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## Review

# Reconciling viability and cost-effective shape memory alloy options – A review of copper and iron based shape memory metallic systems

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## ABSTRACT

Shape memory alloys (SMAs) are group of alloys that display anthropomorphic characteristics. These alloys recover their pre-deformed morphology when heated above their transition temperatures after being deformed in their lower temperature phase (martensitic phase). This unique material behavior is explored in industrial and technological applications where capacity for strain recovery is a key design parameter. Copper and iron based SMAs are largely viewed as potential cost effective substitute to Ni–Ti SMAs judging from their promising shape memory properties, damping capacity and other functional properties. Despite their outstanding potentials, the susceptibility of copper based SMAs to phase stabilization, transition hysteresis, aging and brittleness creates doubt on the possibility of transiting from the realm of potential to functional long term use in engineering applications. On the other hand the low percentage shape recovery in the Fe based SMAs also creates a gap between the theory and potential use of these alloys. This paper takes a critical look at the science of shape memory phenomena as applicable to copper and iron based SMA systems. It also covers the limitations of these systems, the effect of processing parameters on these alloys, proposed solutions to limitations associated with this group of shape memory alloys and thoughts for future consideration.

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## 1. Introduction

The quest to ably address the rising sophistication, complexity and stringency in service requirements for materials has propelled the advancement in material design and development. Several 'super-functional' materials referred to as advance materials which combine unique engineering properties are now being processed for commercial use. A class of advance material which is attracting lot of attention presently is shape memory alloys. Shape memory alloys (SMAs) are primarily characterized by the capacity to restore their original dimensional integrity (pre-deformed shape and size) after undergoing substantial deformation when heated to a certain temperature [1]. This temperature induced strain recovery and other elasticity variants exhibited by SMAs over most other engineering materials (Fig. 1) have made them more appropriate for use in a number of applications. These includes biomedical (blood clot filters, orthodontic corrections), industrial (fluid connectors and coupling), thermal actuators (fire alarms, fire safety valve) and other domestic applications (eye glass frames, brassieres underwires) [2].

Shape memory transformation was first observed when gold-cadmium samples displayed extensive elasticity in a study carried out by Olander in 1932. The phenomena has since been observed in a number of metallic systems like Ag–Cd, Au–Cd, Cu–Al–Ni, Cu–Sn, Cu–Zn, Cu–Zn–X (X = Si, Sn, Ga, Al), In–Ti, Ni–Al, Ni–Ti, Mn–Cu, Fe–Pt, Fe–Mn–Si [3]. The NiTi system remains the most functional, successful and commercially utilized SMAs but its complexity and cost has limited its use in commercial applications. The Cu based alloy systems and Fe based systems are next in ranking of shape memory properties and have significant cost advantages over the NiTi system.

Iron based SMAs have been reported to undergo certain amount of shape recovery. These alloys have good workability and can be produced via conventional steel making processes, and have a cost advantage over NiTi alloys [4]. The Cu based systems are reported

to exhibit superior shape memory functionality compared to the Fe systems and also has a relatively low processing cost advantage [5]. This has made Cu based alloy systems the long term proposed alternatives to the NiTi alloy ahead of the Fe systems for shape memory applications. Despite the cost advantages alongside modest shape memory properties, these alloys (Cu and Fe based SMAs) are yet to replace NiTi alloys in several applications where they have to compete for selection. This has somewhat slowed down the practical exploitation and commercial endorsement of shape memory alloys in a number of application. Several articles have been written to review the shape memory phenomena of NiTi, Cu based and Fe based alloys [3,6–10]. There are however sparse literatures which have attempted to fuse in one review, the fundamental theories of the shape memory phenomena as well as take a critical look at some of the viable low cost SMAs (Cu and Fe based alloys).

## 2. Theories of shape memory phenomena

Shape memory materials exhibit certain properties that characterize their uniqueness and behavior. These materials have two basic phase systems a higher temperature austenitic phase and lower temperature martensitic phase [11]. The transition between the phase systems in these materials is what is known as the shape memory transformation. The driving force for this transformation is the difference in the Gibbs free energy of the phases and can be temperature or stress induced [12]. The temperature or stress dependencies are properties which influence the shape memory behavior of materials.

### 2.1. Thermoelasticity (thermoelastic transformation)

#### 2.1.1. Martensitic transformation

The martensitic transformation is one of the most pervasive phase transformations observed to occur in a number of material systems including metallic, polymeric and ceramic systems [13]. This transformation is a diffusionless solid to solid shear transformation from a higher temperature phase which results in the formation of martensite. The material transforms from a greater crystallographic symmetry phase (austenite phase) to a lower symmetry martensite having multiple symmetry related variants [8]. Martensitic transformations can be thermoelastic (nucleation independent) or non-thermoelastic (nucleation dependent transformations in ferrous alloys).

#### 2.1.2. Shape memory effect

Shape memory effect (SME) is a manifestation of thermoelastic martensitic transformation which is a nucleation independent transformation. It describes the phenomenon where materials assume a particular shape upon deformation in the martensite phase but reverse their original shape (dimension) prior deformation when subjected to temperatures above their transition temperature [14].

The austenite phase which is the high temperature phase is the stronger of the two phases with an opened structure which is either body centered cubic (bcc) or face centered cubic (fcc). The martensite phase is the lower temperature soft phase with a closed structure which is either hexagonal closed pack (hcp) or orthorhombic or monoclinic and easily deformable [12]. Marten-

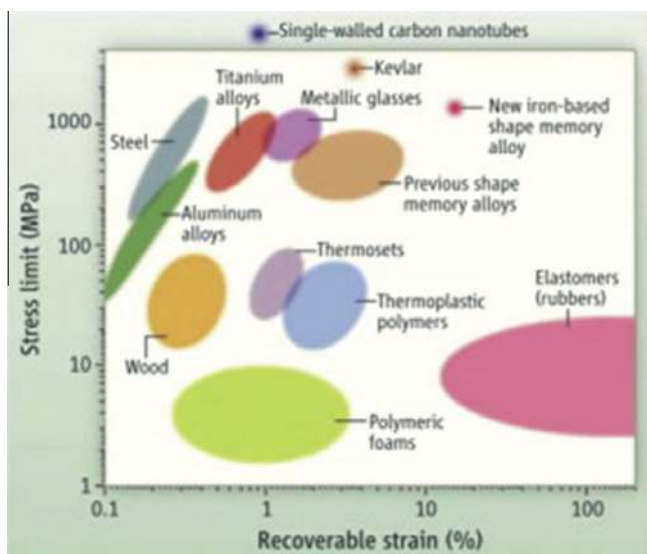
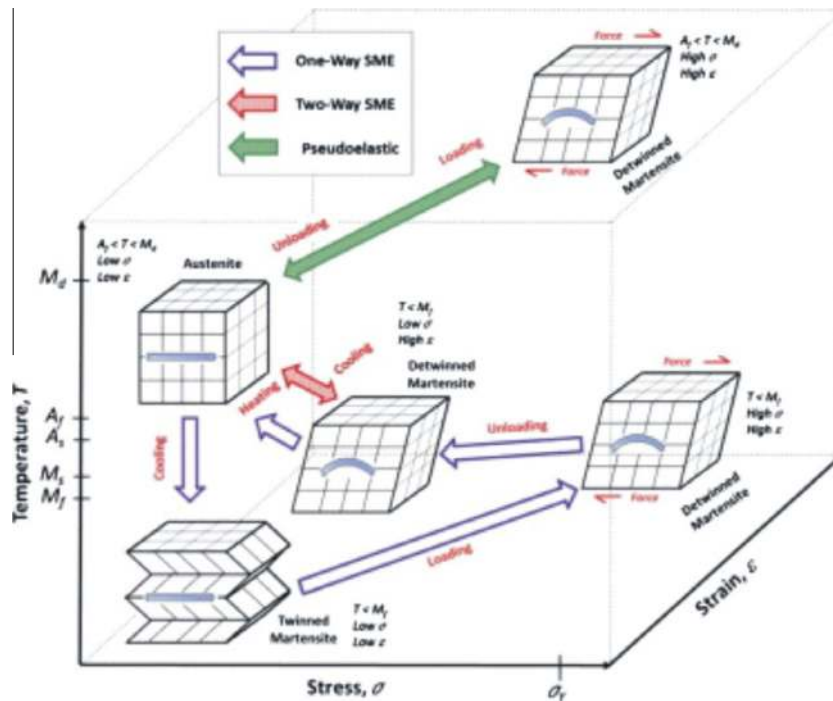


Fig. 1. Typical stress limits and recoverable strain of SMAs compared with other engineering materials (after Jani et al. [9], with permission from Elsevier).



**Fig. 2.** A description of shape memory phenomena – one way shape memory effect, two way shape memory effect and pseudoelasticity (after Jani et al. [9], with permission from Elsevier).

site is formed through lattice deformation and lattice distortion. Lattice deformation or Bain strain involves all atomic movement that results in the formation of the new structure/phase during transformation. The lattice distortion or lattice invariant shear is an accommodation mechanism for the new structure formed involving a shape change and volume change [15]. Shape memory materials undergo only a shape change during martensitic transformations and accommodate the new structure formed by a process of twinning. The martensite phase formed from the twinning process is characterized by self-accommodating twins (variants of martensite with different crystallographic orientations) and are referred to as twinned martensite [10]. The twins are separated by low energy highly mobile twin boundaries making the twinning process respond better to applied stress since there is no need for atomic bond breaking. Prior to deformation both austenite and martensite phases look identical in size and shape on a macroscopic scale. However, on deformation the martensite phase looks different from the austenite phase as a result of lattice distortion. Upon deformation the variants are condensed into a single variant by detwinning causing macroscopic strains and hence distortion in appearance of the deformed martensite [2].

The material's reversibility is associated with temperature sensitive change (thermoelasticity) in martensite either its growth or shrinkage [16]. In the case of shape memory materials, the martensite shrinks to give up the strain energy stored in the material during martensite deformation when heated to certain temperatures above the transformation temperature [17]. This temperature driven crystallographic reversibility of the martensitic structure can also be attributed to low energy and loss of symmetry during martensitic transformation. Lower symmetry detwinned martensite transforming to greater symmetry austenite retaining its original shape on reaching the transition temperature.

Fig. 2 shows a 3D illustration of different shape memory phenomena (one way shape memory effect, two way shape memory effect and pseudoelasticity). The purple colored arrows highlights the transformation from austenite to martensite on cooling

(forward reaction), the deformation of the martensite and the transformation of deformed martensite back to the austenite phase (reverse reaction). In thermoelastic transformations, the transformation from the parent phase to the martensite phase and the reverse transformation temperature are represented by  $M_s$ ,  $M_f$ ,  $A_s$  and  $A_f$  temperatures respectively.  $M_s$  (martensite start) signifies the beginning of the martensite formation and  $M_f$  (martensite finish) signifies complete formation of martensite. The  $A_s$  (Austenite start) is the beginning of the reverse reaction that is the formation of austenite and  $A_f$  (Austenite finish) marks the end of the reverse reaction that is complete formation of austenite [18].

The temperatures that define the transition from martensite to austenite (reverse) on heating differ from the temperatures that define the transition from austenite to martensite (forward) on cooling. This results in a delay in the transformation known as transformation temperature hysteresis. It is defined as the difference between the temperatures at which 50% transformation to austenite occurs on heating and 50% transformation to martensite on cooling [19]. Transformation temperature hysteresis in SMAs is usually between 10 and 50 °C depending on the alloy. In addition the level and type of transformation hysteresis determines the functionality of shape memory material (its application) [20]. The transformation temperature hysteresis forms a loop (hysteresis loop) which is a macroscopic manifestation of the lag between the forward transformation and backward transformation as the material undergoes thermoelastic martensitic transformation [21]. Fig. 3 is a schematic representation of transformation temperature hysteresis in SMAs during forward and reverse martensite to austenite transformation.

**2.1.2.1. One and two way shape memory effect.** SME in materials can be grouped in either of two ways; a one way shape memory effect or a two way shape memory effect. These SMEs are illustrated in Fig. 2 (purple arrows for one way and red arrows for two way shape memory effect).

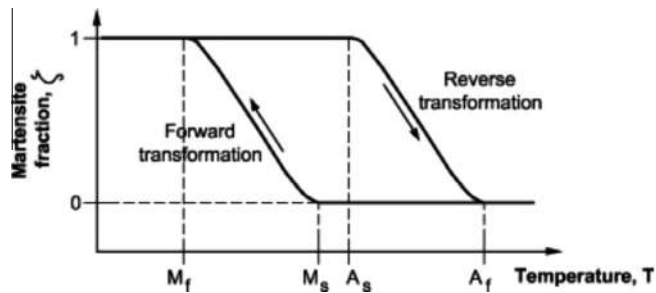


Fig. 3. An illustration of thermal hysteresis during phase transformation between martensite and austenite in SMAs (after Cladera et al. [91], with permission from Elsevier).

In the one way memory effect a material deformed in its lower temperature state (martensite phase) and upon heating above the transition temperature it regains its original morphology [22]. This strain and shape recovery is called a one way SME since only the material's morphology in the higher temperature phase is remembered [23]. This effect is as a result of the inherent material's crystallography reversibility property.

The one way SME is associated with small strains during the forward transformation (austenite to martensite) and reverse transformation (martensite to austenite). It is important to note that in the one way SME the material assumes the same shape in both austenite phase and martensite phase unless it is deformed in the martensite phase and macroscopic change occurs between the phases [24].

The two way SME occurs when the heating (transformation from deformed martensite to austenite) as well as cooling (transformation from austenite to martensite) processes are associated with transformation strains [6]. The two way SME describes the ability of a material to remember two different shapes, a shape in the low temperature phase and another in a high temperature phase. The material exhibits a shape in the high temperature phase and a different shape on cooling to the low temperature phase. This effect is not an intrinsic material property but rather an acquired property which can be obtained by cyclic repetition of certain thermomechanical loading paths (thermomechanical training) [25]. The final shape on cooling is not a function of deformation but as a result of training processes. The training processes are of three categories; shape memory training, pseudoelastic training and thermomechanical training [26]. During thermomechanical training, stress relief occurs when the material is held at high temperatures and on cooling in a constrained condition the overall shape change is minimized. This training makes the component adopt the shape concerned when transformation occurs minimizing the amount of elastic energy recovered.

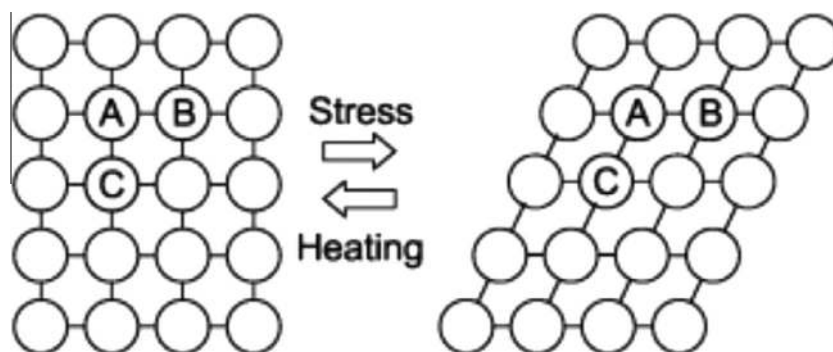


Fig. 4. Schematic illustration of atomic behavior in stress-induced martensite reversible transformation (after Cladera et al. [91], with permission from Elsevier).

## 2.2. Pseudo or superelasticity

Shape memory materials also tend to demonstrate pseudoelasticity or superelasticity. These materials have the ability to undergo extensive deformation when load is applied at specific temperatures and revert back to their original dimension when the load is removed. Phase transformation occurs in these materials by the application of external stress at temperature above its transformation temperature which induces large strain that can be recovered as stress is removed. The transformation is usually above the austenite finish temperature, between  $A_f$  and  $M_d$  where  $M_d$  is maximum temperature at which martensite can be stress induced [27]. Temperatures above  $M_d$  would trigger permanent deformation before martensitic transformation [28]. The martensite formed at this temperature is known as stress induced martensite (SIM), and has a detwinned single variant structure with large strains. Once the applied stress is removed, the material reverts back to the austenite phase and regains its original shape [29]. During this transformation the material undergoes large elastic strain which is not a function of bond stretching but reversible motion of domain boundaries between the variants of martensite. The temperature at which the transformation starts has a direct relation to the magnitude of stress applied; higher stress magnitude implies higher transformation temperature [30]. Fig. 2, illustrates the mechanism of pseudoelastic effect (green arrows) while Fig. 4 demonstrates the atomic behavior during reversible stress induced martensite transformation.

## 2.3. Damping capacity

Damping capacity describes the ability of a material to absorb or suppress vibrational energy [31]. The mechanical damping of a material is as a result of irreversible transformation of mechanical energy dissipated into thermic energy. High damping capacity is desirable in most engineering materials and SMAs exhibit damping capacity higher than most materials [32]. This is attributed to high internal friction during martensitic transformation which is a function of mobility within the interfaces during transformation. The high density of mobile interfaces during martensitic transformation in SMAs makes energy dissipation efficient in these materials. These mobile interfaces are; the interface between the austenite and martensite phase, the interface between the martensite variants and the interface of twin boundaries within the martensite [33]. The damping capacities of SMAs increases in the martensite phase due to the high density of martensite variants present and maximum when stress induced martensite is formed [34].

### 3. Applications based on shape memory properties

The nature of shape memory recovery and transformation has been selectively explored for commercial applications. The categorizations fall into the following broad groupings:

#### 3.1. Free recovery

These are applications based on the ability of the material to deform in its martensitic state and recover its original shape when heated to temperatures above the transformation temperature thereby recovering the deformation strain. These applications employ thermoelasticity and notable applications are in space antenna, eye glass frames (special eye glasses which recover deformation in hot water), blood clot filter, self-expanding stents and atrial septal defect occlusion device used for sealing hole in heart walls [35].

#### 3.2. Constrained recovery

This application employs thermoelastic property but unlike the free recovery, this application is based on partial recovery. The extent of recovery of the shape memory element is not complete but rather restricted to a particular configuration/dimension which leads to the buildup of stresses. The stress generated is the key property of interest in the use of these materials. This means when the deformed martensite is heated to austenite the recovery to the pre-deformed shape is halted after a certain percentage recovery and full recovery is not obtained. The predetermined dimension to be attained in a particular application is specified and the shape memory element is forced to halt its recovery to meet the desired specification. This is used in fastener and couplings (tubes and pipes) for aerospace, marine and orthopedic applications [2].

#### 3.3. Actuators

This application is based on the thermoelastic property of shape memory alloy. The material acts as functional element or component of a larger system. The shape memory element senses a situation and acts in accordance to it depending on the system requirement. The SMA element undergoes activation and deactivation of mechanical work in addition to its thermoelastic property when in use. A fire alarm is an example where this can be applied; the activation of the austenite phase would bring about the turning off of electrical systems and subsequent fire control measures. Fire safety valves, deep fat fryer, temperature fuses are other relevant applications [36].

#### 3.4. Superelasticity

Superelasticity is the shape memory property that has been most explored for commercial use. Its application is guided by the ability of SMAs to sustain large elastic strains at certain temperatures during use. The storage of large amount of energy when stress is applied accompanied by constant unloading of this stress is the basis for applications employing this property [37]. This is seen in eye glass frames, brassieres underwires, medical tools, cellular phone antenna and orthodontic corrections.

### 4. Shape memory alloy systems

Shape memory materials range from metals (alloys), polymers, ceramics, composites and even hybrid systems. SMAs have been the most exploited of all shape memory materials since the Buehler breakthrough in 1961. Buehler and his group in the nineteen sixties discovered the NiTi alloys with shape recovery abilities and modest engineering properties while investigating materials for heat protection [30]. Metallic alloys which display shape memory behavior in addition to other inherent properties (physical, mechanical, electrical) are called shape memory alloys (SMAs).

#### 4.1. Ni–Ti SMAs

Nickel titanium alloys pioneered the applicability of alloys exhibiting shape memory effect for commercial purposes due to their high percentage shape recovery amidst other engineering properties [38]. Nickel titanium alloys also known as nitinol are alloys containing equal amounts of nickel and titanium, whose properties include 6–8% recoverable strain and recoverable stresses of about 90% of the yield strength [39].

The peculiar characteristic of NiTi can be attributed to the presence of equiatomic NiTi intermetallic compound which has moderate solubility for excess Ni, Ti and other alloying elements thereby improving the mechanical and shape memory properties. The shape memory transformation is between a body centered cubic austenite phases (B2) and orthorhombic face centered cubic shape (B19 form) or a monoclinic face centered cubic shape (B19' form) martensite phase [40]. An intermediate phase also occurs between the austenitic/parent phase and the martensite phase known as the R-phase, which is stable at certain temperatures greater than the Martensite start temperature. The R-phase is a rhombohedra distortion of the austenitic phase structure and grows in form of thin plates which can be reverse to the austenitic structure on heating. The transformation temperature hysteresis from the parent/austenitic phase to the R-phase is smaller than that of parent phase to martensite phase hence the R-phase can be desirable for low thermal hysteresis applications [41]. The phase transitions in NiTi SMAs are governed by processing routes, chemical compositions and heat treatment processes. Variations in Ni or Ti content under different process and treatment conditions can lead to the stabilization of the R-Phase [42]. Alloying elements include iron, aluminum, chromium, cobalt and vanadium to sustain stability and ductility while niobium and copper control the hysteresis and martensite strength [14].

NiTi SMAs possess high ductility, excellent corrosion resistance in various environment including body fluids, excel in low cycle fatigue and strain controlled environment [39]. Despite all these properties the commercial application are limited due to expensive cost and complexity of production. The processing procedures required to develop the NiTi with shape memory properties is quite complex. The reactivity of Titanium restricts the melting to vacuum or inert atmosphere and plasma-arc, electron beam and vacuum-induction melting are some of the processes employed. These alloys can be hot worked and cold worked but tend to work harden easily hence frequent annealing is required. Also machining and welding of parts from the NiTi alloy requires special tools and expertise [43]. Grain refinement of NiTi shape memory alloys at room temperature is probable with the use of equal channel angular extrusion but will require having the NiTi samples contained within sheaths [44,45]. These limitations of the NiTi alloy have prompted the search for cost effective and technically efficient substitute for shape memory applications.

#### 4.2. Cu-based SMAs

Cu based SMAs though not having supreme shape memory properties like Ni–Ti alloys, are exploited for their modest shape memory properties (superior to Fe based systems), cheaper production cost and ease of fabrication [46]. They are considered as cost effective because they are easily produced using conventional liquid metallurgy and powder metallurgy routes utilized for processing traditional Cu based alloys [8]. Also, they do not have high reactivity levels which necessitates special furnace environmental conditions during melting as in the case with processing of NiTi [8]. In addition the Cu based alloys have a wide transformation temperature range, a large superelastic effect, small hysteresis and high damping coefficient. All of these desirable properties have

widened the potentials of Cu based in shape memory applications where the NiTi alloy is currently explored.

The main Cu based alloys are the Cu–Zn and the Cu–Al with a third alloying element often added to alter transformation temperature or microstructure. However Cu based SMAs are not easily deformed in the lower temperature martensitic phase which can be attributed to brittleness induced by coarse grain size, high degree of order and elastic anisotropy [47]. These alloys also tend to undergo aging which results in phase stabilization and affects transformation temperatures. Efforts have been made to understand the classes of Cu based SMA and address the setbacks which are currently hindering the use of these alloys in competing applications as the NiTi group.

#### 4.2.1. Cu–Al system

Cu–Al system is a member of the Cu based SMAs (low cost SMAs) and has been alloyed with ternary elements such as Ni, Be, Mn to improve formability and other properties [48]. Addition of a third element to the Cu–Al system broadens the single phase at high temperatures and increases the thermal stability of the alloy. This makes the Cu–Al based ternary alloy applicable in wider temperatures interval than the NiTi alloy though their functional properties are incomparable to NiTi group [49].

**4.2.1.1. Cu–Al–Ni.** Cu–Al–Ni are the most prominent class of the Cu–Al ternary SMAs and are known for their good conductivity (thermal and electrical), high transformation temperatures, thermal stability as well as large recoverable strain [50]. Cu–Al–Ni SMAs are now the only available high-temperature SMA in the Cu based group, which can be used for load bearing high temperature applications. They are however very brittle in polycrystalline state and exhibit low percentage strain recovery [51].

Cu–Al–Ni system usually contains about 4 wt% Ni; beyond this Ni content the alloy becomes increasingly brittle and the transformation temperature of the system is reduced. Cu–Al–Ni are less prone to aging unlike the Cu–Zn–Al but have limited formability due to their brittleness. Alloying elements and processing routes have been seen to influence the shape memory and engineering properties of these alloys. Micro alloying with elements such as Ti, Zr, V and B; rapid solidification technique and powder metallurgy has been seen to improve the ductility and the mechanical properties of Cu–Al–Ni polycrystalline alloys [52].

Saud et al. [53] reviewed the effect of various alloying elements on microstructure and mechanical properties of the Cu–Al–Ni system. Sugimoto et al. [54], Sure and Brown [55], Lee and Wayman [56] all worked on the effect of Zr and Ti on the Cu–Al–Ni alloys. The works by Sugimoto et al. [54], Sure and Brown [55], showed grain refinement and grain growth restriction with these additions (Zr and Ti) and the study of Lee and Wayman [56] focused on the effect of alloy addition on the Ms. Lee and Wayman [56] also reported the effect of Mn and B on grain refinement and stress concentrations relief at grain boundaries. The ductility of Cu–Al–Ni alloys increased with B additions [57] and increase in fatigue life and recoverable strain was also observed with Be additions [58].

The processing routes have also been observed to have an impact on the engineering and shape memory properties of Cu–Al–Ni SMAs. Nanostructured Cu–Al–Ni SMA produced via melt spinning exhibits enhanced shape memory properties and structure stability attributed to extensive dislocation densities which provide numerous heterogeneous nucleation sites for martensite formation [59]. Cu–Al–Ni SMA strips prepared via hot densification rolling subjected to heat treatment experience negligible grain growth and improved mechanical properties attributed to the pinning effect of nano-sized alumina segregated on grain boundaries [60]. Chen et al. [61] also reported significant improvement in ductility and large superelastic and shape memory strains in Cu–Al–Ni

SMAs that were ordinarily brittle when liquid phase (Taylor) wire forming technique was employed in the production process.

**4.2.1.2. Cu–Al–Mn.** Cu–Al–Mn SMAs are reported to have enhanced ductility and formability with Al less than 18% [62]. At low Al concentrations, the shape recovery is also improved because the parent phase (austenitic phase) possesses a low degree of order which favors the martensitic transformation.

The parent phase of ductile Cu–Al–Mn SMA is in the Cu–Al binary region, which extends significantly by the addition of 8 at% Mn and 17 at% Al and results in a combination of grain size and texture control [63]. Cu–Al–Mn alloys also exhibits large superelastic strain comparable to NiTi alloys and other functional properties like two-way SME and high damping property [64].

The addition of Ni to Cu–Al–Mn SMA is reported to be effective in achieving overall fine grain microstructure and superplasticity at a particular temperature range [65]. Micro additions of other quaternary elements to Cu–Al–Mn alloy result in improved shape memory properties but reduced transition temperatures. Thus ternary alloys are better suited for higher transition temperatures [66]. Grain orientation also affects the shape memory behavior of Cu–Al–Mn SMAs as it eliminates barriers to martensitic transformation and increases transformation temperatures simultaneously [67].

**4.2.1.3. Cu–Al–Be.** Be additions to the Cu–Al system reduce the transformation temperature curve in the Cu–Al phase diagram [68]. Low concentrations of Be do not affect composition or transformation start temperature. Cu–Al–Be possess excellent heat resistance like Cu–Al–Ni and adjustable transformation range with increasing concentration of alloying elements like the Cu–Zn–Al. Thermal treatment of this alloy can be used control martensite stabilization and increase its use in a wide range of high temperature applications [69].

#### 4.2.2. Cu–Zn system

Cu–Zn alloy has better shape memory capacities than the Cu–Al alloys and are less prone to grain boundary fracture and are more ductile than the Cu–Al. The Cu–Zn alloys however have a problem of low Ms which is at room temperature. This thermal instability at low temperatures limits their applications to below 100 °C. This has propelled studies focused on developing ternary alloys by addition of Al, Ga, Si or Sn to address the low Ms and stabilize the parent phase/austenitic phase in Cu–Zn alloys. Al has been adopted over the years as a ternary alloying element because it increases deformability at lower temperatures, reduces grain boundary fracture and is relatively easier to melt [70].

In Cu–Zn alloy there is a high temperature disordered phase ( $\beta$ .ase). This  $\beta$ .ase is stable around 450 °C and given that shape memory recovery of the Cu–Zn alloy system takes place below 180 °C. It is necessary to quench the  $\beta$ .ase from its domain of stability to produce a metastable phase at the transformation temperatures. The stability domain of the  $\beta$ .ase for Zn concentrations at ambient temperatures is of a very small range.

**4.2.2.1. Cu–Zn–Al.** Studies on Cu–Zn SMAs pre-dates that of the NiTi but the problem of complex martensitic structure and modest percentage strain recovery diverted attention to NiTi alloys. Cu–Zn–Al alloy was extensively researched for the purpose of commercializing its shape memory property in applications such as fasteners and actuators [71]. Cu–Zn–Al SMAs are the most studied of the Cu based alloys because of its higher percentage strain recovery than other Cu based SMAs. Also it has adaptable production and fabrication routes but these alloys are brittle (due to coarse grain structure) and possess poor mechanical properties such as low fracture and fatigue strength.

Cu–Zn–Al SMAs exhibit shape memory within a certain range of composition. They have disordered bcc structure which is the parent phase stable at high temperatures which is also quenched like in Cu–Zn alloys to retain the  $\beta$  phase for transformation to martensite [72]. This  $\beta$  phase is stable across an extensive temperature range and homogenization of these alloys is easier than the Cu–Zn system.

Cu–Zn–Al SMAs like other Cu based SMAs are susceptible to aging. Aging in these alloys has been a key area of study in understanding these SMAs since it affects the transformation temperatures and limits their long term applications. These SMAs undergo ordered transition from the parent/austenite phase to the martensite phase. The shape memory properties depreciate as a result of incomplete ordering reaction and migration of vacancies at temperatures above 200 °C [73]. Adiguzel [74] also observed that martensite stabilization and ordering in the martensitic state in a Cu–Zn–Al SMA aged at room temperature was dependent on holding time. The stabilization was aided by quenched-in vacancies and structural change which occur during the aging giving rise to the change in the configurational order. Aging in the parent/austenite phase did not affect the transformation temperatures and the arrangement of atoms in the Cu–Zn–Al SMAs but increased As and Af temperatures on account of atom interchange between Cu and Zn [75]. A decrease in stacking fault density in martensite upon aging also contributes to the stabilization of martensite as this takes away a part of the lattice invariant shear preventing the reverse transformation of martensite to the parent phase [75].

The fatigue properties of Cu–Zn–Al alloys can be improved by refining grain sizes and texture of the alloy. Stress concentrations at certain grain boundaries in the parent phase of large grain sized material leads to dislocation pile up due to thermal cycling and eventual premature cracking in the Cu–Zn–Al alloy [76]. Surface defects which lead to fatigue failure are initiated during pseudoelastic cycling and attributed to the formation of a stress induced martensite crystal of width corresponding to the length of the hole created on the surface [77]. Fatigue crack growth rate in Cu–Zn–Al SMA is strongly influenced by the stress ratio value ( $R$ ) which is the ratio of the minimum stress to the maximum stress [78].

Alloying elements like Zr, Ce, Ti, V, Co, B, Fe, Be, Mischmetal have been explored to modify the grain structure of Cu–Zn–Al SMA and improve its mechanical and shape memory properties [79]. Micro alloying Cu–Zn–Al SMAs with Zr brings about grain refined microstructure accompanied with a decrease in all the transformation temperatures (Ms, Mf, As, Af) [80]. Wang et al. [81] also reported unusual grain refining effect of Zr in the Cu–Zn–Al alloy at temperatures above 900 °C attributed to the weakening of the effects Zr on the alloy. B additions in Cu–Zn–Al SMAs lead to an increase in strength and elongation as well as a large percentage of grain refinement attributed to both the presence of refined grains and grain boundary strengthening [82]. A comparative studies on the effect of B, Fe and Ti–B as micro alloying elements on Cu–Zn–Al SMAs revealed B had the maximum refining effect and Ti–B having the least. Grain refinement in Cu–Zn–Al–B was more with increased percentages of B [83]. Cu–Zn–Al alloys also showed significant refinement in grain size when 0.01% of Fe was added as a refiner although no significant improvement in mechanical properties was recorded [84].

4.2.2.2. *Cu–Zn–Ni*. Cu–Zn–Ni SMAs are influenced by Zn and Ni concentrations. These concentrations affect the morphology of martensite formed, the transformation temperatures and strain recovery of the alloys [85]. The transformation temperature decreases with increasing Zn concentrations and increases with increasing Ni concentrations. Lath type martensite was formed in alloys with low Zn concentrations, while alloys with high Zn concentrations recorded a combination of lath type martensite and

spear type martensite and exhibited higher SME. The SME can be attributed to the presence of higher spear type martensite which undergoes martensite to austenite transformation easily. The amount of martensite present in these alloys also affects the extent shape memory transformation since incomplete martensite transformation results in reduced shape recovery [85].

Cu–Zn–Ni SMAs have also been reported to exhibit good corrosion resistance with increasing wt% of the Ni content from 2 to 9 in fresh water, Hank's solution (simulated body fluid) and sea water [86].

4.2.2.3. *Cu–Zn–Sn*. Cu–Zn–Sn SMAs have been studied and reported to have excellent hot workability and SME with varying Sn concentrations [87]. These alloys display high percentage elongations at temperatures ranging from 773 K to 873 K. The transformation temperatures were measured using electrical resistance method and its thermal hysteresis was evidence of a thermoelastic transformation [88]. The transformation temperatures of Cu–Zn–Sn SMA are dependent on the concentrations Sn in the alloys [6] and the enthalpy of heating and cooling increases with increase in mass% of Sn in the alloy [89].

#### 4.2.3. *Cu–Sn*

Cu–Sn alloys undergo martensitic transformations which are not perfectly thermoelastic and suffer from a rapid degradation of shape memory properties during aging at lower temperatures [85]. This aging and narrow parent phase composition range has limited studies in the area of Cu–Sn alloys. The addition of Mn to the Cu–Sn results in the development of an alloy with more thermal stability than Cu–Zn–Al alloys and increased parent phase (austenitic phase) composition range and higher ductility. The shape memory transformation in Cu–Sn–Mn is formed based on the structure of the austenitic/parent phase and stabilized at room temperature by rapid cooling from the parent phase [90].

### 4.3. *Fe-based SMAs*

This is the third most prominent group of SMAs after the NiTi and Cu based alloys. This class of SMA has a cost advantage over the NiTi alloy system due to relatively cheap alloying constituent and ease of fabrication since the facilities for conventional steel making can be employed [91]. Fe based SMAs are also known as shape memory steel (SMS) and include Fe–Pt, Fe–Pd, Fe–Mn–Si, Fe–Mn–Al, Fe–Ni–C and Fe–Ni–Co–Ti [92]. Fe based SMAs or SMS however have a lesser shape memory capacity than the Ni based and Cu based SMAs, and undergoes large transformation hysteresis which limits their area of application. Also production rates of SMSs must be as high as plain carbon steel for the process to be economically viable [93]. Table 1 summarizes the relative advantages and limitations of the three prominent SMA systems, namely: Ni–Ti, Cu-based SMAs and Fe-based SMAs.

**Table 1**

Presents the three major shape memory alloy systems and highlights their relative advantages.

Process factors	NiTi	Cu-based	Fe-based
Maximum recoverable strain	8% [122]	5% [61]	Less than 5% [123]
Cost	High [124]	Low [125]	Low [92]
SME	High [12]	Moderate [126]	Low [109]
Workability	Moderate [14,111]	Low [127]	Good [115]
Fabrication Processing	Low [128] Demanding [14,43]	Good [46] Easy [129]	Moderate [110] Easy [91]

Fe based SMAs/SMSs undergo both thermoelastic and non thermoelastic transformation from an austenitic structure to a martensitic structure depending on the alloy constituents. The SME is as a result of the formation of Shockley partial dislocation during heating [94] and the reversibility of these dislocations and stress induced martensite formed during martensitic transformations [95]. The transformations in SMSs are of three categories; face centered cubic (fcc) – face centered tetragonal (fct), face centered cubic (fcc) – body centered tetragonal (bct) and face centered cubic (fcc) – hexagonal closely packed (hcp). Fe based SMAs can be grouped according to transformation type as follows; (a) fcc–fct: Fe–Pt, Fe–Pd (b) fcc–bct: Fe–Ni–C and Fe–Ni–Co–Ti (c) fcc–hcp: Fe–Mn–Si, Fe–Mn–Al. The fcc–bct and fcc–hcp are the most common transformations in Fe based alloys of shape memory importance in engineering applications [96]. The other transformations are limited to academic research because of their high cost of development. The shape recovery property of SMSs after deformation of alloy in the martensite phase is dependent on the chemical composition (alloying elements) and grain size in the austenite phase [97].

#### 4.3.1. Fe–Mn system

These alloy systems are considered a new area of interest in the subject of Fe based SMAs but have poor SME and large hysteresis [98]. This SME is also influenced by percentage Mn in the alloy. Ternary additions of Si, C, Cr, Co and Ni are added to improve the engineering and shape memory properties of the Fe–Mn shape memory system [95].

**4.3.1.1. Fe–Mn–Si.** Fe–Mn–Si alloys have recently become the most explored SMSs despite their wide thermal hysteresis due to their workability, machinability, weldability coupled with low cost. These SMAs undergo non thermoelastic martensitic transformation from the gamma fcc austenite phase to epsilon hcp martensite phase. The SME in Fe–Mn–Si is dependent on the reverse motion of Shockley partial dislocation created during deformation and the volume of epsilon martensite induced and reversed during the transformation [99].

The shape memory capacity of Fe–Mn–Si based SMAs varies with annealing temperatures. High annealing temperature favors the transformation from the austenitic phase to the epsilon martensite because of reduce density of dislocation structures while low temperatures retards this transformation [100]. The volume fraction of the stress induced martensite is affected by both  $M_s$  and Neel temperature ( $T_n$ ) in Fe–Mn–Si. The Neel temperature is the magnetic transformation temperature from a paramagnetic to antiferromagnetic phase with increasing Mn content. Below the  $T_n$  antiferromagnetic ordering takes place stabilizing austenite and suppressing martensitic transformation [98]. However the percentage recoverable strain in Fe–Mn–Si SMAs is small and this has prompted alloying Fe–Mn–Si based SMAs to improve shape memory properties [101].

Fe–Mn–Si–Cr and Fe–Mn–Si–Cr–Ni are the common Fe–Mn–Si based SMAs with increased percentage strain recovery among other engineering properties [102]. Fe–Mn–Si based SMA can be strengthened by grain structure refinement which improves the yield stress and total area of grain boundaries which affect the partial dislocation motion involved in the transformation [103]. Grain size reductions in Fe–Mn–Si–Cr–Ni result in improved structural and shape memory properties due to increase reversibility of martensite [104]. Fe–Mn–Si based SMAs, reports varied corrosion resistance in NaCl environment which increases after subjection to heat treatment [105].

Thermomechanical treatment has an effect on Fe–Mn–Si–Cr–Ni based SMA producing thin plates of reversible epsilon martensite with improved shape memory properties [106]. Since this

improvement route is rather tasking and expensive the addition of Nb and C equally improves the shape memory properties due to presence of NbC particles producing thin martensite plates at a lower cost [107]. Pre deformation of Fe–Mn–Si based SMA with NbC at temperatures above room temperature also increases shape recovery and recovery stress by creating nucleation sites for NbC particles precipitation which further aids martensite formation and reversion [108]. The deformation at room temperature did not achieve the same percentage shape recovery as the other (above room temperature) due to a large increase in recovery stress during cooling [109]. Carbon additions without Nb can also lead to improvement of recovery strain for large deformations of these alloys after thermomechanical training [110].

Fe–Mn–Si based SMAs have shown improvement in strain recovery attributed to thermal training, alloying and processing techniques. However this alloy system does not undergo superelasticity due to non thermoelastic nature of the martensitic transformation it undergoes from the austenite phase to the epsilon martensite phase [111].

#### 4.3.2. Fe–Ni–Co–Ti system

These alloys undergo fcc–bct transformation from austenite to the martensite phase. The SME in these alloys is observed after thermal treatments (ausaging) to create a two phase structure of austenite and  $(\text{Ni}, \text{Co})_3\text{Ti}$  coherent precipitates [112]. The precipitation of fine particles of  $(\text{Ni}, \text{Co})_3\text{Ti}$  is a condition for shape memory transformation to occur in these alloys. This leads to a decrease in thermal hysteresis and shearing of these particles lead to the formation of a tetragonal structured martensite [113]. Increase in Co contents of this alloy depletes the alloy of Ni and hinders the precipitation of the  $(\text{Ni}, \text{Co})_3\text{Ti}$  precipitates. This thermal treated Fe–Ni–Co–Ti tends to be brittle due to the precipitates forming at grain boundaries and hence reduces the deformability of the alloys [114].

Recent studies have reported high superelastic strains for new SMS. Greater than 13% for Fe–28Ni–17Co–11.5Al–2.5Ta–0.05B [115] and greater than 6% for Fe–34Mn–15Al–7.5Ni [116] however no improvement has been for recovery strain. The low strain recovery of Fe based SMA is attributed to interactions between the stress induced martensite and the large number of twin boundaries. Therefore reducing the density of twin boundaries can help increase percentage strain recovery in these alloys [92].

### 4.4. Other shape memory systems

#### 4.4.1. Nickel–aluminum

Ni–Al, near equiatomic composition exhibits all the attributes one would think are needed for a significant SME with good strength at high temperature and resistance to corrosion [6]. These alloys are however brittle with transformation temperature well above room temperature dependent on Al content. The addition of Fe has been recorded to increase the ductility of the material without any change in the martensitic transformations but lower the transformation temperatures [117]. The lower transformation temperatures in Ni–Al–Fe alloys can be catered for by adding Mn or lowering the Al content of the alloy [118].

#### 4.4.2. Beta titanium alloys (Ti–Nb, Ti–Mo, and Ti–V)

SMEs in beta titanium alloys have been well known since the early 1980's after research on NiTi. The hypersensitivity and toxicity of the NiTi group led to research on development of Ni free alloys with better biocompatibility. The goal was to stabilize the parent Ti phase with the right amount of stabilizers. The resulting alloys have a disordered structure unlike NiTi with a body centered cubic (bcc) austenitic structure that transforms to orthorhombic martensite or hexagonal martensite on cooling. SME has been



reported in Ti–Nb, Ti–Mo alloys and Ti–V alloys. However, the Ti–Mo based alloys are susceptible to phase embrittlement and the Ti–V alloys are not suitable for biomaterial because of its cytotoxicity [119]. Ti–Nb alloys are reported undergo a decrease in Ms with 1 at% increase of Nb content and superelastic behavior stabilized by increase in critical stress for slip [120]. The changes in transformation strain and temperature in Ti–Nb content can also be attributed to the combined effect of work hardening and age hardening [121]. These titanium alloys are easier to hot and cold work than the NiTi alloys but exhibit a large hysteresis with poorly defined shape recovery attributes compared to NiTi. Although Ti based alloys have not been commercialized till date, they are probably the most active area of investigation outside of NiTi for bio-compatible applications.

## 5. Conclusion

This paper presents SMAs and their growing application to the modern world and focuses on Cu and Fe based SMAs as low cost options for strain recovery in engineering applications. Economic consideration has been a major stimulus for the attention both SMA systems are receiving as the base metals Cu and Fe are cheaper than Ni and Ti; also Cu and Fe based SMAs can be easily produced using traditional metal processing technologies. The Cu based SMAs are promoted for applications which would recover low percentages of strain recovery, low thermal conditions (less than 100°), low cyclic conditions and low tendency to fracture. They are mostly employed in actuator applications in devices such as fire safety devices, anti-scald in shower heads, deep fat fryers among others. The Fe based alloys are used in applications that require large production rates and low percentage recovery such as fasteners and pipe coupling. These SMAs (Cu and Fe) have been reported as individual potential replacement for the popular NiTi group. Cu based alloys on account of their cheaper cost of production ease of fabrication, excellent strain recovery and high damping capacity while good workability and ease of processing for Fe based group.

The enormous service application of Cu based alloys are however hindered by their intrinsic brittleness, grain boundary fracture, aging and poor fatigue life which limits formability, material life and shape memory capacity of the system. Processing parameters and techniques such as melt spinning and hot densification rolling are useful in curtailing some of these limitations. Alloying helps in grain refinement which increases formability in the martensitic phase, heat treatment also helps controlling the transformation temperatures thereby increasing the life of the alloy. However, one cannot concretely say the Cu based alloy can completely substituted the NiTi group in actuator applications this is because the problems posed to their use have not been adequately addressed. The Cu based SMAs would still continue to undergo martensite stabilization as a result of aging which would affect the transformation temperatures and retard the material's shape recovery unless solutions are proffered to eliminate it. On the other hand the low percentage strain recovery and absence of superelasticity in the Fe–Mn–Si based SMAs are the problems encountered by this group of SMAs and until this is resolved they lack the ability to compete with Ni–Ti SMA.

As exciting as the notion of low cost alloys (Cu and Fe based alloys) as technically efficient and cost effective alternatives to NiTi alloys the practical transition cannot be achieved just yet. In this regard, the NiTi alloys are still most commercially developed shape memory alloys despite their economic implications and complexity of production. In general the use of shape memory alloys would still be limited to applications where they are technically efficient and of economic benefit. The transition to low cost effective shape

memory alloys would only be possible if the problems at hand are understood and adequate solutions proffered.

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