Superelastic and Superplastic of Structure-Function Alloys

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Abstract

Smart shape memory alloys (SMAs) have dual functions of actuation and sensing. Excellent superelasticity and fatigue resistance are crucial to the service reliability and stability of the alloy. This review summarizes the microstructure, functional properties, strengthening mechanism and failure mechanism of the most widely used NiTi SMA, novel- NiMn-based SMA and new developed Fe-base alloy. The high strength and toughness of NiTi memory alloy achieves excellent fatigue cyclic performance through microalloying, structure, and grain size engineering. The texture toughening strategy overcomes the intergranular brittleness of traditional NiMn-based memory alloys, which enhances the recoverable strain and fatigue resistance substantially. Strategies based on the alloy design to obtained iron-based superelastic alloys with near-constant critical stress temperature dependence, which breaks the traditional nature of superelastic alloys where the temperature decreases with higher strength.The induction and conclusion of the control strategies of superelasticity/superplasticity of shape memory alloy provide a benefit guidance for the design and application of structure-function integrated materials.

Keywords

Superelastic/Superplastic Alloy; Fatigue Resistance; NiTi; Novel NiMn-based Alloy; Fe-based Alloy.

1. Introduction

The excellent mechanical properties of metal materials are the basis for realizing functional characteristics. Traditional metal materials have exposed shortcomings such as poor stability, single structure, and poor adaptability, making it difficult for the functional and engineering application. Therefore, high-strength, superplasticity and superelasticity metal materials are developed via various strategies to achieve functional characteristics, such as shape memory effect (SME) [1-3]. For the structural materials, how to strengthen the materials while maintaining excellent superplasticity is a long-term tricky trade-off. For the shape memory alloys (SMAs), how to enhance their superelasticity and fatigue resistance while maintain the functional characteristics still requires strategic efforts [4,5].

Recently, microalloying, heterostructure and oligocrystalline structure design have been proven to be an effective way to overcome the strength-ductility trade-off [6-14]. SMAs is a smart metal material that integrates the intelligent driving and temperature sensing. Large reverserable strain, including superelastic strain, can be obtained during the load-unload process through the reversible martensitic transformation. The superelasticity of SMAs exhibit nonlinear stress-strain relationships due to elastic migration during thermoelastic martensitic phase transformation, these characteristics promotes the SMA applied in biomedicine [15], aerospace [16], and civil engineering [17], as shown in Figure 1.

The fatigue cyclic resistance of SMAs that undergoes multiple load-unload loops during the transformation process without the performance degradation is crucial for the engineering application. It is generally believed that the functional degradation is due to the production of dislocations and initiation of microcracks during the stress-induced irreversible processes in the two-phase transition layer, and finally induced failure of materials [18,19]. Additionally, the high yield strength, functional stability and fatigue resistance of SMAs is difficult to achieve in a uniform coarse-grained structure. Nanonizing the grain size [8,20-22], establishing heterostructures [7], and introducing nanoprecipitation [7,12,23-28] can hinder dislocation movement, improve damage tolerance, enhance functional stability and anti-fatigue purposes. This research progress on the superelasticity and functional stability of several typical SMAs, aiming at providing guidance for material selection and device design.

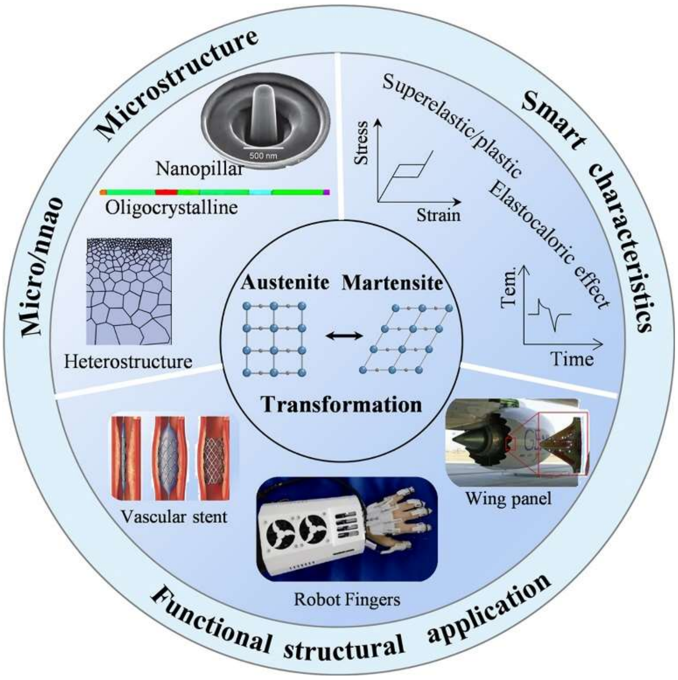

Figure 1. Characteristics and application of SMAs.

2. Superelasticity/Superplasticity Metal Materials

Elasticity is the ability of a material to return to its original shape after deformation and is characterized by the recoverability of strain. Typically, the elastic strain of most metals is a well-known 0.2 percent. In SMAs and high entropy alloys, the elastic strain can reach a few percent, called hyperelasticity, and is induced by external stresses. In SMAs, the essence is a martensitic phase transition. in NiTi-based SMA, phase transition process for the parent phase B2-B19' martensite structure of the transformation process will involve the presence of the intermediate phase R phase, the smaller the R-phase transition hysteresis is more conducive to the superelasticity; NiMn-based SMA martensitic structure of the five-layer modulation martensite The NiMn-based SMA martensite structure has five-layer modulated martensite (5M, pseudo-tetragonal), seven-layer modulated martensite (7M, pseudo-orthorhombic), and non-modulated martensite (NM, quadrilateral), the NM structure is more stable than the first two and is able to obtain better superelasticity; the Fe-based phase transformations are mainly the FCC austenite, the martensite of the HCP and the BCC/BCT structures, and precipitation phases and nano-twins allow the generation of the thermoelastic martensitic transformation to obtain superelasticity.

2.1 Ni-Ti SMAs

Ni-Ti shape memory alloy (Ni-Ti SMAs) is a typical kind of smart alloy material which not only has excellent superelasticity and shape memory effect, but also has superior damping performance and biocompatibility. It has been widely used in biomedicine, aerospace and aviation. Shape memory effect, superelasticity and fatigue cyclic are usually related to the alloy composition, grain size, crystal orientation, phase and deformation method [29-36]. The superelasticity and shape memory effect can be improved by tuning the alloying concentration, fabrication process, precipitate phase size and crystalline texture [30-32,35-38]. Generally, one-dimensional nanomaterials, such as independent nanowires andpillars, have higher elastic strains (4%–9%) comparing with the bulk materials.

NiTi SMAs is the most potential elastic thermal refrigerant in solid-state refrigeration technology. It has an orderly transformation from body-centered cubic structure β phase at high temperatures to a CsCl-type B2 phase at room temperature. When it occurs, the B2 phase can be directly transformed into the monoclinic structure B19' phase or intermediate R phase to obtain the 19' phase. However, bulk polycrystalline NiTi SMAs has poor superelasticity and cyclic instability [39-47], which will significantly reduce the efficiency of the refrigeration system. The main cause of performance degradation is dislocation slip caused by lattice incompatibility between austenite and martensite or stress concentration at the triple-phase junction. The generation and accumulation of dislocations are detrimental to recovery and finally lead to functional deterioration after cycling. Therefore, improving the functional cycle stability of SMAs is crucial for engineering application. Studies have shown that the introduction of secondary phases can improve the cyclic stability of NiTi SMAs. The formation of Ti_3Ni_4 nanoprecipitation NiTi alloys could hinders dislocation movement and produces good cycle stability effectively [23,24,50]. In the $Ni_{50.4}Ti_{49.6}$ (at.%) alloy prepared by selective laser cladding, the presence of Ti_3Ni_4 nanoprecipitates (~50 nm) enables the alloy to obtain a stable tensile recovery strain of up to 3.74% after 20 load-unload cycles [51].Chen et al. [26] has shown the $Ni_{50}.8Ti_{49.2}$ SMA prepared by cold processing and annealing treatment induce a stable tensile recovery strain of 4.7%, which attributes from the formation of nanoscale B2 grains and coherent Ti_3Ni_4 nanoprecipitates (~ 100nm). Grain refinement, another kind of method for improving performance, is widely used. Impeding dislocation movement by reducing grain size can enhance superelasticity and shape memory effect [52-54]. In recent years, nanometerization of the size of metallic materials has been considered as a very promising method to improve mechanical properties [55]. It is reported that the influence of grain size (GS) on phase transformation and mechanical properties can be mitigated through severe plastic deformation and thermomechanical treatments, including high-pressure torsion (HPT) and equal channel angular extrusion (ECAE) [22]. It has been demonstrated that GS can inhibit thermally induced martensitic transformation when it is refined to below 60 nm [21,56]. The thermal cycle stability of the $Ni_{49.7}Ti_{50.3}$ alloy with GS of 100–300 nm prepared by ECAE has been significantly enhanced [57].

The heterostructure, which is obtained through the design of alloys and the implementation of complex manufacturing processes, can further enhance the mechanical properties of brittle SMA in comparison to traditional strengthening methods [58-61]. The realization of high strength and large linear hyperelastic synergy is contingent upon the heterogeneous structure, see Figure 2a. The introduction of nanoscale structures within the austenite matrix enables the original martensite core to be retained, circumventing the conventional martensite nucleation process during the strain process. This results in a reduction in the abrupt stress-induced martensite transformation, which is replaced by a more gradual and continuous transition. Cui et al. [7] constructed a heterogeneous structure containing NiTi nanoparticles and non-converted Nb nanowires, see Figure 2b, c. and achieved a linear elastic strain of more than 6% in $Ni_{41}Ti_{39}Nb_{20}$, with a yield strength as high as 1.6 GPa, see Figure 2d, e. Moreover, the superelastic NiTi nanocomposite [8] with a heterogeneous structure obtained through severe plastic deformation and low-temperature annealing exhibits a recoverable strain of 4.3% and a super high yield strength of 2.3 GPa. The NiTi crystalline-amorphous nanocomposite (CAN) is composed of parallel crystalline nanolayers embedded in an amorphous matrix, with an average thickness of approximately 8 nm. The average grain size is approximately

110 nm. In NiTi CAN, the strong constraint of the amorphous phase precludes grain boundary sliding, enhances dislocation movement resistance, and suppresses the generation and propagation of phase change-induced dislocations in the nanocrystalline phase during the cyclic phase change process. In the nanoscale amorphous phase, the crystalline phase impedes the formation and propagation of shear bands. NiTi CAN thus demonstrates remarkable functional stability under applied tensile stress of up to 1.8 GPa. This is beneficial from the synergistic effect of the nanocrystalline phase and the amorphous phase, which enables NiTi CAN withstand 10^8 compression cycles. Furthermore, the $Ni_{51.5}Ti_{48.5}$ alloy produced via additive manufacturing techniques exhibits a nanocomposite microstructure with a dendritic structure. This induced 10^6 superelastic cycles in NiTi SMAs.

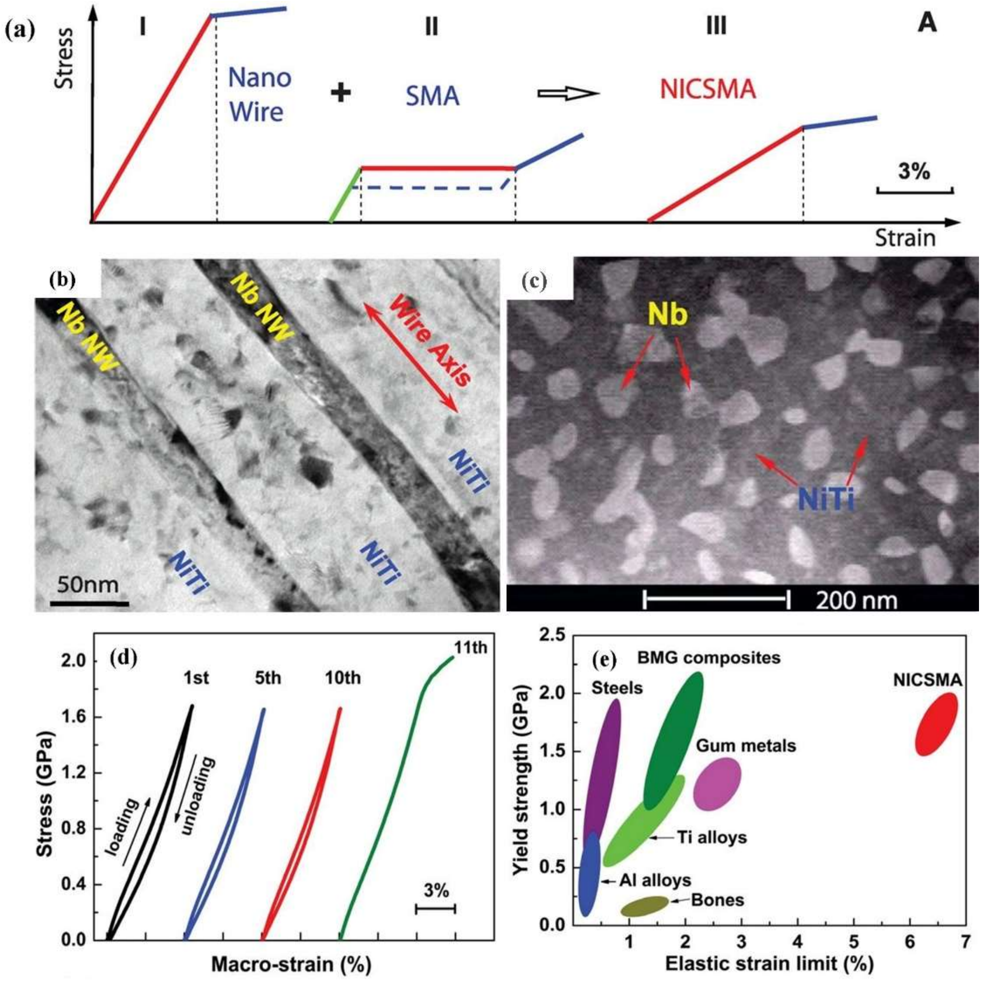

Figure 2. Schematic diagram of the design concept of NiTi nanocomposites (a) [7]. TEM bright field image of the longitudinal section of $Ni_{41}Ti_{39}Nb_{20}$ nanocomposite wire (b) and the transverse section (c). Tensile stress-strain cycle curve of $Ni_{41}Ti_{39}Nb_{20}$ nanocomposite wire at room temperature (d). Comparison of yield strength and elastic strain limit of different materials (e).

The presence of precipitated phases can result in the introduction of additional dislocations and grain boundaries within the matrix, thereby enabling the attainment of Strength Matching In addition to the precipitated phases formed by Ni and Ti, the precipitated phases formed by the third-party elements can enhance the compatibility of interfaces, fatigue resistance, and superelasticity.

2.2 NiMn-based SMAs

NiMn-basedd SMAs exhibit distinctive properties in response to external stimuli, including stress, temperature, and magnetic fields. This makes them suitable for a range of applications, including actuators, sensors, and solid-state refrigeration equipment [62-64]. The Ni-Mn-Ga SMA is a typical

Heusler alloy that has attracted increased attention due to its outstanding superelasticity, shape memory effect, and magnetocaloric properties. The martensitic phase transformation is a non-diffusion phase transformation for the Ni-Mn-Ga alloy. During the phase transformation, the presence of other phases may result in incomplete transformation of martensite, which may in turn induce the microcracks initiation and growth at the grain boundaries simultaneously, and ultimately result in poor cycle performance. Numerous reports have been dedicated to overcome the intrinsic brittleness of polycrystalline alloys and the difficulty of plastic deformation, aiming to improve the fatigue cyclic performance of SMAs [7,8,23-25]. Single crystal Ni-Mn-Ga SMA is devoid of internal constraints, which results in superior mechanical properties. Nevertheless, the production of single crystals is a time-consuming process. The fabrication of polycrystalline Ni-Mn-Ga SMA is a relatively straightforward and inexpensive with melt spinning or the Taylor-Ulitowski method method. Triangle junctions between the grains are generally the origin of brittle cracks during deformation, rarely exhibit large recoverable strains. Dunand and Müullner [65] proposed a strategy to make the grain size comparable to one or more of the characteristic sample dimensions (film thickness, filament or holder diameter, ribbon width, or particle size) through grain growth or sample shrinkage, see Figure 3a. At this point, the size effect assist coordinated deformation between grains and this approach has also been validated in fibers and foams [68,69].

The combination of microalloying and size control was found to be an effective method for improving the cyclic performance of NiMnGa SMAs. The Taylor-Ulitowski method can prepare glass-coated microwires with a diameter of 5–200 μm. It can also reduce the geometric constraints between grains and introduce orientation, thereby improving the superelasticity and ductility of SMA. Xuan [25] enhanced the compatibility between the martensite and austenite lattices through the formation of γ nanoprecipitates by doped Fe and Cu elements in the Ni-Mn-Ga microwires. The oligocrystalline microstructure enables the SMA microwire to exhibit multi-step superelasticity comparable to that observed in Ni-Mn-Ga-Co-Cu [74], see Figure 3b, c. Microwires with a bamboo-like particle structure were prepared by the Taylor method. During the loading process, existing γ precipitates generate elastic incompatibility stress, which is then relaxed during unloading through reversible twinning. On this basis, the oligocrystalline microwires with nearly <001> porientation prepared by Ding [70] showed a fully recoverable strain of >10% and multi-step superelastic behavior. The phase transformation temperature of Ni-Mn-Ga alloy increased by introducing of Co and Cu, promoting the microwires from austenite state to martensite at room temperature. Meanwhile, the austenite transforms into martensite can be drived by temperature, see Figure 3d, e.

The formation of an oligocrystalline structure in microwire samples permit polycrystalline alloys to exhibit properties comparable to those of single-crystal alloys. The oligocrystalline structure provides a free surface that reduces the grain boundaries constraints, thereby facilitates the coordinated deformation between grains. Currently, the oligocrystalline structures are introduced in some other types of SMA, such as microfilaments [11,70] and porous foams [71,72]. Stian M. Ueland [75] prepared a Cu-Al-Zn microwire with an oligocrystalline structure with the fatigue life improves two orders than its counterpart. The crystal formation confers an advantage in improving the fatigue properties of the alloy. Also, Chen [76] prepared Ni-Mn-Fe-Ga microwires with an oligocrystalline structure and a large recoverable strain of up to 15% and stable superelasticity after 1200 cycles. The oligocrystalline structure, when combined with a favorable grain orientation, serves to suppress intergranular fracture and to enhance the superelasticity and fatigue cycling performance of the material.

The oligocrystalline structure and nanoprecipitation achieved by microalloying and size effect in the previous studies facilitate the lattice compatibility and enhance the superelasticity and functional stability of nickel-manganese-gallium (SMAs), which is of great scientific significance and engineering value for the intelligence and miniaturization of devices.

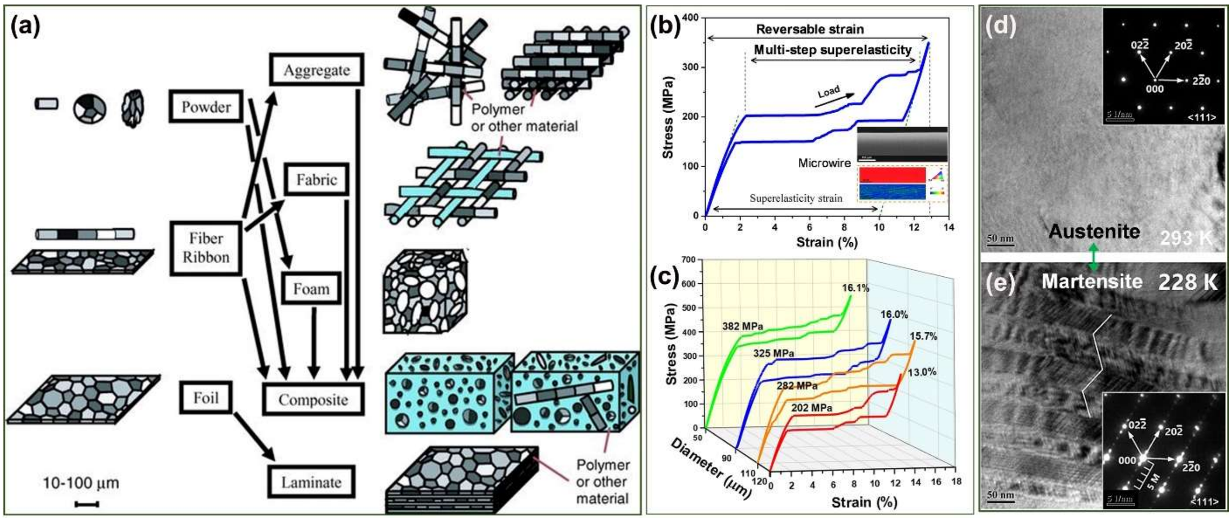

Figure 3. Size effect of NiMn-based SMAs superelasticity [65] (a). Uniaxial tensile stress-strain curve of NiMnGaCoCu alloy at 300 K [25] (b). Stress-strain curves of microwires with different diameters at 573 K [25] (c). Diffraction spots of austenite at 293 K (d). Diffraction spots of martensite at 228 K (e) [70].

2.3 Fe-based SMAs

Fe-based SMAs have unique advantages such as high strength, superplasticity, good shape memory properties and low cost, but most of the Fe-based SMAs are non-thermally elastic martensitic transformation and thus cannot exhibit superelasticity, and non-thermally elastic to thermally elastic martensite transformation can be achieved by introducing precipitation phases and nano-twins, and the thermally elastic phase transformation is the transformation between austenitic (fcc) and martensitic phases (bcc/hcp), see Figure 4. Fe-based SMAs exhibit remarkable properties under extreme environmental service conditions. This allows them to be used as fishplates for heavy machinery tracks, seismic dampers, and rail couplers for novel material-intensive applications [77]. However, the high superelasticity of iron-based SMAs at room temperature has been an ongoing challenge, and recent studies have shown that the formation of nanoscale precipitates resulting from aging treatments can facilitate the reversible martensitic transformation of iron-based SMAs, thereby enhancing the superelasticity [12,28,78]. A major breakthrough was achieved in the development of polycrystalline FeNiCoAlTaB with the superelastic strain up to 13.5% [12], which is benefit from the synergistic effect of coherent nanoprecipitates and large grain size. Based on the nanoprecipitation strategy, superplastic strain exceeding 5% is obtained in the developed Fe-Mn-Al-Ni [28] alloy at room temperature. Two alloy systems generate high local internal stress and large anisotropy at grain boundaries during martensitic transformation. This can easily lead to brittle fracture and the suppression of superelastic behavior. One effective method for improving the superplasticity of SMAs is to reduce the constraints on grain boundaries, thereby promoting coordinated deformation between grains.

In the case of iron-based alloys, processing is required to facilitate a transition from ordinary plastic deformation to the shape memory effect [85,86,87]. In recent years, the superelasticity of Fe-based SMA has been enhanced through the design strategy, including the strengthening of the matrix with coherent nanoprecipitates, the creation of favorable orientations, and the reduction of grain boundary constraints. In addition, through abnormal grain growth in the α single-phase region and α + γ two-phase region, the grain size is larger than the wire diameter or sheet thickness, resulting in large grains that reduce grain boundary constraints and improve superelasticity [81]. Zhao et al. [82] reported that a recoverable strain of 6% was obtained in samples alloy (Fe-34Mn-15Al-7.5Ni-1.5Co) prepared with directional solidification (DR) treatment that induced abnormal grain growth of larger than 20 mm. The constraints between grain boundaries are suppressed, which weakens the resistance to the reversible transformation of martensite. The above strategies can reduce the reversible transformation resistance of martensite, and thereby enhance the reversible strain. Besides, the temperature dependence of the critical stress is another essential feature of the martensitic transformation. Alloying of the temperature-invariant elements represents an effective strategy for overcoming this disadvantage. For instance, the doping of the Cr element has been shown to alter the temperature dependence of critical stress in the temperature range above 50 K without increasing the strain hysteresis in Fe-Mn-Al-Cr-Ni single crystal alloys [13]. The precipitates with a B2 structure and are arranged in a relatively irregular stacking order, which results in distortion of the thermoelastic martensite. Interestingly, the superelasticity of NiMn-based alloys is unstable in a wide temperature range, but $Fe_{34}Mn_{13.5}Al_3Cr_{7.5}Ni$ single crystal obtains nearly constant superelastic strain in a wide temperature range of 10 -300 K, with a recoverable strain of up to 3.5%, see Figure 5a, b. The realization of near-constant superelasticity in a wide temperature range is attributed to the temperature-invariant elements and the formation of precipitated phase.

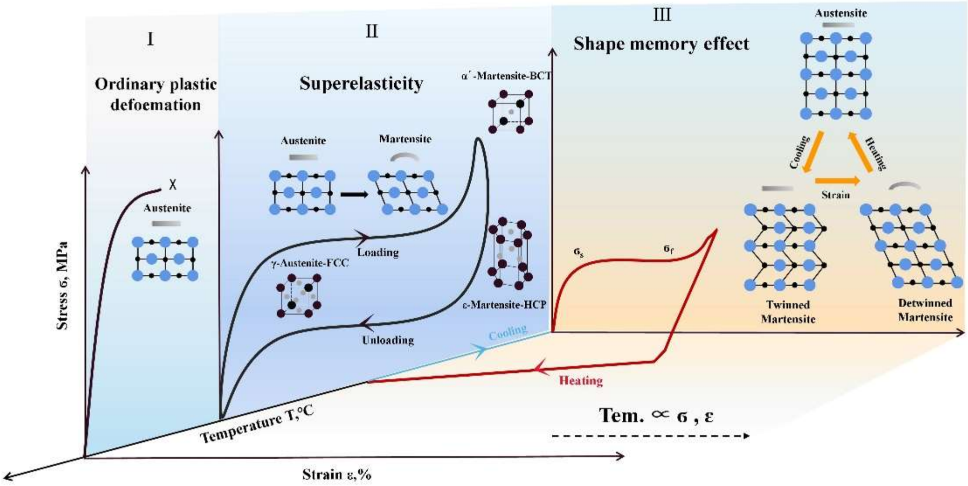

Figure 4. Typical stress–strain–temperature diagrams for SMAs (Ni–Ti alloy as an example).

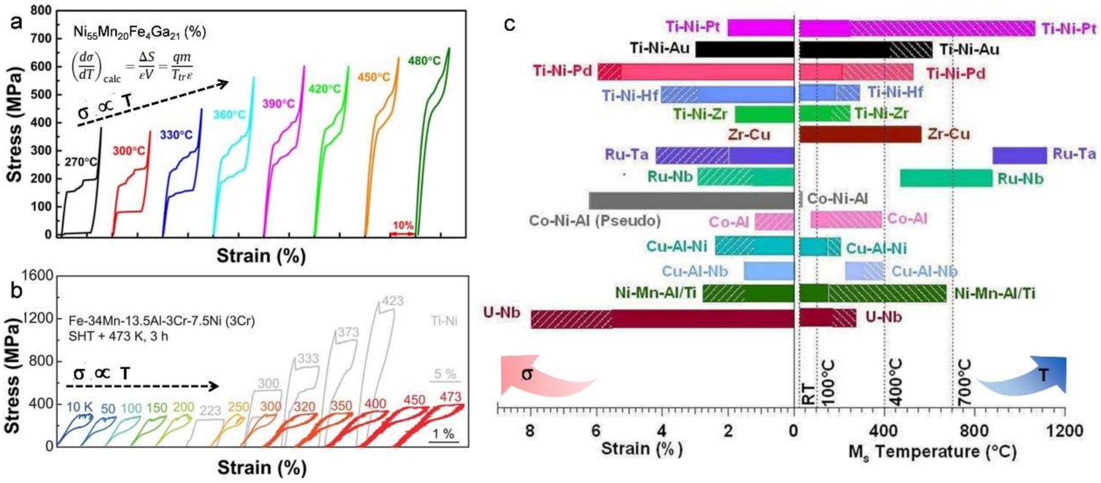

Figure 5. Stress-strain curves of $Ni_{55}Mn_{20}Fe_4Ga_{21}$ in different temperature ranges [76] (a). Comparison of stress-strain curves between $Fe_{36}Mn_{11}Al_{7.5}Cr_3Ni$ and NiTi in different temperature ranges [13] (b). Relationship between strain and temperature of different types of alloys (c).

However, the fatigue failure of the Fe-based SMA under cyclic loading conditions is mainly due to the obstruction of the reversible martensitic phase transformation, resulting in the accumulation of residual strain [83]. There are relatively few studies on the cyclic stability of Fe-based SMAs. Figure 6 is a comparison chart of the cyclic stability of different types of SMAs. It can be seen that the functional stability of Fe-based SMAs is lower than that of NiMn-based and NiTi-based counterpart. Herein, we expect to improve the cyclic stability of iron-based SMA by avoiding martensite interface pinning and residual strain accumulation during cyclic phase transformation. If the reversible movement occurs through a specific lattice path, the defects can be eliminated at the earliest stages, thus stabilizing energy losses during subsequent transformations. Finally, the dispersed nanoprecipitates can induce back stress on the martensite laths and are beneficial for the interface movement along a specific path between the parent phase and ε-martensite phase. Thus, the formation of ε-martensite can be synergistically enhanced during prestressing by increasing the formation of stacked faults, and the reverse transformation can be realized during unloading. Stress induced ε-martensite undergoes a process of formation and decomposition during repea-ted tensile and compressive cycles. The repetitive phase transformation is beneficial to reduce the internal stress concentration induced by cyclic loading and inhibit the accumulation of local dislocations, thus suppressing the generation and extension of fatigue cracks [84]. The introduction of sufficient slip resistance at acceptable transformation stresses can result in a reduction in the plasticity produced at the martensite-austenite interface. The functional stability of iron-based SMA is achieved through the synergistic effect of structural design and the control of precipitation phase.

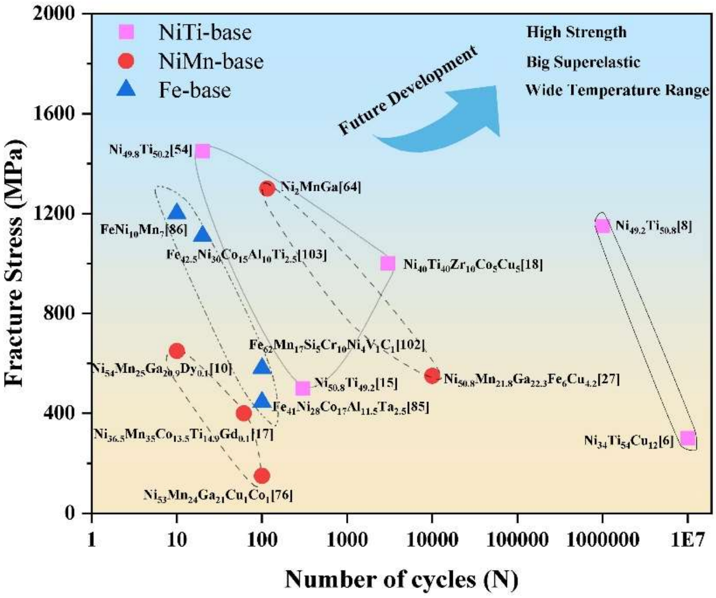

Figure 6. Comparison of cyclic stability of various types of SMAs at room temperature [6,8,10,14,15,16,25,52,62,74,83,84,87,90].

The high superelasticity and functional stability of Fe-based SMAs over a wide temperature range give them great potential as high damping and sensor materials, and can be used as infrastructure for applications in extreme environments such as the Moon, Mars, etc, which is of great importance for carrying out aerospace and large-scale engineering seismic projects.

2.4 Comparison of the Structural-Functional Integrated Materials

Excellent mechanical properties support the action of the material's multifunctional properties. NiTi-based shape memory alloys exhibit a number of distinctive properties, including unique functional characteristics, biocompatibility, and damping properties [7,45-47]. The ultra-high strength of these alloys, achieved through the utilization of the special mechanical properties inherent in the separate nanowires, can be employed in a variety of demanding smart devices [7]. Additionally, NiTi's exceptional functional stability renders it the most attractive material for alloys.

Magnetically driven shape memory is a unique property of NiMn-based shape memory alloys, where macroscopic strains can be generated by the rearrangement of martensitic variants under the presence of a magnetic field. Larger than 10% magnetic field-induced strain was obtained in martensitic phase Ni-Mn-Ga-based single crystal alloy [89-91], which make it used to design actuators, sensors and harvesters. Interestingly, heat exchange was usually accompanied during phase transformation driven by stress [92] or magnetic field [93], elastocaloric effect [94] or magnetocaloric effect [95], such as the reported NiMnCo(Sn,In) alloys [96-99]. Basically, the enhanced superelastic properties of NiMn-based memory alloys provide a fundamental support for the implementation of multifunctional properties of the materials.

High strength, large strain and superelasticity are the essential properties of the iron-based superelastic shape memory alloys [12,28,77,78]. Besides, the new developed Fe-Mn-Al-Cr-Ni have a controllable temperature dependence (10-300 K) of critical stress by optimizing the Cr content, which applied in precision metrology to avoid thermal expansion. Meanwhile, the lower cost and better cold-workability make it as an advanced structural-functional integrated materials [100,101].

3. Summary and Prospect

With the advent of the smart era and the booming of high-end equipment manufacturing, the development of high-performance and functional SMAs and HEAs is imminent. In SMAs, it is a challenge to improve yield strength and fatigue resistance in a uniform coarse grain state. Size effects in the material help to reduce geometrical constraints between grains and significantly improve lattice compatibility between martensite and austenite. This contributes to the functional stability of the material. Heterogeneous structures are microstructures with significant strength/ductility differences in the spatial range from the atomic level to tens of nanometers. These heterostructures generate reactive forces at the interface, harmonizing plastic compatibility while increasing the yield strength and plasticity of the material.

Moreover, the interconnection of cavities and the movement of dislocations between the two-phase structures serve to reduce stress concentration and achieve superplasticity. In addition to NiTi SMA, further efforts are required to achieve high energy efficiency, large-scale production, and application for the functionality and damage resistance of other SMAs and HEAs. Although the incorporation of heterostructures and nanoscale precipitates can enhance the overall properties of alloys, the development of novel strengthening strategies remains a crucial area of research.

Acknowledgments

The authors acknowledged the financial supports from National Natural Science Foundation of China (Grant Nos. 51771121, 52303091), Science and Technology Committee of Shanghai Municipality(20ZR1437500) and from Shanghai Yangfan Program (22YF1430200). Shanghai Yangpu District Medical Key Discipline Construction Fund (22YPZA08).

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