Effect of Temperature on Phase Transformation of NiTi-based Shape Memory Alloy

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Abstract. For NiTi-based alloys, the phase transition temperature directly affects and limits their application fields. In order to apply the NiTi-based shape memory alloy in the wider field, it is necessary to control the phase transformation temperature. Studies have shown that the content of Ni element in the NiTi-based alloy and the precipitates of the alloy, such as NiTi2, Ni3Ti2 and Ni4Ti3, will affect the phase transition temperature of the alloy. At the same time, adding a third or even a fourth element to the NiTi binary alloy can also effectively regulate the phase transition temperature of NiTi-based alloy. We then pay attention to the problems confronting the current state of the NiTi-based shape memory alloy. We have confidence that the NiTi-based shape memory alloy have a bright future in the development and innovation of excellent properties.

1. Introduction
Shape memory alloy is a kind of alloy material with excellent mechanical properties such as shape memory effect and superelasticity. The shape memory effect was discovered in metals as early as 1930. In the 1980s, stainless steel base, iron base and Fe-Mn-Si base shape memory alloys with many advantages of simple processing and low cost have been widely concerned and developed. Since then, a great deal of research has been carried out on the transformation mechanism of shape memory alloys and related superelastic effect mechanism. At the same time, the double path shape memory effect, R phase transformation, omnidirectional shape memory effect and other phenomena have been discovered. This series of research results open up a broad prospect and market for the application of shape memory alloy. At present, the successfully developed shape memory alloys mainly include NiTi based shape memory alloys, such as NiTi, NiTi-Cu, NiTi-Nb, NiTi-Hf, etc. Copper based shape memory alloys, such as Cu-Zn-Al, Cu-Al-Ni, Cu-Zn, Cu-Sn, etc. And 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. Shape memory alloys have developed rapidly, with more than ten thousand patents on shape memory alloys. The application of shape memory alloy is extremely wide, including all fields of aviation, aerospace, electronics, machinery, energy, medical and other industries[1]. Among them, NiTi shape memory alloy (48at.%-52at.%Ni) with near equal atomic ratio has outstanding functional properties: one-way shape memory effect and superelasticity can reach 8%. The double path shape memory effect is stable and can reach millions of times when the strain is less than 1%[2]. And the alloy grain size is relatively small, so it has excellent mechanical properties, can be used to manufacture thin plate and fine wire materials. In addition, it also has high biocompatibility and corrosion resistance. At the same time, it has high resistivity, can be heated by electric current in a short time and other excellent characteristics, so it has been widely studied and applied[3]. Since 1990, shape memory alloy materials with excellent properties such as wide hysteresis and high temperature have become a new
direction of research, and the research on shape memory alloy thin film materials has been advancing with The Times[4].

For the most widely used NiTi alloys, the phase transition temperature directly affects and limits their application areas. In order to be able to apply NiTi alloy in a wider field, it is necessary to control the transformation temperature of NiTi alloy effectively and accurately.

2. Effect of deformation on phase transition temperature

For the application of shape memory alloys, it is very important to control the phase transition temperature effectively. Using deformation to control phase transition temperature is one of the methods. This phenomenon was first discovered by Melton et al.[5]. A large number of studies have shown that NiTi-Nb alloy at martensitic stage can significantly increase the transformation temperature As and Af after severe deformation. Lin et al. also found the same phenomenon in NiTi binary alloy[6]. The phase transition temperature As increases with the increase of the total stress. In other words, the deformation of the alloy in the martensite stage can make the martensite to achieve stabilization. At the same time, the rise of the initial temperature of martensitic reverse transformation As is accomplished overnight, and As almost remains unchanged in the second heating process.

For martensite stabilization, Lin et al. drew some conclusions from dislocation and defects caused by structural distortion and deformation, and they believed that martensite boundary formed by dislocation led to martensite stabilization[7]. On the other hand, Piao et al. believed that the elastic energy stored in the rmoelastic alloys during cooling impeded the phase transition[8]. According to the above theory, Piao et al. conducted experiments with single crystal Cu-Al-Ni alloy and found that deformation at martensitic stage could indeed lead to an increase in the transformation temperature As. This increased phase transition temperature, As, returns to normal after undergoing the reverse phase transition of the first thermal cycle. This is due to the emergence of multiple martensite variants during cooling. Thus, the one-time stabilization of martensite is explained. The same experiment was performed with NiTi polycrystals, and the deformation of the alloy produced a large number of dislocations at the martensitic stage. Due to the constraints of grain boundaries in polycrystalline alloys, the elastic strain cannot be unloaded by twin grain boundary motion, but by dislocation slip. Thus, the stabilization of martensite can be given a qualitative explanation[8].

3. Effect of composition and precipitation on relative phase transition temperature

3.1. Chemical composition and element occupation of alloys

The martensitic transformation temperature is highly dependent on the composition of the alloy and the alloying treatment. At present, the following factors influence how the elements added to the alloy will occupy the role of alloying:

The first factor is the electron configuration of the alloying elements. Elements added to the alloy will preferentially replace atoms with similar electron configurations. Obviously, Zr and Hf have similar outer electron configuration with Ti, and their outer configuration is ALSO ND2. Thus Zr and Hf will replace Ti atoms but not Ni atoms in the alloy. On the other hand, Fe and Co are closer to Ni in the periodic table, so Fe and Co will replace Ni atoms in NiTi-based alloys.

Nakata et al. experimentally determined the placeholders of some elements in nitin-based alloys[9-11]. They found that Fe, Co and Pd tended to take the place of Ni atoms Mn, Cr and Cu can take the place of both Ti and Ni. That is, although electron configuration plays a key role in atomic space occupying, chemical affinity and atomic size also influence whether elements added to the alloy replace Ni or Ti atoms. If the added element has a strong affinity for Ti atoms (in the form of a large enthalpy of formation) and only a small affinity for Ni, it will take the place of Ni, even though it has similar chemical properties to Ni [19]. Co and Fe satisfy this condition, so Co and Fe will take the place of Ni atoms. In addition, the size of the atom is another factor. Other things being equal, elements added to the alloy will replace elements with similar atomic volumes[12].
3.2. Effect of Ni content on phase transition temperature of NiTi base alloy

A large number of experiments have confirmed that the martensitic transformation temperature of NiTi based shape memory alloy depends on the alloy composition and component elements. In most cases, a change in the composition of 1% nickel will even lead to a change in the 100K phase transition temperature. Therefore, a relatively efficient way to change the alloy phase transition temperature is to change the composition proportion of the alloy. The effect of composition change on the phase transition temperature of NiTi binary alloy is discussed firstly, and then the effect of adding elements on the phase transition temperature of NiTi based ternary alloy is discussed.

NiTi binary alloy is not an ordinary disordered metal, but a metallic compound with B2 structure. But it's not a linear compound with a fixed composition. It has a certain solubility for additional Ni in the Ni-rich region, but does not dissolve excess Ti. Figure 1 shows the phase diagram of NiTi alloy[13]. It can be seen that the Ti-rich region is basically vertical, while the Ni-rich region has a certain solubility at high temperatures (approximately 6at.% at 1000°C). After quenching at high temperature, the solid solution without precipitated phase can be presented at room temperature. This makes it possible to study the effect of Ni content on martensitic transformation temperature.

![Figure 1. Phase diagram of NiTi alloys](image)

3.3. Effect of alloying elements on phase transition temperature

The addition of alloying elements can change not only the phase transition temperature, but also the phase transition products and the phase transition path. Typical NiTi binary alloys generally have a direct B2→B19’ one-step phase transition, while NiTi-Fe alloys with Fe element added have a B2→R→B19’ two-step phase transition[14]. The separation of B2→R phase transition and R→B19’ phase transition increases with the increase of Fe element addition. This property allows the R phase properties to be unaffected by the R→B19’ phase transition over a wide temperature range.

Another important alloy system is NiTi-Cu alloy. Cu makes the phase transition temperature of the alloy less sensitive to changes in composition. This makes it easier to control memory performance. Another good feature of Cu addition is the high phase transition temperature (above room temperature) of NiTi-Cu alloy. This makes it possible to achieve shape memory effects at room temperature. The phase transition path of the alloy can be changed into B2→B19→B19’ by adding more than 5at.% Cu. The B2→B19 phase transition is also related to the thermal hysteresis (Cu content is 20at.%), the thermal hysteresis is about 4 K, which is the same as the B2→R phase transition. However, it is much smaller than B2→B19’ phase transition (about 30K). These good properties make NiTi-Cu alloy a very promising application shape memory alloy.

The addition of Pd element to NiTi alloy can replace the position of Ni atom, and with the addition of Pd element, the phase transition temperature will initially decrease. However, with the increase of Pd element addition, the phase transition temperature of the alloy will gradually increase with the
addition of Pd element[15]. At the same time, the phase transition products of the alloy also changed from B2→B19’ to B2→B19. At present, NiTi-Pd alloy and Ti-Pd alloy system have been studied as high-temperature memory alloys [16].

4. Conclusion
For NiTi-based alloys, the phase transition temperature directly affects and limits their application fields. Studies have shown that the content of Ni element in the NiTi-based alloy and the precipitates of the alloy, such as NiTi2, Ni3Ti2 and Ni4Ti3, will affect the phase transition temperature of the alloy. At the same time, adding a third or even a fourth element to the NiTi binary alloy can also effectively regulate the phase transition temperature of NiTi-based alloy. It is confidence that the NiTi-based shape memory alloy have a bright future in the development and innovation of excellent properties.

Acknowledgments
The Natural Science Foundation of Inner Mongolia, grant number 2019BS03010; the PhD Start-up Foundation of Baotou Medical College, grant number BSJJ201808.

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