Shape memory alloys: Smart materials with long memory

Dinumol Devasia

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Shape memory alloys (SMA) are smart materials that can "remember" their original shapes. In these metallic alloys, deformation (change in shape) can be induced and recovered through temperature or stress changes. SMA materials are used for the fabrication of structures capable of changing their shape and vibration parameters such as stiffness, natural frequency, and damping. SMAs are lighter and stronger than conventional metals leading to their increased demand in the market. In 1932, Olander first discovered and reported the remarkable rubber-like elastic behavior of a AuCd alloy at room temperature¹ followed by the discovery of SME in NiTi alloy (Nitinol) in 1961.² Shape memory effects and thermoelastic martensitic transformation in Ni_{50%at}Ti alloy discovered in 1963 by Buhler, resulted in the first commercial application of NiTi alloy in joints of hydraulic installation of F-14 aircraft (1971).³

Shape memory effect and pseudoelasticity (superelasticity) are unique properties exhibited by SMA because of the solid-solid phase transformation.⁴ The shape memory effect is the effect due to which shape memory alloys regain their original shape. The SME effect is a stress and/ or temperature induced shift in the crystalline structure of the material between low symmetry martensite and high symmetry

austenite.

SMA has two phases, high temperature phase austenite and low temperature phase martensite, each with different crystal structures and hence different properties.⁵ Austenite is generally cubic whereas martensite exhibits tetragonal, orthorhombic or monoclinic crystal structure. The transformation from one crystal structure to the other is shear dominant diffusionless that occurs by the nucleation and growth the of martensitic phase from a parent austenitic phase and the process is called as martensitic transformation (figure 1). In the absence of applied stresses, twinned martensite is formed combination selfby the of



Figure 1. Schematic diagram of crystal structure evolution of NiTi SMA subjected to martensite reorientation and detwinning.¹⁴

accommodated martensitic variants. By applying mechanical loading, the martensitic variants reorient (detwin) into a single variant with large macroscopic inelastic strains. But while heated above the transition temperature, the martensitic phase returns to the austenitic phase recovering the inelastic strains. This is the so-called shape memory effect (SME). The superelastic behavior is observed when the loading and unloading of the SMA occur above the austenitic transition

temperature in which case detwinned martensite is directly produced from austenite. As austenite is the thermodynamically stable phase at this temperature, under no-load conditions, the material goes back to its original phase (austenite). This extraordinary elasticity is called pseudoelasticity or transformational superelasticity.⁶

The most popular shape memory alloys include NiTi based alloys, Cu based alloys, and Fe based alloys. NiTi alloy, commonly called as Nitinol has been used for various practical applications like automotive, aerospace, eyeglasses, window frames, pipe couplings, antennae for cellular phones, actuators, sensors, shock absorbers etc. Transformation temperatures of nitinol are well below or close to body temperature, which is why nitinol has many applications as a biomaterial. Nitinol is an ideal material for biomedical implant because of its low elastic modulus close to natural bone material and compressive strength higher than natural bone material.⁷ It can also be used as blood clot filters and stents in cardiovascular treatments. It has applications in artificial organs, artificial kidney, and are good candidates as microactuators for microrobots.

Superelasticity or the non-linear pseudoelasticity has applications in various fields like orthodontic arch wire that has transformed the orthodontic surgery effective and easier. SMAs have been used as guide wires for catheters in medical use. A catheter is a standard tool used to diagnose the circulatory system by injecting a contrast medium to the blood vessels.⁷ When a foreign object comes in contact with blood, proteins adsorb onto its surface initiating various biological reactions like platelet activation, thrombus formation etc. intended to provide immunity. This leads to biocompatibility issues with bioimplants. It has been suggested that hydrophobhic surfaces can decrease the protein adsorption and hence Ni-Ti alloys with superhydrophic surface and Ni-Ti-Cu alloys with antibacterial properties have been fabricated which are highly beneficial for biomedical applications.⁸

Cu based shape memory alloys, with excellent conductivity of heat and electricity, are best for high temperature applications ~ 473 K.⁷ Numerous studies have been done on the modification of shape memory alloys especially Ni-Ti alloy modified with ternary elements to satisfy the high and low temperature applications. Electronic studies have been performed on them to understand the mechanism. It has been found that the ternary and quarternary alloying elements alter the number and concentration of valence electrons and therefore change the transformation temperatures.⁹ In situ observation on temperature dependence of martensitic transformation and plastic deformation in superelastic NiTi shape memory alloy was also carried out.

The use of SMAs as couplings, actuators stem from their shape memory effect. SMA actuators were used in electric appliances, automobile devices, and robotics. SMA actuators are superior to wax actuators because of their good thermal conductivity resulting in an excellent thermal response. Ni-Ti alloy thin films have gained attention in the field of microelectromechanical systems (MEMS) to fabricate thin microscopic devices without sacrificing the bulk properties. Ti-Ni is a good candidate to be used as a microactuator in MEMS, due to its large recovery forces and high recoverable strains.¹⁰ Interestingly, the shape memory effect of Ni-Ti alloy has been exploited in the study of electrochemical catalysis on the surface of a Pt nanofilm.¹¹

Magnetic shape memory alloys (MSMAs), also called as ferromagnetic shape memory alloys (FSMAs) are a subgroup of shape memory alloys that produces motion and deformation in response to a magnetic field (exhibits ferromagnetic behavior). Typically, MSMAs are alloys of Ni-Mn-Ga. The first report on MSM effect was in 1996. They are prospective materials for interconversion of magnetic and mechanical energies since they combine large strain capability of ordinary SMA with the fast and remote actuation or sensing that is possible using magnetic fields.¹²

Recently, large field induced-strains in single-crystal Ni-Mn-Ga alloys have also been observed near structural transition points. Large magnetoresistance and entropy change have also been reported. The studies on ferromagnetic SMAs have revealed the presence of magnetocaloric effects and barocaloric effects making them promising materials to renew the existing cooling devices.¹³

There are still some difficulties that need to be overcome to use the shape memory alloys to their full potential. These alloys are relatively expensive to manufacture compared to steel and aluminum. Also, the fatigue properties are not very impressive compared to steel. Still, they are involved in rebuilding the world.

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