Cu-Au-Sn, Cu-Zn, Cu-Zn-Al, Cu-Zn-Sn, Cu-Zn-Ga, Cu-Zn-Si, In-Ti, Ni-Al, Ni-Ti, Fe-Pt, Fe-Pd, etc. However, mainly three alloy systems generally known to exhibit the Shape Memory phenomena have been the focus of research and development. They are Ni-Ti, Cu-Al and Fe based alloys. Of these, the Ni-Ti based alloys are commercially available and the most used mainly for biomedical applications due to their excellent biological compatibility. In other applications, Cu-based SMAs would be preferred over Ni-Ti ones due to its low cost. Cu-based SMAs are in the forefront of R&D since many decades now, yet their commercial availability is poor across the world.

When the shape memory effect of thermo responsive SMAs 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 material during the high temperature phase. The areas where SMAs can be applied are ever increasing utilizing the mechanical energy resulting from the shape transformations. The areas of application now include low to high end products in engineering and medical sectors.

Developmental activities in SMAs is not very new; however there are a number of areas that are still emerging as potential areas for R&D with capability to develop materials with better shape memory properties in terms of superior transition temperature, mechanical properties, fluid flow capability and new materials. In recent years, attention is being paid to synthesis of (i) newer class of SMAs (ii) develop cost effective and more sensitive SMAs (iii) improve the transition temperature and performance of already existing SMMs through proper composition, heat treatment etc. (iv) fabrication of new SMAs like thin films, porous and amorphous/nano crystalline types and (v) fabrication of SMAs with temperature memory effect (TME), which appears after an incomplete reverse MT. This effect is characterized by a neat delay of the thermally induced transformation to higher temperatures where an additional calorimetric peak appears.

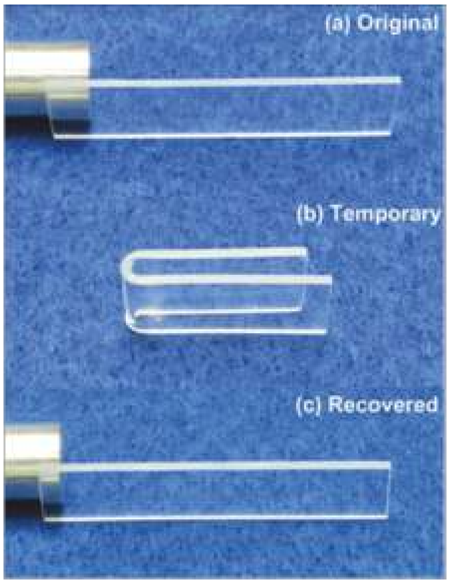


Methods of Making Shape Memory Alloys and Thermo Mechanical Processing:

Shape memory alloys are conventionally made either through liquid or powder metallurgy routes unless single crystals have been grown. In the liquid metallurgy route which has been more commonly used, usually an induction furnace has been used and melting was carried out either in vacuum or in an inert atmosphere like Argon. In most cases, purity levels of metals used is high as the chemical composition plays a major role in the expected shape memory properties and transformation temperatures. Powder Metallurgy is used to produce near net shape alloy products as this has better controllability on the composition and grain size. In the case of making the alloys through powder metallurgy route, premixed elemental powder mixtures in the ratio of the designed alloy are used. Care is taken to select the median size and purity of the powders. In most cases, the elemental Cu and Ni powders are annealed in an H_2 atmosphere at 600ºC for 30 minutes to reduce the surface oxides present on the powder. Ball milling is applied to convert the elemental powder mixtures of Cu, Al and Ni into prealloyed powders; ordinary ball milling is being replaced by high energy planetary ball milling to obtain better properties. The milling time affects the final composition and particles size. The elemental powder mixture was cold compacted in dies. The green compacts are sintered usually in a stepwise manner and preferably in a hydrogen atmosphere. However, SMAs are invariably used in the wire or sheet form made from cast alloys either through powder metallurgy or liquid metallurgy as discussed above. For making sheets, homogenized alloys are hot-forged and finally cold-rolled into thin plates. The plates are then heated to relieve stress created by forging and rolling/drawing. Cold rolling is carried out in steps down to the required thickness corresponding to a definite reduction ratio, which varies according to the machine used and requirement; in between the different rolling procedures the material is solution treated. For wire drawing, ingots are usually hot rolled to a given size. The obtained specimens were then cold-drawn down to a diameter corresponding to an expected reduction ratio with annealing in α (face-centered cubic, fcc) + β (body centered cubic, bcc) region. Shape memory properties are attained only in the presence of the martensitic phase. To attain the desired phase, quenching is to be performed from the region in the phase diagram of the particular alloy system where the martensitic phase(s) are formed. The ageing temperature and time needs to be optimised to retain only the martensitic phase so that SM properties are observed. In most cases, the final wire or sheet is subjected to the heat treatment cycle to retain/attain the shape memory properties.

The Shape Memory Effect:

Shape memory effect results from a displacive, first-order phase transition called martensitic transformation, which is one of the most interesting variants of structural phase transition in solids. The so-called “shape memory effects” are the direct result of thermoelastic martensitic transformation. In this kind of transformation, a balance is struck between chemical free energy change which accompanies the transformation and the elastic energy built up around the martensite crystallites. The parent-to-product transformation can be induced by either decreasing the temperature or applying a stress on the specimen. In the early stages of the transformation, martensite plates form in the specimen and grow continuously through the specimen as the temperature decreases or stress increases. When temperature is increased and/or the stress is removed, the



plates formed during the transformation shrink away to reform the original parent phase. Shape memory behaviour is characterised by stress free recovery experiments where the specimen is deformed in martensite, unloaded, and then allowed to recover its shape upon heating under no external stress. The forward and reverse thermoelastic transformation behaviour has been studied by voltage measurement.

Training for SM Property:

The shape memory effect is exhibited either one way or two way. The two-way shape-memory effect is the effect that the material remembers two different shapes: one at low temperatures and one at the high-temperature shape i.e. the material shows a shape-memory effect during both heating and cooling is called two-way shape memory. This can also be obtained without the application of an external force (intrinsic two-way effect). The reason the material behaves so differently in these situations lies in training. Training implies that a shape memory can "learn" to behave in a certain way. Under normal circumstances, a shape-memory alloy "remembers" its high-temperature shape, but upon heating to recover the high-temperature shape, immediately "forgets" the low-temperature shape. However, it can be "trained" to "remember" to leave some reminders of the deformed low-temperature condition in the high-temperature phases. There are several ways of doing this. A shaped, trained object heated beyond a certain point will lose the two-way memory effect; this is known as "amnesia". In most cases, shape memory alloys are supplied as raw materials, i.e. without shape memory. Various training methods have been proposed which include:

1. To memorize a certain shape, heat treatment is normally required. This is usually done by fixing the shape memory alloy into a required shape and then heating it up for a certain period of time at a high temperature. After this, one-way shape memory alloy is formed. Next, same procedure is repeated again but with different clamped shape of SMA and different heat treatment time. This is training TWSMA by reheat treatment. In general, either thermal/mechanical cycling or severe (plastic) deformation is essential. From fabrication and stability points of view, they are either non-convenient or have a lack of reliability. Shape-setting occurs in a furnace. To shape-set in a furnace by placing the fixture in the chamber prior to turning on the oven, heating the oven to the desired temperature, holding it for optimised time and allowing the oven to cool over several hours. Because this approach unavoidably holds the wire at high temperature for long periods of time, the result was a brittle wire that weakly exhibited the shape memory effect.

2. An alternative approach to shape-setting involves resistive heating. Using high currents (3 - 5 A), the wire can be heated on ceramic fixtures; when a wire that has been shape-set and straightened is heated above the transformation temperature, the location of the curves is evident although the exact shape that was set is not fully recovered. In this case perhaps the wire does not heat evenly as the ceramic fixture acts as a heat sink. The advantage of this process is that the shape training can be completed easily if power supplies are available and, if proper precautions are taken, the safety risk is much lower.

3. A uniaxial two way shape memory effect can be induced in wire specimens by thermo mechanical training. The wire specimens were thermally cycled through the temperature range of phase transformation under a constant load that has been applied at room temperature. Heating was done by direct passage of current, cooling and pressurized air. The change in length during the transformation cycles was measured using chemical edges for micro strain measurement with strain gauge. Length and temperature are continuously recorded. After training, the specimen is unloaded and the shape change upon free thermal cycling – representing the induced intrinsic TWSME- determined.

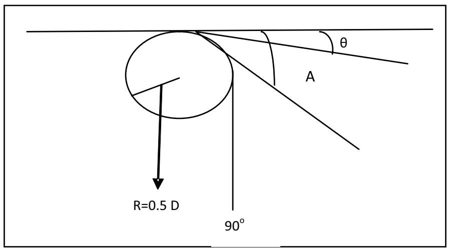
4. The simplest of methods for laboratory studies where the specimen (wire/thin sheet of Cu-bases SMA) is uniformly fixed by bending up into 'U' shape on a mound with requisite diameter and thermal cycling conducted between boiling water and 12C water i.e. the sample underwent constrained cycling training. After a certain number of training cycles, the sample relieving the constraint was put into boiling water for 8 hours aging.

Evaluation of SM Property:

The shape memory ratio, η, of the alloy is measured by bending the strip to 90° around a circular cylinder at room temperature and then heated above the Af temperature. The residual angle was then measured. The shape memory ratio, η, and the maximum deformation strain, ε, can be calculated by:

$$\eta = (1- \theta/90) \times 100\%; \varepsilon = [t/(D+t)] \times 100\%$$

where θ is residual angle after the sample is heated above the Af temperature, t is the specimen thickness and D is the diameter of the cylinder, i.e. the diameter of curvature. The sketch of recovery measuring is shown below.



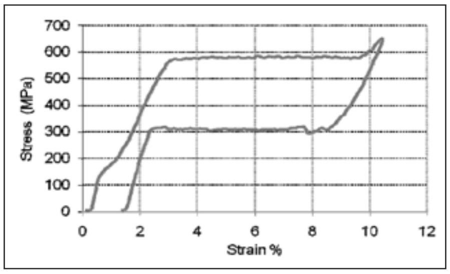
Pseudoelasticity and Temperature Memory Effect:

Pseudo-elasticity is another phenomenon exhibited by SMMs. It occurs in shape memory alloys when the alloy is completely composed of Austenite (temperature is greater than Af). Unlike the shape memory effect, pseudo-elasticity occurs without a change in temperature. The load on the shape memory alloy is increased until the Austenite becomes transformed into Martensite simply due to the loading. The loading is absorbed by the softer Martensite, but as soon as the loading is decreased the Martensite begins to transform back to Austenite since the temperature of the wire is still above Af, and the wire springs back to its original shape. In the pseudoelastic condition SMAs can undergo nonlinear deformations under loading that can be recovered on subsequent unloading. This ability of the material to exhibit large recoverable strains is attributed to a mechanism called "stress induced martensite transformation". A typical stress-strain plot obtained on a pseudoelastic alloy in a complete loading cycle is shown below. It is seen that the threshold stress values at the apparent yield point associated with the onset of stress induced transformation during loading and its reversal during unloading are not the same, causing a large hysteresis in the response curve. The presence of such a hysteresis indicates that a significant dissipation of energy takes place during such a loading-unloading process leading to the expectation that a pseudoelastic alloy could function as an effective damping material for incorporation in structures prone to seismic vibrations. Problems Associated with SMAs:

There are mainly two types of problems generally associated with SMMs.

(i) Shape Memory Fatigue: The main issue of concern of the potential offered by the thermo-mechanical properties of shape memory materials is the long-term predictability of the material behaviour and the fatigue lifetime of the macro structural elements arising from repeated use of the shape-memory effect may lead to a shift of the characteristic transformation temperatures. This effect is known as functional fatigue, as it is closely related with a change of microstructural and functional properties of the material.

(ii) Stabilization of Martensite: The plateau region of the stress-strain graph shows the region of recoverable strain in an SMA. This strain is accommodated in the martensite



phase. The two common problems that hinder the commercial use of these SMAs are natural ageing and grain growth during thermo mechanical processing. Ageing in martensite, which is accompanied by a gradual change in physical properties, can result in loss of memory behaviour. Stabilization is directly related to disordering in martensitic state and the spacing differences (Δd) between selected pairs of diffraction planes reflect the degree of ordering in martensite. The natural ageing degrades the material and the affects the transformation temperature. They also have the very large grain size which makes them essentially very ductile but the addition of grain refiners can solve this problem. To increase the strength some alloying additions are made like cobalt, titanium, vanadium and boron. These additions keep the grain size low and hence improve the mechanical properties. However, the amount of these additions should be carefully monitored because it can disturb the structure which is responsible for shape memory effect.

Application Potential and Presently Available Commercial SMAs: If correctly harnessed, SMMs becomes a lightweight, solid-state alternative to conventional actuators such as hydraulic, pneumatic, and motor-based systems using the pseudo-elastic properties of the material during the high temperature phase. The areas where these can be applied are ever increasing utilizing the mechanical energy resulting from the shape transformations. The areas of application now include low to high end products in engineering and medical sectors. The many uses and applications of shape memory alloys ensure a bright future for these materials and with innovative ideas for applications, the number of products on the market using such materials is continually growing. The range of applications for SMAs has increased in recent years; the medical, aerospace and marine industries are the largest consumers of shape memory components. However, the medicinal applications are restricted to Ni-Ti alloys due to its excellent bio-compatability. However, there are many possibilities for thermo responsive SMMs in the manmade world to improve/add new dimension to its performance. These include:

- **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 affect self repair.

- **Smart Materials in Aerospace:**

Some materials and structures can be termed 'sensual' devices. These are structures that can sense their environment and generate data for use in health and usage monitoring systems (HUMS).

- **Smart Materials in Civil Engineering Applications:**

However, 'sensual structures' need not be restricted to hi-tech applications such as aircraft. They could be used in the monitoring of civil engineering structures to assess durability. This would influence the life costs of such structures by reducing upfront construction costs and by extending the safe life of the structure. 'Sensual' materials and structures also have a wide range of potential domestic applications, as in food packaging for monitoring safe storage and cooking.

- **Adaptive materials:**

Smart materials and structures offer the possibility of structures which not only sense but also adapt to their environment. Such adaptive materials and structures benefit from the sensual aspects highlighted earlier, but in addition have the capability to move, vibrate, and exhibit a multitude of other real time responses.

- **The automotive industry:**

Is eager to incorporate intelligent materials technology. Projects are being undertaken to develop smart car seats that can identify primary occupants and adapt to their preferences for height, leg-room, back support, and so forth. Technology also exists to enable cars to tell owners how much air pressure tires have, when oil changes are needed, and other maintenance information. Developing solid state and smart materials technologies will bring costs down.

- **Mechatronics:**

Mechatronics relating essentially to hybrid mechanical and electronic systems are smart materials, where sensing and actuation occurs at the atomic or molecular level.

- **Industrial**
  - Aircraft : use shape memory alloy that reduces aircraft's engine noise.
  - Piping: for better and leakfree fitment using the constraint property of the material.
  - Intelligent materials systems will enable composite structures to relay their life experiences, including stresses and weaknesses, and allow for a "graceful retirement."
  - Robotics : These materials in robotics, as they make it possible to create very light robots.
  - Medicine
    - Optometry
    - Dentistry
    - Blood-clot filter
    - Connection between intervertebral disc
    - Shape memory alloys are also applicable in medical accessories like in an example of Wagner's thermo-lock, where a shape memory spring is used to lock sterilization containers.
    - Actuated implantable drug delivery system Micro actuators
    - Defence: Shape-memory alloys will allow construction of more comfortable and lighter bullet-proof vests.

Future of SMMs:

Although developmental activities in SMMs is not very new; however there are a number of areas that are still emerging as potential areas for R&D with capability to develop materials with better shape memory properties in terms of superior transition temperature, mechanical properties, fluid flow capability and new materials. In recent years, attention is being paid to synthesis of (i) newer class of SMMs (ii) develop cost effective and more sensitive SMMs (iii) improve the transition temperature and performance of already existing SMMs through proper composition, heat treatment etc.

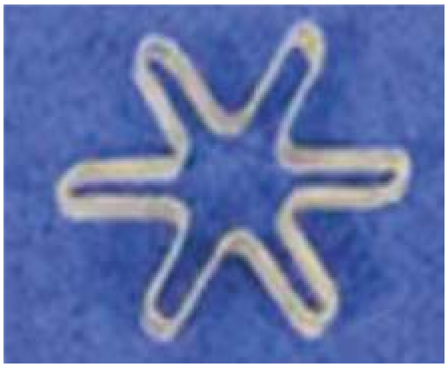
CSIR-AMPRI, Bhopal's Foray in R&D in SMMs:

In line with the R&D focus on an international scale CSIR-AMPRI, Bhopal has since a couple of years directed its R&D activities in the area of thermo-responsive shape memory materials with a focus on developing either new or improved materials of different varieties but pertaining to thermo responsive SMMs. The areas and focus of R&D is being directed to address problem areas in the mentioned areas identified after a thorough literature review. Keeping in mind the knowledge gaps and scope of research in the mentioned areas, the Institute has chalked out its research plan and deliverables in each field mainly with an objective to overcome the shortcomings and add scientific knowledge in each of the chosen areas to be as follows:

- **SMA Foam**: On SMA foam, even in international scenario, very limited literature is available and is the research stage. The polycrystalline SMAs have isotropic properties and have random orientation of the grains. These nullify some effects of its shape memory characteristics. SMA foams made of alloys having shape memory characteristics would have the advantage of reducing grain orientation by increasing the grain size as well as through proper orientation of the grains. In case of foams, the cell walls/cell edges are very thin and thus number of grains would be less and in these walls and edges, the grains will not be so randomly oriented. Because of less number of grains and less degree of randomness in grain structure, it is expected that SMA foam could give improved shape memory effect provided purity and proper phase transformation is ensured. In addition, the SMA foam will have the characteristics of variation of cell size and its overall size and shape which could be used for fluid flow controls, microsurgery, bone implants, sensors etc.

CSIR-AMPRI in its effort in synthesis and processing of closed cell and open cell SMA foam for impact and energy absorbers and insert for control fluid (liquid/gas) flow using liquid and powder metallurgy route aims to attain an optimised process for developing closed and open cell foams from both Cu-Al and Ni-Ti based alloy compositions with reproducible physical characteristics like uniform cell size [in the range of 0.1 to 2 mm], porosity [up to 70%] and shape memory properties with pseudo-elasticity ~3% along with thermal stability.

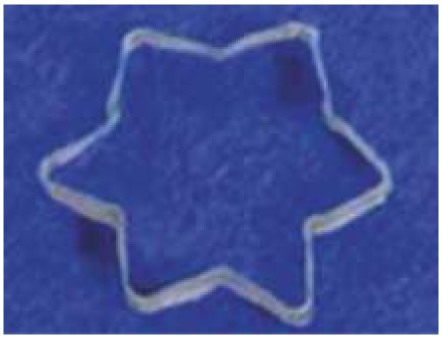
- **Cu-based SMAs through L/M & P/M routes:** In spite of the decades of research in the area of SMAs and their various industrial applications, some challenges still remain right from its synthesis. This is since the shape memory effect (pseudoelastic behaviour) of the alloys is very sensitive to chemical composition and microstructural features. Moreover, common contaminants such as



oxygen, carbon, and nitrogen can cause a dramatic shift in the transformation temperature while degrading the mechanical properties of the alloys. Further, cost presents a further barrier to SMA development. The presently available non ferrous SMAs find use only in high end products. The temperature up to which their pseudoelastic behaviour can be maintained needs to be enhanced.

CSIR-AMPRI in its effort in this direction aims to arrive at optimised alloys composition and heat treatment cycles to maximise the Shape Memory Effect [SME] and thermal stability in the wire and strip form for (i) Cu-Al-Ni system for improved mechanical properties (ii) Cu-Zn-Al for high transformation temperatures and (iii) Cu-Al-Mn series for compositions for high ductility.

- **Nano Structured Ni-Ti based SMAs through powder metallurgy**: Despite considerable efforts being made globally to produce nanostructured shape memory alloys through different routes, R&D activities in India in this context are not much reported. This suggests the need to direct R&D efforts towards generating research expertise in the area of nano



structured SMAs in the country to tap the immense market potential in the near future. Worldwide very limited literature is available pertaining to the development of SMA based composites.

CSIR-AMPRI aims is to develop a novel, cost-effective process for the synthesis and subsequent processing of shape memory NiTi alloy and their composites containing TiC/TiB_2 particles for engineering application.

- **Carbon Nano Tube (CNT)/nano particles dispersed Shape Memory Polymers:**

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 process of temperature change. Insulating tendency also restricts its response to temperature. Short carbon fibres and carbon black have been reported to double the conductivity of SMPs and improve glass transition temperature. Different compositions and dispersion methods are being employed to have a breakthrough to have recovery stress more than 3 MPa that has been reported.

CSIR-AMPRI in its effort in attempts to improve recovery stress and switching efficiency of Shape Memory Polymers by reinforcing them uniformly with Carbon Nano Tube (CNT)/nano particles followed by thermo-mechanical programming to impart two-way training to the dispersed SMPs.