STUDIES ON SHAPE MEMORY ALLOYS – A REVIEW

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ABSTRACT
Shape memory alloys (SMAs) are metallic systems that "remember" their original shapes. These alloys undergo martensitic phase transformations because of applied thermo mechanical loads and are capable of recovering permanent strains when heated above a certain temperature. What makes SMAs remarkably different from other materials are primarily the shape memory effect (SME) and pseudo elasticity, which are associated with the specific way the phase transformation occurs. SMAs are useful for such things as actuators, which are materials that "change shape, stiffness, position, natural frequency, and other mechanical characteristics in response to temperature or electromagnetic fields". This paper on "shape memory alloys" carries out simplified study of the crystallographic structures/ transformation of SMAs, general characteristics, working principles, commonly used alloys, and applications. The potential uses for SMAs have broadened the spectrum of many scientific fields and the study of the history and development of SMAs can provide an insight into a material involved in cutting-edge technology.

KEY WORDS
Shape memory effect, Pseudo Effect, Damping Properties, Applications

1. INTRODUCTION
The key characteristic of all SMAs is the occurrence of a martensitic phase transformation between the austenitic phase and the different variants of the low temperature, low symmetry martensitic phase. Arne Olander first observed these unusual properties in 1938 (Otsuka and Wayman [4]), but not until the 1960's were any serious research advances made in the field of shape memory alloys.

William J. Buehler, a researcher at the Naval Ordnance Laboratory in White Oak, Maryland, was the one to discover Ni-Ti shape memory alloy. Since these alloys have unique property in remembering the shape, having an actuator function, and having super elasticity, they are now being used for various applications such as pipe couplings, various actuators in electrical appliances, automobile applications, antennae for cellular phones, medical implants and guide wires etc. The diverse applications for these metals have made them increasingly important and visible to the world.

2. FABRICATION

Most popular amongst the SMAs are the Ni-Ti alloys, known as a 'Nitinol'. There are various ways to manufacture Nitinol. Current techniques of producing nickel-titanium alloys include vacuum melting techniques such as electron-beam melting, vacuum arc melting or vacuum induction melting (Figure 1). Further this cast ingot (Figure 2) is press-forged and/or rotary forged prior to rod and wire rolling. Hot working to this point is done at temperatures between 700°C and 900°C (Stoeckel and Yu, [3]).

At the bottom of small ingots (Figure 3a) typical solidification structures can be observed: i) small grains at the outer part due to the rapid solidification; ii) a columnar grains region obtained by an high radial temperature gradient during the solidification; iii) equiaxial grains in the central part. The central small ingot area of Figure 3b, instead, shows long columnar grains due to a different solidification condition. The difference in grain morphology is likely due to the variation in feeding rate resulting from a manual cast operations, and it could cause a variation in the workability properties during the subsequent ingot hot working.

For all the lengths of bigger ingots (20 Kg each) the solidification structure shows a more equiaxed grain growth and a typical cross section is reported in Figure 3c.

The Ni-Ti alloys are also subjected to cold working, where the procedure is similar to titanium wire fabrication. Carbide and diamond dies are used in the process to produce wires ranging from 0.075mm to 1.25mm in diameter (Stoeckel et al. [3]). Cold working of Nitinol causes "marked changes in the mechanical and physical properties of the alloy" (Jackson et al. [1]); (Figure 4).
3. CRYSTAL STRUCTURE

Exactly what made these metals "remember" their original shapes was in question after the discovery of the shape-memory effect. Dr. Frederick E. Wang, an expert in crystal physics, pinpointed the structural changes at the atomic level that contributed to the unique properties these metals possess (Kauffman and Mayo, [2]).

The two unique properties (shape memory effect and pseudo elasticity) are made possible through a solid-state phase change that is a molecular rearrangement, which occurs in the shape memory alloy. A solid-state phase change is similar in that a molecular rearrangement is occurring, but the molecules remain closely packed so that the substance remains a solid. In most shape memory alloys, a temperature change of only about 10°C is necessary to initiate this phase change. The two phases, which occur in shape memory alloys, are Martensite, and Austenite.

Since properties of shape memory alloys are closely related to martensitic transformation (MT), a brief notion of MT is given in an oversimplified manner. Martensitic transformation is diffusion less transformation in solids, in which atoms move cooperatively, and often by a shear like mechanism. Usually parent phase (high temperature phase) is cubic and martensite (lower temperature phase) is of lower symmetry. Martensitic transformations are usually categorised into two groups—thermoelastic and non-thermoelastic. The non-thermoelastic transformations occur mainly in ferrous alloys and are associated with non-mobile martensite-parent phase interfaces pinned by permanent defects and proceeds by successive nucleation and growth. Due to re-nucleation of austenite during the reverse (martensite to austenite) transformation, these transformations are crystallographically non-reversible in the sense that the martensite cannot revert to the parent phase in the original orientation. Whereas thermoelastic martensitic transformations are associated with mobile interfaces between the parent and martensitic phases. These interfaces are capable of “backward” movement during the reverse transformation by shrinkage of the martensitic plates rather than nucleation of the parent phase, which leads to a crystallographically reversible transformation (Otsuka et al. [4]). The unique properties of SMAs are the result of thermoelastic martensitic transformation.

When temperature is lowered below critical one, MT starts by a shear like mechanism, as shown in Figure 5. The martensites in region A and B have same structures but the orientations are different. These are called correspondent variants of martensite. Since martensite is lower symmetry phase, many variants can be formed from same parent phase. Now if the temperature is raised and martensite becomes unstable the reverse transformation (RT) starts and if it is crystallographically reversible, the martensite reverts to parent phase, in the original orientation.

4. GENERAL CHARACTERISTICS AND DISCUSSIONS

4.1. Shape memory effect

Martensite is the relatively soft and easily deformed phase in shape memory alloys, which exists at lower temperatures. The molecular structure in this phase is twinned. Austenite, the stronger phase of shape memory alloys, occurs at higher temperatures. The shape of the Austenite structure is cubic. The un-deformed Martensite phase is the same size and shape as the cubic Austenite phase on a macroscopic scale, so that no change in size or shape is visible in shape memory alloys until the Martensite is deformed. The temperatures at which each of these phases begin and finish forming are represented by the following variables: $M_s$, $M_f$, $A_s$, $A_f$. The amount of loading placed on a piece of shape memory alloy increases with the values of these four variables.

The shape memory effect is observed when the temperature of a piece of shape memory alloy is cooled to below the temperature $M_f$. At this stage, the alloy is completely composed of Martensite, which can be easily deformed. After distorting the SMA, the original shape can be recovered simply by heating the wire above the temperature $A_f$. The heat transferred to the wire is the activation energy, driving the molecular rearrangement of the alloy, similar to heat melting ice into water, but the alloy still remains solid. The deformed Martensite is now transformed to the cubic Austenite phase, which is configured in the original shape of the wire (Figure 6).
applied load is necessary to induce detwinning and/or reorientation and to bring the SMA specimen into a new deformed shape that can be recovered upon heating above $A_c$. There is no transformation strain induced during the cooling of the material. If transformation strains are generated during both heating and cooling of the material, then this property is known as the two-way shape memory effect and was observed for the first time by Perkins (1974)[6]. In contrast with the SME, discussed earlier, or the pseudo elasticity, which will be described in the next section, the two-way shape memory is not an intrinsic but an acquired characteristic.

4.2 Pseudo elasticity:
The pseudo elastic behaviour of SMAs is associated with stress induced strain recovery upon unloading at temperatures above $A_c$. Under most general conditions, pseudo elastic thermo-mechanical loading paths start at zero stress in the austenitic region, then move to the de-twinned martensite region and then unload again to the starting point. Examples are the isothermal and isobaric loading paths as shown in Figure 7. For clarity, the initial loading from austenite to achieve the required constant stress for the isobaric path is not shown. Note that isothermal condition can be achieved only by quasi-static (small strain increments) loadings, so that the latent heat generated/ absorbed during the phase transformation has time to dissipate. For simple understanding, in this paper mostly isobaric or isothermal loading paths will be considered.

4.3 Damping properties
The damping capacity, which consists of the dissipation of mechanical energy into heat, is not a characteristic behaviour that is specific to shape memory alloys alone, all materials exhibit this property. However, shape memory alloys exhibit a damping capacity that is far greater than that of standard materials. This is linked to the existence of the numerous interfaces related to the martensitic transformation: those between austenite and martensite, those between the different variants of martensite, and the twin boundaries inside the martensite itself. In spite of the thermoelastic character of the transformation, many irreversible events occur (production of defects, movement of dislocations, etc.). Hysteresis observed in pseudo elasticity is one of the energy dissipation manifestations (Stoiberet [7]). During a transformation cycle (or a reorientation one), the damping of an isotropic material is characterized by the ratio of the dissipated energy to the total energy developed. This ratio depends on the excitation frequency, its amplitude and temperature. For shape memory alloys, it also depends on the difference between the operating and transformation temperatures. In general, three damping regimes are distinguished in SMAs:

a) For the alloy initially in the austenitic phase, operating temperatures higher than $M_s$ and weak mechanical excitation the SMA remains in the austenitic phase. The damping capacity is small.

b) The damping capacity increases for operating temperatures below $M_s$. This can be attributed to the large number of interfaces present in the material in the martensitic phase.

c) For operating temperatures above $A_c$ and stress levels high enough to induce stress induced martensite, the damping capacity reaches its maximum. Creation and displacement of austenite–martensite interfaces during the loading cycles are accompanied by a strong level of defect production and large thermo-mechanical coupling.

5. COMMON SHAPE MEMORY ALLOYS
Nickel-titanium alloys have been found to be the most useful of all SMAs. Other shape memory alloys include copper-aluminium-nickel, copper-zinc-aluminium, and iron- manganese-silicon alloys. The thermo mechanical properties of SMAs depend crucially on their chemical composition, cold work, heat treatment, and thermo mechanical cycling. In this section the properties of common SMAs of different chemical compositions are summarized.

5.1. Nitinol
Shape memory alloys based on Ni and Ti has today provided the best combination of material properties for most commercial applications. The discovery took place at NOL, the Naval Ordnance Laboratory and hence the acronym NiTi-NOL or Nitinol (Buehler et al., [9]; Buehler et al. [10]). One of the first rigorous characterizations of NiTi has been performed in the early 1970s (Jackson et al. [1]). Although its cost is still high, it is popular due to its strong SME behaviour with transformation strains of approximately 8% (Melton et al. [8]). A wide range of transformation temperatures for typical NiTi alloys have been reported in the literature with $M_f = 288 \pm 40 \text{ K}$ and $A_f = 362 \pm 80 \text{ K}$.
The variation in the transformation temperatures is due to different methods of cold work and thermo-mechanical treatment. The properties of Nitinol are particular to the exact composition of the metal and the way it was processed. The physical properties of Nitinol include a melting point around 1240 °C to 1310°C, and a density of around 6.5 g/cm³ (Jackson et al. [1]). The large force generated upon returning to its original shape is a very useful property. Other useful properties of Nitinol are its "excellent damping characteristics at temperatures below the transition temperature range, its corrosion resistance, its nonmagnetic nature, its low density and its high fatigue strength" (Jackson et al. [1]). Nitinol is also to an extent impact- and heat-resistant (Kaufman et al. [2]). These properties translate into many uses for Nitinol.

5.2. Cu based alloys

The main copper-based alloys are found in the Cu–Zn and Cu–Al systems b-domain. The presence of a third element allows the adjustment of the transformation temperatures by a wide margin (about 370°C). The transformation temperatures are highly dependent on the composition. Copper-based alloys generally exhibit less hysteresis than NiTi. The Cu–Zn–Al alloy is easy to create and rather cheap. However, it exhibits a high tendency of decomposing into its equilibrium phases when overheated, thus bringing about a stabilization of the martensite. The presence of additives, such as Co, Zr, B or Ti, is necessary to produce grains from the martensite. The presence of additives, such as overheated, thus bringing about a stabilization of decomposing into its equilibrium phases when rather cheap. However, it exhibits a high tendency to improve their properties in some crystalline form to improve the ductility of the material. e.g. - CuAlNi, CuZnSn, CuAlBe. Copper-based alloys are also used in single crystaline form to improve their properties in some industrial applications.

5.3. Fe-based alloys

Iron based alloys are known to exhibit less SME than many other alloys types. FeMnSi alloy is a widely studied example of a Fe based SMA. The martensitic transformation, considered non-thermoelastic, leads to an incomplete one-way shape memory effect; pseudo elasticity is weak or non-existent. The performance of these alloys is very sensitive to thermo mechanical treatments. To avoid corrosion, Cr and Ni are sometimes added, diminishing the memory effect (Maki, [5]).

6. APPLICATIONS

- Bioengineering: Biomedical applications of SMA have been extremely successful because of the functional properties of these alloys, increasing both the possibility and the performance of minimally invasive surgeries. The biocompatibility of these alloys is one of the important points related to their biomedical applications as orthopaedic implants, cardiovascular devices, and surgical instruments, as well as orthodontic devices and endodontic files. Broken bones can be mended with shape memory alloys. Memory metals also apply to hip replacements, considering the high level of super-elasticity. For clogged blood vessels, an alloy tube is crushed and inserted into the clogged veins. Since the memory metal has a memory transfer temperature close to body heat, the memory metal expands to open the clogged arteries. Dental wires used for braces and dental arch wires, memory alloys maintain their shape since they are at a constant temperature, and because of the super elasticity of the memory metal, the wires retain their original shape after stress has been applied and removed.

- SMAs can be designed to restrict water flow by reacting at different temperatures, which is important to prevent scalding.

- Fire and security systems lines in industries that involve petrochemicals, semiconductors, pharmaceuticals, and large oil and gas boilers.

- For many applications that deal with a heated fluid flowing through tubes, or wire and ribbon applications where it is crucial for the alloys to maintain their shape in the midst of a heated environment, memory metals are ideal.

- In certain commercials, eyeglass companies demonstrate eyeglass frames that can be bent back and forth, and retain their shape. These frames are made of memory metals as well, and demonstrate super-elasticity.

- In helicopter blades: Performance for helicopter blades depend on vibrations with memory metals in micro processing control tabs for the trailing ends of the blades, pilots can fly with increased precision.

7. CONCLUSIONS

The many uses and applications of shape memory alloys have ensured a bright future for these metals. Main advantages of shape memory alloys may be summarised as - Bio-compatibility, Diverse Fields of Application, and Good Mechanical Properties (strong, corrosion resistant) However, there are still some difficulties with shape memory alloys that must be overcome before they can live up to their full potential. These alloys are still relatively expensive to manufacture and machine compared to other materials such as steel and aluminium. Most SMA’s have poor fatigue properties; this means that while under the same loading conditions (i.e. twisting, bending, compressing) a steel component may survive for more than one hundred times more cycles than an SMA element. Researches are progressing at many robotics departments and materials science departments, with the innovative ideas for applications of SMA’s and, the number of products on the market using SMAs continually growing, advances in the field of shape memory alloys for use in many different fields of study seems very promising.

REFERENCES

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