Microstructure and Phase Transition Characteristics of NiTi Shape Memory Alloy

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Abstract: Shape memory alloy (SMA) with shape memory effect and superelasticity has had an increasing interest for researchers of mechanics of materials in recent decades. With the deepening of theoretical research, the applications of SMA have also made considerable progress. SMA has a unique solid phase transformation characteristic that is thermoelastic martensitic transformation. The high temperature phase of SMA is austenite, while the low temperature phase of SMA is martensite. Because of the biocompatibility and the corrosion resistance, NiTi shape memory alloy has been widely used in biomedical and aerospace. However, the NiTi binary alloy can only be applied to the ambient temperature, because the phase transformation temperature is lower than 100 centigrade. In order to apply the NiTi based shape memory alloy in the wider field, it is necessary to control the phase transformation temperature, thermal hysteresis latent heat of phase change and other phase transformation behavior and mechanical property effectively and accurately. Thus, it is important to add a third or fourth element to NiTi alloy to form a new type of NiTi based shape memory alloy. The results show that NiTi alloy contains many precipitates such as NiTi$_2$, Ni$_3$Ti$_2$, Ni$_4$Ti$_3$. Adding the third or even the fourth element to the NiTi binary alloy can effectively adjust the phase transition and related mechanical properties of NiTi alloy. In this paper, the research progress of NiTi binary alloys is summarized, the microstructure, types and structures of properties, types and properties of phase transitions of NiTi alloys are introduced respectively, the problems faced by NiTi alloys are analyzed and their prospects are prospected, so as to provide reference for the development of shape memory alloys with better properties.

1. Introduction

The NiTi based alloys are the most important practical shape memory alloys (SMA) with excellent mechanical properties. Although there had been many controversial problems in the past as described below, most of them have been solved by now. Thus it will be useful to review them in a unified manner on an up-to-date basis. Secondly, there are many phase transformations in NiTi based alloys system, which include not only diffusionless/martensitic transformations, from which shape memory and superelastic effects arise, but also diffusional transformations. Thus even the latter transformations have been used effectively to improve shape memory characteristics. Thus the alloy system will serve as an excellent case study of physical metallurgy, as is the case for steels where all kinds of phase transformations are utilized to improve the physical properties.

The unique shape memory effect in an equiatomic NiTi alloy was first found by Buehler et al. in 1963[1]. Although the same effect was found in Au–47.5at.%Cd and In-Ti alloys earlier, it had not attracted much attention of researchers[2-4]. In contrast, the NiTi alloy became quite popular soon after the discovery, partly by the world-wide publicity by the people in Naval Ordinance Laboratory who found it, and partly by the good mechanical properties of the alloy, which were suitable for...
applications. Despite the fact, the understanding of the phenomena and the martensitic transformation, from which the phenomena originate, did not develop rapidly. This is because the NiTi alloy system is quite a complicated system, as it turned out later. By the 1970s, Cu-Al-Ni, Cu-Zn-Al and NiTi based shape memory alloys had been developed[5, 6]. In the 1980s, shape memory alloys, such as stainless steel based SMA, iron base and Fe-Mn-Si based SMA, which have many advantages such as simple processing and low cost, were widely concerned and developed. Since then, a lot of researches have been carried out on the phase transition mechanism of shape memory alloys and the related hyperelastic effect mechanism. At the same time, such phenomena as two-step shape memory effect, R phase transition and omni-directional shape memory effect have also been discovered. This series of research results have opened up a broad prospect and market for the application of shape memory alloy[7, 8]. So far, the successful shape memory alloys that have been developed mainly include NiTi based shape memory alloys (such as Ni-Ti, Ni-Ti-Cu, Ni-Ti-Nb, Ni-Ti-Hf, etc.) copper based shape memory alloys (such as Cu-Zn-Al, Cu-Al-Ni, Cu-Zn, Cu-Sn, etc.), iron-based shape memory alloys (such as Fe-Mn-Si, Fe-Pd, Fe-Pt, Fe-Ni-Co-Ti, etc.), and Ag-Cd, Au-Cd, In-Ti, etc.

In the 1980s, shape memory alloys developed rapidly, and more than 10,000 patents related to shape memory alloys were issued. Shape memory alloys are widely used in all areas of the aerospace, electronics, machinery, energy, medical and other industries[9]. The NiTi shape memory alloy (48at.-%52at.%Ni) with nearly equal atomic ratio has outstanding functional characteristics: the single-pass shape memory effect and superelasticity can reach 8%. Two-way shape memory effect has good stability and can reach millions of times when the dependent variable is less than 1%[10]. Moreover, the grain size of the alloy is relatively small, so it has excellent mechanical properties and can be used in the manufacture of sheet and filament materials. In addition, it has high biocompatibility and corrosion resistance. At the same time, it has high resistivity, can be heated in a short time by current and other excellent characteristics, so it has been widely studied and applied[11]. Since 1990, shape memory alloy materials with wide lag and high temperature have become a new research direction, and the research on shape memory alloy film materials has been advancing with the times[12].

2. Basic concepts of shape memory alloys
Thermoelastic martensitic transformation is the fundamental reason for the shape memory effect and other excellent properties of shape memory alloys, such as hyperelasticity[13]. Martensitic phase transition is a solid phase transition that can occur in many kinds of nonmetals and metals. In essence, martensitic transformation includes shear transformation and displacement transformation. The martensitic phase transition is characterized by the regular motion of individual atoms. This atomic migration is similar to that which occurs in mechanical twins. Among them, the distance of atomic migration is generally no greater than the atomic distance of a single atom. This is different from some solid phase transitions controlled by diffusion, such as eutectoid decomposition, and martensitic phase transition belongs to diffusion free phase transition. Shape deformation is the most significant geometric feature of martensitic transformation. In general, austenite surface is relatively smooth, and when it transforms into martensite through phase transition, clear surface distortion can be observed. When austenite is converted into martensite, the plane is converted into a plane and the straight line into a straight line, so obvious surface buoyancy can be observed. Although the crystal structures of austenite and martensite are not the same, there is some lattice orientation relationship between the two phases. In austenite, there exists a plane that separates austenite from martensite during the phase transition. This plane neither rotates nor deforms during the phase transition, which is called the habitus plane[13].

2.1. Thermoelastic martensite transformation
There are two most common crystal structures in NiTi based shape memory alloys: Body centered cubic Austenite phase of the B2 structure (A, Austenite), and monoclinal martensite phase of the B19' structure (M, Martensite). Austenite is the high temperature parent phase and martensite is the
low temperature phase. In the process of Martensitic transformation, $M_s$ is generally used to represent the starting temperature of martensitic transformation, while $M_f$ represents the ending temperature of martensitic transformation. In the process of inverse phase transition (Austenite phase transition), $A_s$ is generally used to represent the starting temperature of inverse martensitic phase transition, and $A_f$ to represent the ending temperature of inverse martensitic phase transition. Compared with martensite, austenite has higher symmetry in structure. When the austenite is transformed into martensite, its symmetry is significantly reduced and many variants of martensite with crystallography equivalent but different habitus surfaces are produced. It is precisely because of the thermoelastic Martensitic transformation that shape memory alloy has two unique properties: shape memory effect and superelasticity. The thermoelastic martensitic transformation is closely related to temperature and stress[9, 14].

2.2. Shape memory effect
Shape Memory effect (SME) is a special effect in which a material has the ability to remember its initial shape. Generally, the material is kept in a certain shape under the condition of high temperature, and then reaches room temperature by cooling treatment, and residual deformation is generated by external force. If heated from its phase transition temperature, the material can still eliminate residual deformation and return to the shape it possessed at high temperature, a phenomenon known as shape memory effect. The shape memory effect can be divided into the following three types[15]. One-way Shape Memory Effect (OWSME), Two-Way Shape Memory Effect (TWSME) and All-Round Shape Memory Effect (ARSME). Table 1 compares the above three shape memory effects.

|               | OWSME | TWSME | ARSME |
|---------------|-------|-------|-------|
| Initial shape |       |       |       |
| Low temperature deformation |       |       |       |
| Heating       |       |       |       |
| Cooling       |       |       |       |

2.3. Superelasticity
Superelasticity is when an external force is applied to a shape memory alloy that has elasticity. If the alloy remains more inelastic than before, it can bounce back immediately after the applied stress is removed. Different from the elastic deformation of ordinary metals, the stress-strain relationship of shape memory alloy is nonlinear and its recoverable strain is much larger than that of ordinary metals.

When the ambient temperature is greater than $A_s$, the material exists in austenite state. If external stress is applied to the material at this time, the material will undergo stress-induced martensitic phase transition. When the ambient temperature is higher than $A_f$, the austenite phase in the material is in a thermodynamic stable state, while the martensite phase is in an unstable state. Therefore, the martensite phase can return to the austenite state through the inverse phase transition after the unloading of the external force[16].

3. Crystal structure of NiTi alloy
In NiTi shape memory alloy, there are three typical types of martensitic phase transition, and these three types of phase transition involve four different phases[17]. They are high-temperature austenite parent phase A, martensite phase M, B19, and intermediate phase R. Each phase corresponds to a corresponding crystal structure. The high temperature austenite parent phase A is the body centered cubic B2 structure, the low temperature Martensite phase M is the monocline B19'structure, the intermediate phase R is the tricline structure, and the B19 phase is the orthogonal structure. The phase transition process is shown in Fig. 1.
3.1. Crystal structure of the B2 austenite
In NiTi binary alloy, austenite phase (parent phase) is body centered cubic (bcc) B2 structure. B2 phase is a typical CsCl type body centered cubic structure. Ni atoms occupy every angle of the cube unit cell, Ti atoms are located in the central position of body centered cubic cube, and lattice constant a =0.3014nm[18].

3.2. Crystal structure of the B19' martensite
The crystal structure of such martensite had been an unsolved problem for many years after the first report as hexagonal by Purdy and Parr in1961[19]. However, the specific structure of martensite at that time is not very clear, there are some disputes. It was not until 1971 that Sandrock and Heheman proposed HS structural parameters and Otsuka et. al. proposed OSS structural parameters[19, 20]. After a lot of research, they think martensite structure is monoclinic structure. The structure of martensite described by many researchers is similar, but there are slight differences in the direction of irregular distorted crystal plane and monobevel angle. However, these two structures still have some problems in interpreting some diffraction patterns. Ten years later, Sinclair and Michal proposed an MS structure model of spatial group P21/M based on HS model, and analyzed the position of atoms[20]. Buhrer et al. obtained martensite as a P21/M spatial group through Rietveld analysis technique and established the STRUCTURE model of BGKMS[21]. Kudoh et al. further analyzed the structure of martensite by means of single crystal diffraction, and confirmed that martensite belongs to the P21/M space group, and also established the KTMO model[22]. KTMO parameter model is the most perfect NiTi alloy martensite structure model from the first principle calculation and relevant experimental data. Table 2 shows the comparison of the above five martensite structural parameter models. These constants vary slightly with the composition of the NiTi alloy[23].

| OSS  | HS    | MS    | BFKMS | KEMO  |
|------|-------|-------|-------|-------|
| a (nm) | 0.2889 | 0.2883 | 0.2885 | 0.2884 | 0.2898 |
| b (nm) | 0.4120 | 0.4117 | 0.4120 | 0.4110 | 0.4108 |
| c (nm) | 0.4622 | 0.4623 | 0.4622 | 0.4665 | 0.4646 |
| β (°)    | 96.8   | 96.8   | 96.8   | 98.1   | 97.78 |
| Atoms per unit cell | 4      | 4      | 4      | 4      | 4      |
| Space group | P2/c   | P21/m  | P21/m  | P21/m  | P21/m  |

3.3. Crystal structure of the B19 martensite
The structure of the martensite in the first stage of Ti_{50}Ni_{50-x}Cu_{x} (x=10-30) alloys were first reported by Shugo et. al. as orthorhombic (B19), and then confirmed by Tadaki et. al.[24, 25]. The structure is simple and is essentially the same as those of γ2 martensite in Au–47.5Cd and γ1 martensite in Cu–Al–Ni alloy etc. (i.e. 2H structure in Ramsdel notation). The lattice parameters of the parent phase and
the martensite in Ti$_{49.5}$Ni$_{40.5}$Cu$_{10}$ alloy reported by Saburi et. al. are: \(a_c = 0.3030\) nm (for parent phase), \(a = 0.2881\) nm, \(b = 0.4279\) nm, \(c = 0.4514\) nm\([26]\).

3.4. Crystal structure of the R-phase

The so-called R-phase appears under certain conditions prior to the transformation to B19$'$ phase. However, it is now established from the following reasons that this phenomenon is a martensitic transformation from B2 parent phase to R-phase, which has a distinct crystal structure. Firstly, R-phase martensite plates are clearly observed by electron microscopy\([27]\). Secondly, the direct transformation from B2 to B19$'$ without precursory effect occurs depending upon conditions. Thirdly, the shape memory and superelasticity effects are also observed associated with this phenomenon\([28]\). This simply means that B2–R transformation is a martensitic transformation, which competes with B2–B19$'$ transformation. If R-phase appears first, the successive transformation occurs such as B2–R–B19$'$. However, if B19$'$ transformation occurs first, R-phase transformation is suppressed\([29]\). Fig. 2 shows two structural diagrams of R phase of NiTi alloy.

![Fig. 2 Schematic illustration of the P3 model (a) and the p31m(1) model (b) for R-phase of Ni-Ti alloys](image)

4. Phase transition types of NiTi alloys

For NiTi shape memory alloy, the martensitic phase transition process of the alloy will be changed by different composition proportions, different degree of addition of the third group of elements, and even the subsequent thermo-mechanical treatment under different conditions. It can be a one-step phase transition, a two-step phase transition, or even a multi-step phase transition\([17]\).

4.1. One-step phase transition

NiTi binary alloys generally undergo a B2–B19$'$ phase transition directly after solid solution
treatment[30]. This phase transition is a first order phase transition, and surface convexity is generally observed. The transition from B2 austenite to B19’ martensite is called a one-step martensite transition, and does not require any other phase transition.

4.2. Two-step phase transition
The R phase transition may occur if the NiTi binary alloy is properly treated (aging treatment, thermal cycling, cold working, incomplete annealing, etc.) or the third group of elements is added. Then the alloy goes through a two-step phase transition of B2–R–B19’[31]. Generally, Ni-rich NiTi binary alloys (Ni>50.5at.%) undergo B2–R phase transition after aging treatment, and the reason for R phase transition is the precipitation of Ni3Ti2[32]. On the other hand, when Cu is added to the NiTi binary alloy to replace Ni, another type of two-step phase transition occurs, B2–B19–B19’, when the Cu content exceeds 7.5at.%[33]. However, if strictly speaking, this is not a single phase transition, but two continuous processes that occur in overlapping regions of similar temperature.

4.3. Multi-step phase transition
A large number of studies have shown that NiTi binary alloys generally undergo a one-step phase transition of B2—B19’ or a two-step phase transition of B2—R—B19’. However, under some conditions, there are other phase transitions, which are called abnormal multistep martensitic transformations[34].

5. Problem and prospect
Although NiTi shape memory alloys are developing rapidly and widely used, there are still some problems to be solved in the research and application of NiTi shape memory alloys. One of the key issues is the phase transition temperature. There are many factors affecting the phase transition temperature of shape memory alloy. How to obtain the phase transition temperature required in various fields without decreasing or even improving the other properties of the alloy has always been the focus and difficulty of the research. In addition, the shape memory effect of shape memory alloy is mainly dependent on martensitic transformation. The material change is hysteresis, so the alloy must be repeatedly loaded and unloaded, cooling and heating. Therefore, shape memory alloy is only suitable for low-frequency narrowband vibration. In addition, the structure of memory alloy has some defects such as crack damage, which limits its application to a great extent. On the other hand, in order to improve the application level of NiTi shape memory alloy, the alloy needs to be further miniaturized, so the research and application of shape memory alloy thin films also need to be further explored.

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