Patents on Superelastic Shape Memory Alloy

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Abstract: Innovative investigations, discoveries and recent patents regarding superelastic shape memory alloy (SMA), a novel material, are briefly discussed in this review paper. Known as a functional material, SMA can recover large strains in two ways: shape memory effect (SME) and pseudoelasticity. SME is by virtue of temperature induced martensitic transformation while pseudoelasticity (also called superelasticity) happens because of stress induced martensitic transformation (SIMT). SMA is one of the most widely used functional materials in many adaptive structures, as well as in medical and biomedical applications.

Because of SME, SMA can be mainly used for active control of adaptive structures. On the other hand, having pseudoelasticity SMA can be used for passive damping of a vibrating structure. Superelastic SMA is also widely used for applications like: antenna of portable phones, headband of headphones, in the ballpoint pens and eyeglass frames etc. This study will focus mainly on pseudoelasticity of SMA and its potential characteristics.

Keywords: Shape memory alloy, stress induced martensitic transformation, pseudoelasticity (superelasticity), nonlinear stress-strain curves, tension-compression asymmetry.

INTRODUCTION

The shape memory alloys, termed as functional materials, show two unique capabilities: shape memory effect (SME) and superelasticity (SE), which are absent in the traditional materials. Both, SME and SE largely depend on the solid-solid, diffusion-less phase transformation process known as martensitic transformation (MT) from a crystallographically more ordered parent phase (austenite) to a crystallographically less ordered product phase (martensite) [1-3].

The phase transformation (from austenite to martensite or vice versa) is typically marked by four transition temperatures, named as Martensite finish (M_f), Martensite start (M_s), Austenite finish (A_f), and Austenite start (A_s). Let us assume, $M_f < M_s < A_s < A_f$. Thus, a change in the temperature within $M_s < T < A_s$ induces no phase change and both martensite and austenite may coexist within $M_f < T < A_f$.

It is seen that the phase transformations may take place depending on changing temperature (SME) or changing stress (SE) [1-3]. Let us first discuss the SME. Suppose $T > A_f$, so the SMA is in the parent austenite phase with a particular size and shape. Under stress free condition, if the SMA is cooled to any temperature $T<M_f$, martensitic transformation (MT) occurs as the material converts to product martensite phase. It should be noted that MT is basically a macroscopic deformation process, though actually no transformation strain is generated due to the so-called self-accommodating twinned martensite Fig. (**1**). If a mechanical load is applied to this material and the stress reaches a certain critical value, the pairs of martensite twins begin 'detwinning' (conversion) to the stress-preferred twins. The 'detwinning' or conversion process is marked by the increasing value of strain with insignificant increase in stress Fig. (**2**). The multiple martensite variants begin to convert to single variant, the preferred variant determined by alignment of the habit planes with the axis of loading. As the single variant of martensite is thermodynamically stable at $T<A_s$, upon unloading there is no reconversion to multiple variants and only a small elastic strain is recovered, leaving the materials with a large residual strain (apparently plastic). Next, if the deformed SMA is heated above A_f, SMA transforms to parent phase (which has no variants), the residual strain is fully recovered and the original geometricconfiguration is recovered Fig. (**2**). It happens as if the material recalls from 'memory' of its original shape before the deformation and fully recovers it Figs. (**1**, **2**). Therefore, this phenomenon is termed as shape memory effect (more specifically, one way SME). However, if some end constraints are used to prevent this free recovery to the original shape, the material generates large tensile recovery stress, which can be exploited as actuating force for active or passive control purpose.

Having an idea of what SME is, we can now discuss the second feature of SMA, that is, pseudoelasticity. The superelastic SMA has the unique capability to fully regain the original shape from a deformed state when the mechanical load that causes the deformation is withdrawn. For some superelastic SMA materials, the recoverable strains can be on the order of 10% [1-3]. This phenomenon, termed as the pseudoelasticity or, superelasticity (SE) is dependent on the stress-induced martensitic transformation (SIMT), which in turn depends on the states of temperature and stress of the SMA.

To explain the SE, let us consider the case when the SMA that has been entirely in the parent phase ($T>A_f$), is mechanically loaded. Thermodynamic considerations indicate that there is a critical stress at which the crystal phase transformation from austenite to martensite can be induced. Consequently, the martensite is formed because the applied stress substitutes for the thermodynamic driving force usually obtained by cooling (for the case of SME). The load, therefore, imparts an overall deformation to the SMA specimen as soon as a critical stress is exceeded. During unloading, because of the instability of the martensite at this temperature in the absence of stress, again at a critical stress, the reverse phase transformation starts (from the SIM to parent phase). When it is complete the SMA returns to its parent austenite phase Figs. (**3**). Therefore, superelastic SMA shows a typical hysteresis loop (known as pseudoelasticity or superelasticity) and if the strain during loading is fully recoverable it becomes a closed one [1-3]. It should be noted that SIMT (or the reverse SIMT) are marked by a reduction of the material stiffness Fig. (**3**). Usually, the austenite phase has much higher Young's modulus in comparison with the martensite phase.

For $T<A_s$, there is no pseudoelastic recovery and the residual strain can be recovered by heating above A_f (SME). For any temperature, there exists a critical stress for irreversible plastic slip to occur in the material (this critical stress value decreasing with increasing temperature), and if the stress is exceeded, then the residual strain can't be recovered by heating or unloading [3].

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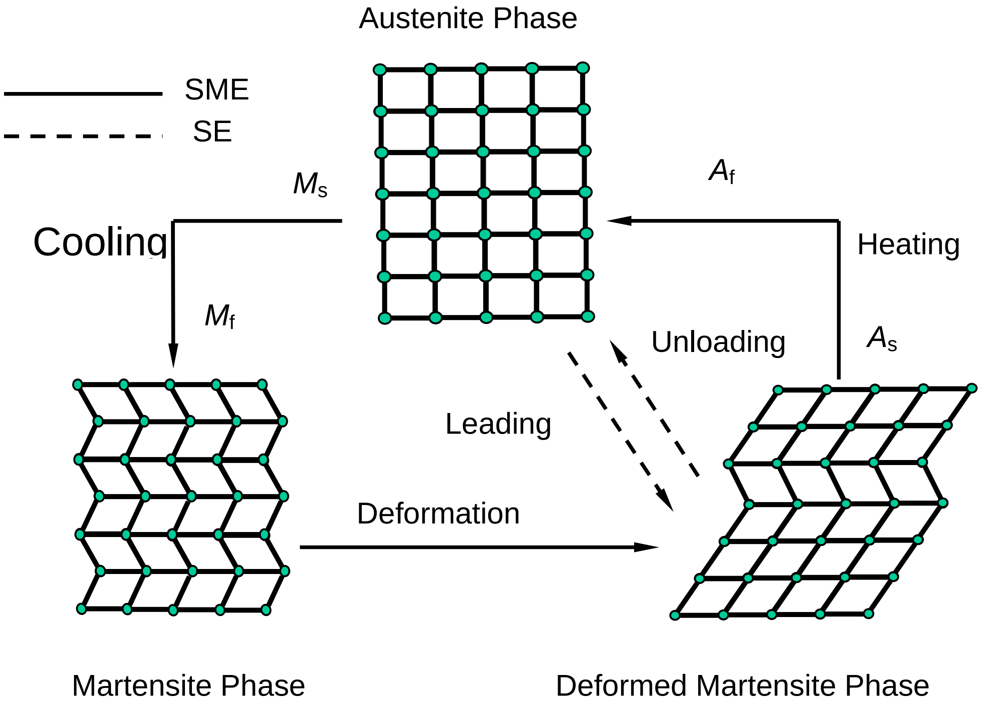

Fig. (1). Crystal lattice deformations during SME and SE.

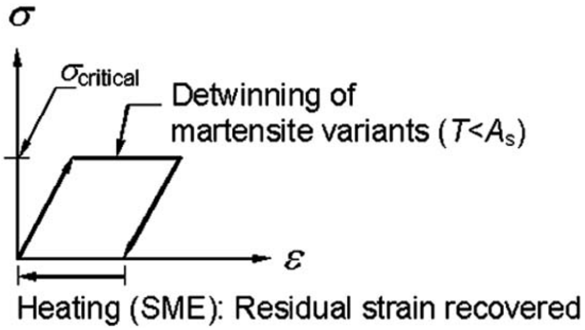

Fig. (2). Idealized stress-strain diagram showing SME.

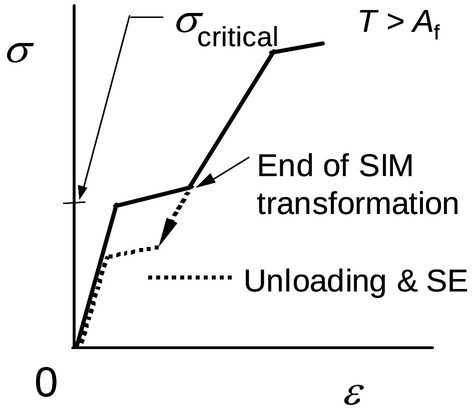

Fig. (3). Idealized stress-strain diagram of the superelastic SMA.

The following advantages of the SMA's have made them popular as smart actuators and sensors: very high force to weight ratio, high adaptability, and compactness. Among the SMA materials, the most popular and widely used Nickel titanium alloys (abbreviated as Nitinol or TiNi) have strong actuating capability with almost 8% recoverable strain and the tensile recovery stress can be as large as 700 MPa. Thus powerful actuators can be designed within these extreme limits.

Besides the actuators, the major applications of SMA have been as pipe couplings and electrical connectors. Both, SME and SE enable the SMA to have excellent medical applications [1].

Having the unique feature of superelasticity (usually at room temperature) SMAs are used in various applications. Superelasticity has been extensively used in the medical and clinical applications (orthodontic wires, self-expanding micro-structures used in the treatment of hollow-organ or duct-system occlusions). Applications of the superelastic elements have the advantages: light weight, retention of shape even if misused and being comfortable to use. Some of the latest applications of the superelastic wires include antenna of portable phones, headband of headphones and eyeglass frames. They are also used to retain the shape of shoes for comfort [1].

RECENT PATENTS ON SUPERELASTIC SMA

Superelastic SMA can demonstrate a number of peculiar and useful characteristics apart from superelasticity. Therefore, inventors and researchers have been reporting many patents on them. This paper shall, however, review only a few and the recent ones, giving the readers an idea of how superelastic SMA's functional characteristics can be exploited for fruitful applications.

Regarding patents of this wonderful novel material, Marthinus, Attila, Masters and John [4] reported a patent utilizing the high energy absorbing capability of the superelastic Nitinol SMA: (Ni) and Titanium (Ti), which are mixed in an approximate ratio of 55% by weight Ni and 45% by weight Ti, annealed to form the desired shape. According to the invention, highly deformable pseudoelastic memory alloy materials are used to improve the energy absorption of mechanical components used in structures subjected to impact loads. Specifically, the patent has focused on optimizing the material's inherent strain energy absorbing capability for enhancing the crashworthiness of aircraft seats. The NiTi is being integrated in the seat support to reduce the loads on an occupant in a crash, thus increasing the chances of survivability. This is due to the fact that in addition to the high strain recovery capability (as much as 7%), the material can sustain an enormous fracture strain (as much as 60% or more).

Schneider [5] has patented a polymer composite structure having resin matrix interlayers reinforced with SMA particles of different shapes (cylindrical, oval or spherical). The SMA particles provide superelastic reversible strain properties that significantly improve the damage resistance, damage tolerance and elevated temperature performance of the composite structure without negatively affecting the hot-wet compression strength of composite structure. The polymer composite is ideally suited for aerospace and aircraft applications where lightweight and structurally strong materials are essential.

Since SMAs display superelastic hysteresis behavior over large strain ranges, a significant amount of energy dissipation is possible. Thus, superelastic SMAs can be suitably used in the structures as dampers.

As far as vibration damping of a rotating body is concerned, Sherwin and Ulmer [6] have reported a patent for vibration damping in a turbine using superelastic SMA's typical hysteresis. The method includes performing structural dynamics analysis on the turbine to determine at least one area of high vibrational stress on the turbine, and performing thermal analysis of the turbine to determine at least an approximated maximum operating temperature at the area of vibrational stress. Next, the hysteresis of superelastic SMA is utilized to dampen the turbine's operational vibrations. The hysteresis damping essentially includes selecting an SMA having a martensite-to-austenite transformation temperature substantially similar to the approximate maximum operating temperature of the component at the area of high vibrational stress, and disposing the selected SMA on the turbine on the related area of high vibratory stress.

In terms of medical applications, Pelton [7] has patented a radiopaque nitinol stent for implantation in a body lumen. The stent is made from superelastic nitinol, and includes a ternary element including tungsten. The nitinol stent is found to improve the radiopacity comparable to that of a stainless steel stent of the same strut pattern coated with a thin layer of gold. Furthermore, the nitinol stent has improved radiopacity yet retains its superelastic and shape memory behavior and further maintains a thin strut/wall thickness for high flexibility.

Nakamura and Takeuchi [8] have patented eyeglass frame made of superelastic SMA. They also report fabrication method: plastic working a composition containing Ni and Ti, and subjecting the composition to heat treatment at a temperature between 600 and 880^o C in order to impart shape memory.

CURRENT AND FUTURE DEVELOPMENTS

So far researchers have mainly focused on the superelastic properties of the SMA for many medical and structural applications through publications of patents. An enormous volume of literature on superelastic SMA shows that this unique novel material has so many potential features that are difficult to describe in a single article. Therefore, only a few features of superelastic SMA, that can be utilized in future patents, will be highlighted in the following paragraphs.

Superelastic SMAs inherently demonstrate highly nonlinear stress-strain curves that are non-symmetric in tension and compression [9]: this peculiar point can also be focused through patents.

Apart from superelasticity, short columns made of SMA posses remarkably high buckling strength. For example, Urushiyama, Lewinnek, Qiu and Tani [10] discovered that a bent column, made of Cu based SMA, tends to become straight under axial load; consequently a bent column's buckling resistance is found to be more than that of a straight column. They also showed that short SMA columns carry higher buckling loads compared to steel columns [10]. Rahman, Qiu and Tani [11] also demonstrated similar facts: having the same sizes and slenderness ratios, short superelastic SMA columns made of NiTi have a buckling load significantly higher than that of a stainless steel column.

Moreover, uniaxial tension of a superelastic SMA rod shows that during SIMT and reverse SIMT, the local strain is found to be zero while the total strain increases monotonously [12,13]. Therefore, some patents, based on these features of superlastic SMA, would be really interesting.

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