Shape memory alloys: a state of art review

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Abstract. Shape memory alloys (SMAs) are the special materials that have the ability to return to a predetermined shape when heated. When this alloy is in below transformation temperature it undergoes low yield strength and will deform easily into any new shape which it will retain, if this alloy is heated above its transformation temperature it changes its crystal lattice structure which returns to its real shape. SMAs are remarkably different from other materials are primarily due to shape memory effect (SME) and pseudoelasticity which are related with the specific way the phase transformation occurs, biocompatibility, high specific strength, high corrosion resistance, high wear resistance and high anti-fatigue property. SMA are used in many applications such as aerospace, medical, automobile, tubes, controllers for hot water valves in showers, petroleum industry, vibration dampers, ball bearings, sensors, actuators, miniature grippers, micro valves, pumps, landing gears, eye glass frames, Material for helicopter blades, sprinklers in fine alarm systems packaging devices for electronic materials, dental materials, etc. This paper focuses on introducing shape memory alloy and their applications in past, present and in future, also revealed the concept and mechanism of shape memory materials for a particular requirement. Properties of SMAs, behaviour and characteristics of SMA, summary of recent advances and new application opportunities are also discussed.

1. Introduction

Shape memory alloys are the designed materials in which large distortion can be stimulated and regained through temperature changes or stress changes which results martensitic phase change and induced elasticity at high temperatures. These special materials kept on being developed for intensify the accomplishment as per the need for the engineering field. Shape-memory alloys (SMAs) are a class of novel materials that exhibit two outstanding unique properties namely the shape-memory effect and super elasticity. These properties make them different from the ordinary materials based on
the diffusion less transformation in solid. Shape memory effect is one of the unique property which returns to the actual shape during heating, after being deformed. In other words it has the ability of the material to regain from plastic deformation through thermal processing. During hysteretic loop, super elasticity has the ability to recover from large elastic strains (up to 8%) also permits the material to resist large cyclic deformations, without residual strains. due to these immanent wonderful properties, SMAs are adopted in new technological applications related to energy dissipation in civil engineering structural designs, vibration control devices[1, 2].Super elasticity is obtained in a limited temperature range just above its transformation temperature, heating is not required for getting undeformed shape to recover and exhibits enormous elasticity, associated with large non-linear recoverable strains. The technology pushes towards ‘Smart materials ‘with adaptive or innovative functions makes use as sensors, actuators and micro-controllers, which results a disagreeable increase in weight and volume of the related machine components. The development of high ‘functional density’ and ‘smart materials’ applications must conquer technical and commercial provisions, such as available space, environmental conditions, response time and allowable cost [3].

2. Methods of preparation of shape memory alloys:

2.1. Melting:
SMA can be produced by many ways one of the most important method is vacuum melting. In addition to the vacuum melting other melting techniques like electron beam melting and plasma melting can also be adopted. Vacuum induction melting works on Electromagnetic induction works by inducing electrical eddy currents in the graphite crucible and in the metallic charges. Furthermore electro dynamic force is adopted for excellent stirring and mixing of the melt. NiTi alloys are melted by VIM in graphite crucible carbon content increases and forms TiC in the alloy, due to this transformation temperature decreases. By using electro graphite crucible [4] SMA can achieve low carbon concentrations. The advantage of VIM is achieving of chemical composition homogeneity throughout the ingot and controllability of chemical composition [5]. Vacuum arc re-melting (VAR) doesn’t have problem of contamination of carbon in the alloy due to the absence of graphite crucible and gives high purity. VAR classified in to two types with respect to the heating system first method is non consumable electrode and is preferred in laboratories and is applicable to many varieties of alloys in this method raw materials to be melted are placed in a copper mould and irradiated by the argon arc from an electrode made of a tungsten rod. When the alloy melts it resembles button shape due to the surface tension effect, the button shape again re-melted number of times in order to get homogeneity composition. Second method is consumable electrode consists of two sources one is heating source and another one is material source the electrode is heated by the argon arc and the molten alloy drops down on to the mould and forms a cylindrical ingot[6,7,8]. A drawback of melting multiple types results oxygen and carbon pick up if any leakage of vacuum occurs. Double melting process using VIM primary followed by VAR is often used to get further refining. Electron beam melting utilizes high voltage electron beam as a heating source this method is mainly adopted for NiTi SMA which doesn’t need accurate or definite control of transformation temperature. Plasma melting method uses a low viscosity electron beam discharged from a hollow plasma cathode, this method results very less loss of the alloy element .composition distribution is uniform inspite of the use of water cooled copper mould [5]
2.2. Heat treating:
NiTi samples must be cold worked before heat treatment in order to achieve optimized properties. If we consider super elastic nitinol, heat treatment may be adopted at a temperature of 500°C, for shape memory alloys it usually lies between 350°C- 450°C. Unique properties like SME and pseudo elasticity is good at a Nickel composition of 55.5(wt %). At high temperatures these properties will achieved by solution treatment and aged at a temperature around 400°C rich Ni- phases [10] precipitates and as the composition of matrix varies [11] transformation temperature increases.

2.3. Powder metallurgy:
Powder metallurgy is an essential technique for producing near net shape components of NiTi alloys. In case of copper based shape memory alloys a grain refinement to enhance fatigue properties is targeted. There are two kinds of powder metallurgy techniques for preparing NiTi alloys, one is raw metal powder sintering and another one is alloy powder sintering. The homogeneity of NiTi alloy can be improved compared with raw metal powder sintering. Different powder metallurgy methods have been developed for Ni Ti in which both elemental powders and pre alloyed powders can be used as starting materials by hot isostatic pressing (HIP) [12], hydriding and pulverization [13]. HIP is most commonly adopted sintering technique powders are filled in evacuated and gas tight welded cans will transfer the pressure to the powder. Samples prepared by this method having combined advantages of theoretical density and high homogeneity. If we require high amount of complex near net shape parts Metal injection moulding (MIM) becomes a cost effective. It is a combination of polymer injection moulding and powder metallurgy (PM), due to low density their yield strain is only 1%

2.4. Thermal spray:
Thermal spray process is mainly used for producing NiTi foils or NiTi tubes, thin walled mill products and other 3D shapes. It offers near net shape processing to reach the advantage of processing of highly reactive materials under controlled conditions. This process can be done by two methods one is low pressure wire arc spraying and another one is vacuum plasma spraying technique. Smart NiTi alloys which are difficult and expensive to manufacture by conventional methods. Low pressure thermal spraying process technology will reduce lead time, production cost for semi finished NiTi foils and tubes. The microstructure of the NiTi foils or tubes can be improved by hot rolling [14].

2.5. Thin film fabrication:
NiTi thin films can be fabricated by using vacuum sputter deposition of multiple layers, micro electromechanical systems (MEMS) and photolithographic steps [15]. Chemical composition of sputtering targets is the primary determinant of phase transition temperatures. In NiTi if titanium possess more composition produces best results, this technique eliminates the difficulties of joining, welding, or bonding of nitinol films. Presently fabrication of medical devices is most successful by planar sputters on three dimensional substrate or multiple layer method. Compositions for Nitinol thin film noted in various studies include binaries in the range of 48.2-51.9 atomic percent Ni [16,17], NiTiHf [18] and NiTiCu [19] using either pre-alloyed or elemental targets.

3. Crystal structures of shape memory alloys:
Different metals and alloys will possess different crystal structures and all the metals and their alloys will not show the Shape memory effect. The constitutional changes occurred at the atomic level that contributes the particular properties [20] like Shape memory effect and Superelasticity which are attainable through a solid state phase change having similar that of a molecular re-arrangement but the molecules which remains close packed. SMA can exist in two different phases (Parent phase Austenitic and Daughter phase Martens tic) with three different crystal structures (twinned marten site, de-twinned marten site and austenite) six possible transformations [21][22].Parent Austenitic phase is strong having 35000 to 100000 psi yield strength and daughter martensitic phase is fairly weak 10000 to 20000 psi deformation stress able to absorb 8% Recoverable strain. The structure of the high
The temperature Austenitic phase of Nitinol alloy is B2 type ordered structure and this structure was finally determined by using single X-ray diffraction method and least square analysis [23]. Monoclinic martensite is quite different from martensitic structures in β - phase alloys due to the difference in mechanical properties of high temp Austenite and low temperature martensite. Martensitic transformations are classified into thermo elastic and non thermo elastic. Non-thermo elastic transformations occur mainly in ferrous alloys thermo elastic martensitic transformations are associated with an interface between austenite phase and martensite phase. According to Otsuka et al. [24] during the rescind transformation there will be shrinkage of martensitic plates will be preferred than nucleation of the high temperature austenitic phase which cause to a crystallographically reversible transformation. The unique properties like Shape memory effect (SME) and super elasticity of SMA results of thermo elastic martensite transformation.

4. Properties of SMA:

4.1 Shape memory effect:
During martensitic phase transformation the molecular structure is twinned. On a macroscopic scale the size and shape of undeformed martensite phase is same as the cubic austenitic phase. The temperature at which starting and finishing of both parent austenitic phase and daughter martensitic phase has characterized by the following variables $M_S$, $M_F$, $A_S$, $A_F$. $M_S$ is the martensite start temperature upon cooling and $M_F$ is the martensite finish temperature upon cooling, during heating $A_S$ and $A_F$ are the temperatures of the austenite starts and finishes. The loading quantity of SMA increases with the four variables ($M_S$, $M_F$, $A_S$, $A_F$), shape memory effect (SME) is noticed when SMA temperature is below $M_F$, when the alloy is in deformed martensite, SMA will be recovered the original shape by heating the specimen above $A_F$.

![Figure 2 SMA phases and crystal structures][25-27]

![Figure 3 Temperature Hysteresis in SMA][28]

![Figure 4 Stress-strain temperature of NiTi SMA][29]

Normally SME refers to the one-way SME in which external load makes to include de-twinning brings the SMA in to a current distorted structure that can be regain on heating above $A_F$. In this type there is
no transformation strains are induced during cooling. Two-way SME is the one in which transformation strains are persuaded during heating or cooling of SMA [30]. Two-way SME is not an essential, but a developed characteristic.

4.2 Pseudo elasticity:
Super elasticity or pseudo elasticity of SMA involves stress induced strain recovery upon unloading at a temperature above $A_f$. In general super elastic thermo mechanical loading path starts at zero stress state where de-twinned martensite is stable examples of this characteristic are isothermal (constant temperature) and isobaric (constant pressure) loading paths indicated in (Figure 5). For achieving the required constant stress by austenite is not shown in the constant pressure path. The point which we remember is the constant temperature conditions carry out only by quasi-static loading which we can treat as small strain increments. During phase transformation, there is a dissipation of latent heat which was generated during quasi-static process. For easy understanding this review paper concentrates mostly constant pressure and constant temperature loading paths will be considered.

During loading at a temperature above $M_f$ the transformation occurred at critical stress levels from austenite to martensite that stress is called as Transformation stress (a-b). This phase transformation usually occurs during (b-c) path. During thermo elastic critical stress level large in elastic strains are going to be developed. If the load increased further de twinned martensite region (c-d) does not produce any more phase transformation, during multi-axial loading there may be re-orientation of martensite twins will occur. At point (d) there will be Reverse transformation (RT) from martensite to austenite which will leads to recovery of in elastic strains. At point (e) there will be a complete transformation from martensite to austenite and the final element of the loading path (e-a) is identified by regaining of thermo elastic strains which leads to zero macroscopic strains upon completion of the path. This transformation process concludes in a hysteresis which returns the energy dissipated in the cycle.

4.3 Damping properties:
It is very important property for all the materials which are going to use in any specific application. SMA having high damping capacity compared to the remaining materials. Damping property mainly deals with the dissipation of mechanical energy in to heat. The numerous interfaces, which exist during martensitic transformation between austenite and martensite, different martensite variants, the boundaries obtained during twinning of martensite instead of thermo elastic transformation. There will be occurrence of many irreversible events like production defects, dislocation movements etc. hysteresis observed during pseudo elastic characteristic is one of the energy dissipation. The ratio of dissipated energy to the total energy obtained during transformation cycle for isotropic materials will develop. This ratio depends on excitation frequency, temperature, amplitude. A novel material like SMA mainly depends on operating and transformation temperatures.
The properties of SMA are determined by their composition and the most commercially adopted shape memory alloys are NiTi (Nitinol) and the Cu-based alloys like Cu-Zn-Al and Cu-Al-Ni. Some of the typical properties of these alloys are listed in below table.

|                         | Nitinol (Ni-Ti) | Cu-Zn-Al | Cu-Al-Ni |
|-------------------------|-----------------|----------|----------|
| Melting temperature(°C) | 1300            | 950-1020 | 1000-1050|
| Density (gcm⁻³)         | 6.45            | 7.64     | 7.12     |
| Resistivity(µΩcm)       | 70-100          | 8.5-9.7  | 11-13    |
| Thermal conductivity (W cm⁻¹ per °C) | 18           | 120     | 30-43    |
| Young’s modulus (Gpa)   | 83(austenite)   | 72(beta phase) | 85(beta phase) |
|                         | 26-48(martensite)| 70(martensite)| 80 (martensite) |
| Yield strength (Mpa)    | 195-690(austenite) | 350 (beta phase) | 400 ( beta phase) |
|                         | 70-140 (martensite) | 80 (martensite) | 130 (martensite) |
| Ultimate tensile strength (Mpa) | 895           | 600     | 500-800  |
| Shape memory strain (% maximum) | 8.5          | 4       | 4        |
| Transformation range (°C) | -200-110       | <120    | <200     |
| Transformation hysteresis (°C) | 30-50         | 15-25   | 15-20    |

5. Behaviour and Characterization of SMA:
Thermo mechanical characterization of SMA gives qualitative indication of the material behaviour and quantitative material properties. Experiments for determining the material property and the behaviour has done on the MTS 810 servo hydraulic loading frame Equipment and Differential Scanning Calorimetry (DSC) and has done in four different conditions, resolving of Zero stress transformation, Monotonic loading and unloading, Resolving SME at non zero stress level and finally effects of repeated loading which includes equilibrium of material. Consider a Nitinol wire with a diameter of 0.091 cm used in actuator application, in order to determine zero stress transformation learning of stress free transformation temperatures is necessary otherwise it is very difficult to determine phase of the alloy at any liable stress and temperature. In order to determine these temperatures a DSC was used. The short DSC sample is slit from large quantity material using saw. The test results will obtain after loading the samples in the DSC machine. In order to measure this heat flow/temperature curve tangent to the start and finish of each peak and if we draw tangent to the base line heat will flows. The different intersection of these lines provides measure for start and finish temperatures of each transformation
Consider monotonic loading of SMA if temperature (T) < Martensite finish (Mf) (e.g. T < -20°C) gives illumination on elastic properties of twinned martensite also identify if the material indicates essential shape memory behavior by checking the potential to express stress free SME. Before testing, sample is first heated to above A\text{f} (e.g. 22°C) to regain any transformation strain and then cooled to below Mf(-20°C) to attain a fully martensite state this leads to elimination of detwinned martensite which formed due to unknown deformations. The fragment is consequently tested at a temperature below Mf, Martensite is the only balanced phase. During the course of testing maximum stress is chosen when detwinning has completed. The specimen is then unloaded and the temperature of the specimen is increased homogeneously above A\text{f} any recoverable strain occur it is going to be examined. From this test de-twinning start and finish stresses obtained are σ\text{s}_1 = 140Mpa & σ\text{s}_2 = 170Mpa and strain recovered is about 6.2% some non recoverable strain will remain at the end of SME test, elastic modulus is found to be 24 Gpa. If T > Mf (e.g. T = 30°C) then monotonic loading is applied to the specimen then full superelasticity property is observed with enduring plastic strain. The martensite elastic modulus is found to be higher in this case T > Mf compared with earlier case T < Mf some portion of austenite may remain after the completion of loading. During unloading elastic modulus will reflect austenite and martensite According to ASTM test method F-2516, during loading upper level of stress at 3% strain is 300Mpa and lower level of stress at 2.5% strain is 100Mpa, elastic modulus is found to be 47 Gpa.

During non-zero stress level especially in actuators it is crucial to examine zero SME and material is capable to accomplish work by providing supplanting under load. Constant stress actuation test or isobaric test is going to be adopted for uni-axial loading, for example SMA sample is heated above A\text{f}...
(22°C) and then stressed to 200Mpa this load held to be constant when the temperature is gradually consistently reduced until forward transformation in to martensite is completed then temperature is raised gently until reverse transformation is concluded. Throughout this experiment, the strain is examined and registered.

During cyclic loading, when the SMA (eg. actuator) deals with multiple transformation cycles a straightforward approach exists of implementing abundant thermal transformation cycles under steady load can be applied. A constant stress of 200Mpa or below is performed for repeated and reversal loading. Overall eighty thermal cycles are adopted. When the material is subjected to cyclic loading, its response has emerged and stabilised. Stresses ranges from 2.5Mpa to 200Mpa in 50Mpa accession, the low stress test is important for determining Zero-stress transformation temperatures and Zero stress transformation strain.

(a) Microstructure of NiTi SMA using SEM (b) Microstructure of NiTi SMA using EDX Spectra

(a) Area A in fig13(a) b) Area B in fig13(a)
Figure (b) shows the EDX spectra of the cast NiTi SMA which exhibits that the matrix phase of the cast NiTi SMA is NiTi and the Ti$_2$Ni phase circulates among the NiTi matrix phases due to this Ti$_2$Ni phase cause the matrix to be rich in Ti. Figure(c) gives DSC curve, the transformation temperatures of the cast NiTi SMA are lowered due to the Ti$_2$Ni phase exists in the NiTi SMA during melting and solidification which increases Ni concentration of the matrix and thereby decreasing of transformation temperatures. Figure(d) gives XRD analysis of cast NiTi SMA consists of B19$'$ martensite phase, B2 Austenite phase & Ti$_2$Ni phase simultaneously at room temperature which is in concord with the DSC test. Martensite & Austenite co-exist because the $M_f$ of the cast NiTi SMA is smaller than the room temperature, which causes insufficient transformation of cast NiTi SMA from Austenite to Martensite at room temperature.

6. Applications of SMA:
In Automobile industries SMA plays a major role. SMA used as actuators, sensors, mini actuators. Automatic valves, we can also use SMA as Solenoids in order to reduce noise and electric generators to generate electricity from exhaust heat. It can also used as air dams to optimize aerodynamics at various speeds. NiTi SMA can be used as a variable area form nozzle which makes jet engines quite and efficient, vibration dampers in jet engines, high shock absorber applications such as ball bearings, & landing gears. SMA having an advantage of reducing weight and increasing efficiency. In Robotics SMA used as Micro actuators or artificial muscles [33-37] the difficulties come across in biomedical fields, small strain output, low efficiency, large hysteresis, slow response times. SMA find varieties of applications such as buildings, & bridges, Intelligent Reinforced Concrete (IRC) is one of the SMA application uses wires embedded with the concrete also it senses cracks and reduce large scale sized cracks. Due to biocompatibility property, SMA used in orthodontic devices, endodontic files, broken bones can have remedy with SMA. In order to prevent scalding SMA can make to restrict water flow by reactors at different temperatures. SMA can also adopted in petro chemicals, semi conductors, pharmaceuticals, oil industries, piping, Engines, crafts, Gas boilers. Applications which deal with damped vibrations, free recovery, wire and ribbon applications, heated fluid flowing through tubes, SMA are ideal. SMA plays a very important role in commercial applications which includes eye glass frames. SMA can also be used as a material for helicopter blades which depends mainly on vibration in Micro processing control tabs for the trailing ends of the blades.

7. Future trends of SMA:
Developments of new SMA have significantly improves the quality of SMA attributes and performances. A new concept called as multiple memory material technology (MMMT) which was developed by researchers at university of waterloo, Canada has transformed SMA in to multiple shapes at various temperatures [38]. Current research focuses on developing iron based shape memory alloys having thermo elastic martensitic transformation are necessary to get shape memory effect (SME). many alloys like Fe-Ni-C[39],Fe-Mn-Si[40],Fe-Mn-Si-Cr-Ni[41], undergoes non thermo-elastic transformation and still exhibits good SME. These alloys are having different characteristics compared with conventional SMA in that they depends on stress-induced martensite for SME also it offers large transformation hysteresis, less (4%) recoverable strain commercial capability of these alloys has still to be determined but the effort has opened up for new classes of alloys which includes β-Ti alloys and iron base alloys. The importance of modern computer design and analysis tools such as CAD & FEA in to innovative and a reliable SMA application which makes interest for accurate 3D
constitute models. Development of new materials which includes composites and hybrid shape memory materials, fabrication technologies and treatment process which makes stable, durable and also develops robust computation models of SMA behaviour. Linear actuator was developed by Velázquez et al. has used mini actuator made of two bias springs has a diameter of 0.15cm and a length of 4.5cm, a weight of 150 milli grams [42] and is capable of developing a draw force of 320 mN (fig.14). Donnellan suggested mini linear actuator which was developed by Starsys Research and Applied physics Laboratory (ALP) [43] for getting larger stroke instead of using SMA wire if we use SMA compression spring of 7.6 mm length and 6mm diameter we can able to get larger stroke of 1.7 cm with an alert time of 1 sec. Elwaleed et al has also developed SMA beam actuator to amplify the actuator strain using elastic beams [44, 45, 46]. SMA wire of diameter of 0.7 mm 150mm gives a displacement up to 2cm which is greater than the unconstrained wire movement. Pittaccio et al has developed the mini linear SMA actuator which is adopted for cyclic and apathetic mobilization of in elastic ankle [47] generates a maximum movement of 8cm. Park et al has developed Mini-rotary-actuators using Nitinol SMA wires [48] having a diameter of 100µm which changes completely from treading rotational motion to the extended rotational motion. Linear actuators in the stroke to volume ratio ($S_R$)-force to volume ratio ($F_R$) plane can trace a straight line through the location of Donnellan’s actuator and parallel to the one representing the ideal SMA mini actuator characteristics. Figure 19 can differentiate in to three areas, the line gives the present implicit technological restriction for developing mini actuators. Below this restriction nearly all the actuators has conferred with in this area with little $S_R$ and $F_R$. Suppose in this area if there is a big $S_R$ and little $F_R$ is very limitedly explored as yet i.e. only Haga’s actuator fall into this region. The third area is presently un-explored, For examining this area for developing SMA mini actuators with mechanical accomplishment that suits high $F_R$ and low $S_R$, a more intricate and challenging imminent goal is to bring close to the SMA mini actuator mechanical accomplishment by changing implicit technological restriction near to the ideal one.
8. Conclusions:
In this review paper the characteristics and applications of SMA makes future of these alloys. The importance of these alloys can be summarized by their advantages like corrosion resistance, recoverable strain Biocompatibility, ductility makes use of emerging applications in the recent years. There are some difficulties to make and forming of SMA, relatively expensive, poor fatigue properties, compared with other materials like Steel and aluminium. Researchers are focusing to reduce the difficulties possessed by these alloys especially in robotic applications. Due to the exclusive properties like Shape memory effect (SME), super elasticity, damped vibrations, there will be lot of scope is there to use these materials in almost all engineering fields. The new ideas, applications, and the number of products produced in the market using SMA is continuously flourishing, there will be development of different SMA which makes use in different areas of applications.

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