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Relatively New Shape Memory Alloys for Possible Applications: A Brief Review

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ABSTRACT

Shape memory alloys (SMAs) are smart metals that can change their shape at cold state and memorize its predeformed shape when heated. From past decades SMAs are on the front line of research and development in several industries and research institutions. Ni-Ti alloy is commercially available most commonly used thermal SMAs today due to its extraordinary behavior of shape memory effect and superelasticity. Demands of Nitinol have been increased for biomedical, industrial, automobiles, aerospace, civil structures, microelectromechanical systems (MEMS), sensing and actuation, vibration damping and robot applications. Ni-Mn-Ga alloys are popular and mostly investigated ferromagnetic shape memory alloys because of their unique properties such as magnetic shape memory effect, magnetocaloric effect and strain induced by magnetic field. Ni-Mn-Z (Z=Sn, Sb, In, Al) are realized as relatively new gallium-free alloys and contributed to overcome limitations of popular Ni-Mn-Ga alloy system.

***Keyword:** SMAs, Ni-Mn-Ga alloys, Ni-Mn-Z alloys, FSMAs, Heusler alloys*

1. INTRODUCTION

SMAs are compact and lightweight, adaptive, have high power to weight ratio, large strains but low energy efficiency and fatigue properties [1]. After 1963, success of Ni-Ti alloys (Nitinol) starts with many commercial applications. Demands have been increased for biomedical, industrial, automobiles, aerospace, civil structures, microelectromechanical systems (MEMS) and robot applications [2]. Increase of temperature in SMAs can brings shape recovery even at high applied force. This results in high energy of actuation. Also, SMAs absorbs and dissipate mechanical energy when subjected to cyclic loading.

Other SMAs include Cu-Al-Ni, Cu-Zn-Al, NI-Al, Fe-Mn-Si, and Cu-Zn-Si. Even though these are low-cost alloys and available easily, but have poor thermomechanical performance and brittleness [3]. In this context, Ni-Ti is still most popular shape memory alloy. Recent progresses on SMAs shown that conventional actuators can be replaced by smart SMAs to reduce size, cost and mechanical complexity. They have higher wear resistance compared with steels and its alloys [4]. High temperature SMAs (operating above 1000C) such as Ni-Ti-Au, Ni-Ti-Pd, Ni-Ti-Pt, Ni-Ti-Zr have been developed for high temperature applications [5]. However, they are difficult to process due to less ductility, poor fatigue properties at room temperature and high cost of manufacturing. In this paper a brief review of relatively new potential SMAs for possible applications has been presented.

SMAs are exclusive materials exhibiting unique properties called shape memory effect (SME) and pseudoelasticity or superelasticity [6]. Based on transformation temperature these metals have high temperature phase called as austenite and low temperature phase called as martensite with different crystal structure and properties. Martensite has tetragonal, orthorhombic while austenite has cubic crystal structure. The transformation process is diffusionless but occurs by shear lattice distortion. This typical transformation is known as martensitic transformation. Martensitic phase usually occurs below transformation temperature and is disorder in nature. Austenite phase is refereed as ordered phase. The phase transformation between austenite and martensite occurs due to change in temperature can be explained by shape memory effect. Martensite exists in more than one variant and with little change in crystal structure and orientation showing twinned structure as shown in Fig.1. This complicated structure of martensite enables shape memory alloy to experience large magnitude of deformation not undergoing plastic strain.

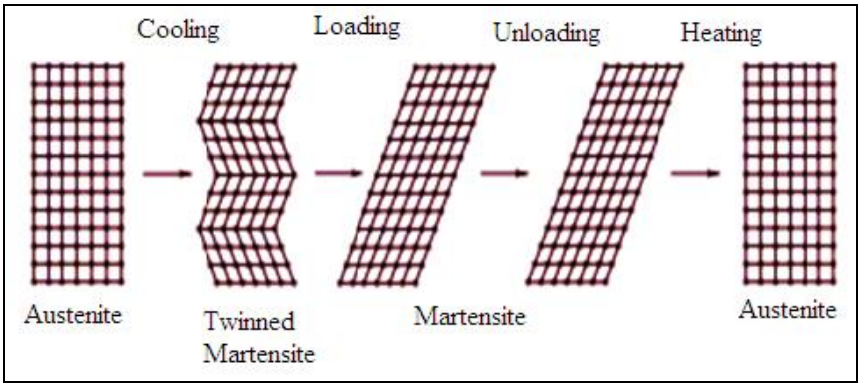

Fig -1 Representation of Shape Memory Effect [6]

2. FERROMAGNETIC SHAPE MEMORY ALLOYS (FSMAs)

Recently, FSMAs also called as magnetic shape memory alloys, the different SMAs which produce forces, motion as well as strain in the presence of magnetic field have been explored. The development of FSMAs started at AdaptaMat, Finland [7] during 1995, which is principle manufacturer of FSMAs for actuators, sensors and energy harvesters. One important limitation of Ni-Ti alloy is the low frequency response. The strain in FSMAs is different from Ni-Ti and also operate at higher frequencies (up to 1KHz) as phase transformation is via magnetic fields which is not affected by relatively slow rate of heat transfer due to temperature change. These alloys show inverse magnetostrictive effect. On compressing or elongating these materials a change in resistance occurs. Magnetic shape memory effect or magnetic field induced reorientation is rearrangement of ferromagnetic martensitic strain with large macroscopic strain up to 10% [8]. Here twin martensitic variants have magnetic moments in different directions. Their de-twinning takes place once high intensity external magnetic field is applied resulting macroscopic deformation. The nature of FSMAs are similar to magnetostrictive materials (Terfenol-D), but allows 50% higher strain. These are materials in between SMAs and magnetostrictive and would be a replacement for valves and motor applications. In conventional SMAs phase transformation occurs by thermal change, while in FSMAs same can be obtained by changing the magnetic flux as well as temperature also.

Ni-Mn based Ni-Mn-Ga is most popular FSMA till date in which austenite and martensite phases are ferromagnetic. Other potential FSMA is Fe-Pd. Magnetic shape memory effect is instrumental in the development of these alloys due to high frequency response and actuation strain. FSMAs can be used in magnetic actuators, energy harvesters [9], pneumatics, medical devices, robotics and mechatronics with application thermal range from -1300C to 700C [10]. In general, FSMAs are brittle and difficult to manufacture, hence commercially not suitable. Therefore, more research to further improve other materials such as Ni-Mn-Sn, Ni-Mn-Al, Ni-Mn-Sb and Ni-Mn-In is required to develop engineering applications.

3. HEUSLER ALLOYS

Often it can be seen from literature that ternary Ni-Mn based Heusler alloys display a shape memory effect. The suitable example is mostly studied Ni2MnGa as a ferromagnetic shape memory Heusler alloy. Friedrich Heusler, German mining engineer and chemist first invented Heusler alloy composed of Cu-Mn-Al in 1903 despite of the fact that there was no ferromagnetic element present in the alloy [11]. These are important intermetallics with fixed stoichiometric composition 2:1:1 (X2YZ) called full Heusler alloys and 1:1:1 (XYZ) called half or semi Heusler alloys, where X and Y are transition metals in 3-12 groups and Z is in groups 13-15, either semiconductor or non-magnetic element.

Heusler alloys exhibits extraordinary properties such as magnetic shape memory effect, inverse magnetocaloric effect and superelasticity for the possible application in the magnetocaloric devices [6]. As most of the Heusler alloys are ferromagnetic, they are primarily studied for magnetic properties from the discovery of Cu-Mn-Al in 1903. Recently they have attracted in the field of thermoelectrics, spintronix [13]. There is prime importance of well-known Ni2MnGa as Heusler ferromagnetic shape memory alloy. Ni-Mn-Ga alloy exhibits ferromagnetism with L21 structure and Fm-3m space group in austenitic phase below 6000C [14]. At low temperatures this alloy undergoes martensitic transition from cubic austenite to martensite phase. After several decades still researchers are active in the development of novel Heusler compounds due to their multifunctional properties.

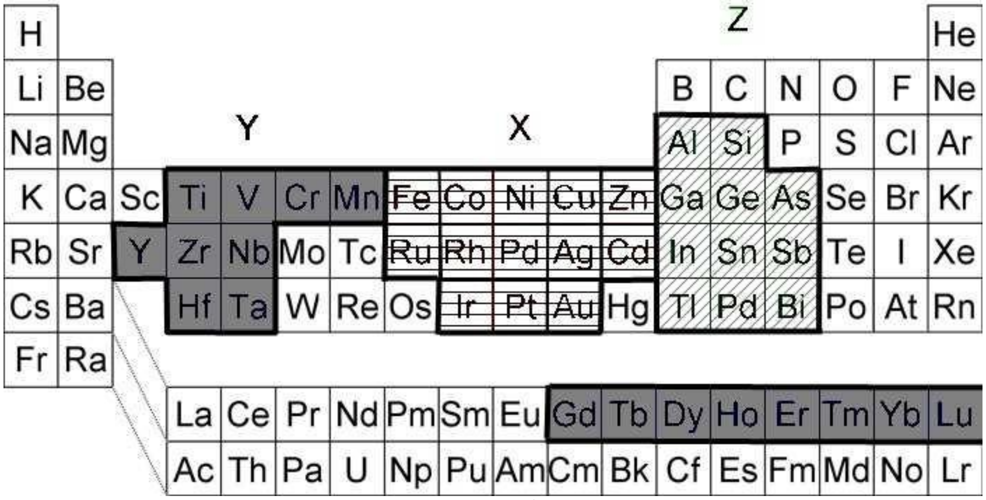

Fig-2 General presentation of Heusler alloys [12]

3. Ni-Mn-Ga ALLOYS

During the year 1974-75 J. Soltys first worked on Ni-Mn-Ga alloys systems. Then Webster et al. [15], Kokorin and Chernenko [16] reported martensitic transformation in Ni2MnGa Heusler alloys. After that Ullakko et al [17] showed possibility of 0.2% magnetic field induced strain in single crystal Ni-Mn-Ga alloy at magnetic field of 800 kA/m. In 2000, Murray et al. [8] determined 6% MFIS within single crystal Ni-Mn-Ga alloy. After that, Sozinov et al. [7] investigated highest 10% magnetostrains along with high frequency response which made single crystal Ni-Mn-Ga alloy extraordinary FSMAs and new material for magnetic actuator applications. Crystal structure of Ni-Mn-Ga Heusler intermetallic alloys have been studied by Ranjan et. al. [18] in 2006 and Pons et al. [19] in 2008. The martensitic structure influences on magnetic and mechanical and thermal properties of Ni-Mn-Ga FSMAs [20]. This structure may occur in orthorhombic and tetragonal form which mainly depends upon Ni/Mn/Ga ratio. J. Pons et al. [19] found these alloys with L21 cubic structure in high temperature austenite phase described by space group Fm-3m. Structural, magnetic and thermal properties of Ni-Mn-Ga FSMAs have been studied earlier and confirmed martensitic phase, transformation temperatures and magnetic behavior using XRD, DSC and VSM instruments respectively [21,22].

Mechanical properties of Ni-Mn-Ga alloy systems have been studied earlier by some researchers [23,24]. Attempts have been made to improve ductility by preparing polycrystalline thin films which showed better mechanical properties [25]. Apart from single and polycrystalline bulk Ni-Mn-Ga alloys forming methods, fine particles synthesized by spark erosion and mechanical alloying (ball milling) method have been developed for the applications of nanomechanical components [26-28]. It is pointed that for such types of alloys high energy ball milling is simple and economical than spark erosion method.

4. Ni-Mn-Z (Z=Sn, Sb, In, Al) ALLOYS

Even though Ni-Mn-Ga alloy systems are well-known Heusler FSMAs, their highly brittle nature, low martensitic transformation temperature, high cost of gallium have put constraints to use these alloys practically. In this respect, Ni-Mn-Z (Z=Sn, Sb, In) alloy system have been recognized as potential FSMAs [9, 29,30]. Ni-Mn-Al alloy system is also studied and characterized for shape-memory effect for stoichiometric (Ni2MnAl) and off- stoichiometric composition exhibiting a martensitic transformation [31-35]. Recently Ni-Mn-Sn and Ni-Mn-Al Heusler alloys are realized as relatively new gallium-free SMAs and contributed to overcome limitations of popular Ni-Mn-Ga alloy system [9,31,35]. Due to their basic mechanism of deformation they attracted researcher for the development of sensors, actuators and magnetic refrigerators. Ni-Mn-based alloys have been synthesized using different techniques such as arc-melting, melt spinning, and MA [9,29,26-28,31]. Ni-Mn-Sn Heusler alloys, due to its comparatively low cost and good ductility than Ni-Mn-Ga and high martensitic transformation temperature has become a choice of study [36,37]. The realization of large magnetostrains in Ni-Mn-Ga activated an interest in the structural and magnetic properties of Ni-Mn-Al alloys. At the beginning they were brought for modifications and to improve the brittleness in the binary Ni-Al alloys [38]. The austenite and martensite phases of Ni-Mn-Sn and Ni-Mn-Al Heusler alloys display same crystal structure as that of Ni-Mn-Ga [39].

Recently, MA has been identified as a cost-effective method for the synthesis of intermetallics and Heusler alloys for industrial applications [9]. Compared to arc melting and other chemical and deposition methods MA offers feasibility in producing mass-scale production at nanoscale range using high energy planetary ball mills, attrition ball mill devices [26] and also practically it is important and easy to mold fine powders into desired shape by consolidation. Coll et al. [29], Behara et al. [40], studied Ni-Mn-Sn shape memory alloy system by varying Sn content. Ni-Mn-Sn polycrystalline ingots were prepared by argon arc melting process. Thermal analysis showed that transformation temperatures rely on the alloy composition. They produced polycrystalline bulk alloys by arc melting and found that increasing Sn content, the transformation temperature of martensite to austenite decreases. Dan et al. [41] investigated magnetic and magnetocaloric properties of Ni-Mn-Sn Heusler alloys by preparing it by arc melting and then carried annealing. They showed the possibility of the alloy for magnetic refrigeration by suitable composition and annealing condition. Saini et al. [42] prepared Ni-Mn-Sn alloy by arc melting technique. The results suggested possibility of Ni-Mn-Sn as Ga- free high-temperature SMAs. Varzaneh et al. [43], Popa et al. [44] investigated structural behavior of Ni-Mn-Sn alloys prepared by MA route using planetary ball mill and the subsequent annealing on the structure of alloys. The results suggested MA as an active method to fabricate SMAs. The magnetization curve revealed soft ferromagnetic nature of the alloy. Very few attempts have been made to study the mechanical properties of Heusler alloys with particular focus on hardness, elastic moduli, bulk modulus, fracture toughness and brittleness or ductility [45-47].

4. CONCLUSIONS

Literature review reveals that in recent years Ni-Mn based Heusler SMAs have generated interest in research for the actuators, sensors and refrigerators applications. Out of these alloys Ni-Mn-Ga are popular and mostly investigated FSMAs. Despite of these properties, its high brittleness, cost of gallium element are big constraints for the practical use of this alloy. To overcome these limitations better gallium-free Ni-Mn based SMAs have been reported during last decades. In this respect Ni-Mn-Z (Z=Sn, Sb, In, Al) have been studied for possible SMAs. It is pointed that research in Ni-Mn-Ga Heusler alloys triggered an interest in the development of Ni-Mn-Sn and Ni-Mn-Al alloys. Literature survey also reveals that arc melting is the general method employed for the preparation of Ni-Mn based Heusler alloys. MA is another interesting, cost effective technique employed to synthesize these alloys using high energy ball mills. Studies on mechanical properties of Ni-Mn based Heusler alloys are lacking, which is limiting its use for practical applications. From literature review it can be realized that some experimental information is available regarding hardness and elastic modulus properties of semi-Heusler alloys, but similar information does not available for Ni-Mn based Heusler alloys.

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