Effects of Cu content and heat treatment on the transformation behaviour and shape memory property of Ti-Ni-Cu alloys

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Effects of Cu Content and Heat Treatment on the Transformation Behavior and Shape Memory Property of Ti-Ni-Cu Alloys

by

Cheng Guiping

Supervisor: Asst/P Xie Zeliang

A thesis submitted to the Nanyang Technological University in
fulfillment of the requirements for the degree of Doctor of Philosophy

School of Materials Science and Engineering

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ABSTRACT

Ti₅₀Ni₂₅Cu₂₅ ribbon is widely studied because of its one stage B2 (austenite) $\leftrightarrow$ B19 (martensite) transformation with small hysteresis and good shape memory property, which can be useful in microactuator appliances. Structure-property relationships are fundamental to optimize properties of shape memory alloys. In order to understand the effects of initial melt-spun structure and post-heat treatment on the shape memory properties (transformation behavior and shape recovery strain) of Ti₅₀Ni₂₅Cu₂₅ ribbon, three different initial structures were selected: fully amorphous, fully crystalline and partially amorphous. In addition, the crystal structure and transformation behavior of bulk Ti-Ni-Cu alloys with different Cu contents were investigated in order to understand the mechanism of Cu addition on the transformation characteristics from a thermodynamic viewpoint. SEM, XRD, TEM, DSC and TMA techniques were used as characterization methods.

The initially amorphous ribbon crystallized at 450°C. With an initial amorphous structure, it was possible via proper annealing to obtain nano-sized martensite without twinning or micro-sized martensite with only one pair of twin variants. Strong preferential orientation was observed to change with annealing from [211]_{B19} fiber to (111)_{B19}[$\bar{2}$ 11]_{B19} sheet texture, B11 TiCu precipitates formed at annealing temperature above 550°C. The initially partial amorphous ribbon shared a similar structure evolution with annealing to the initially amorphous ribbon.

The initially crystalline ribbon contains a mixed structure of B2 austenite and B19 martensite at RT. The two-phase microstructure did not change except that the amount of

B19 phase increased with the increase of annealing temperature up to 550°C, above which B11 precipitation occurred.

In this study, the frequently observed twin was Type I (111) twin and its twinning elements were calculated.

Initial structure has no effect on transformation sequence and hysteresis, but leads to different transformation temperatures and shape recovery strain. All the three annealed ribbons showed a one-stage $B2 \leftrightarrow B19$ transformation and well-defined shape memory effect. Annealing above 550°C decreased transformation temperatures and shape recovery strain of all the three ribbons due to the formation of B11 TiCu precipitates. Initially crystalline ribbon showed much lower transformation temperatures but higher shape recovery strain than initially amorphous and partially amorphous ribbons after annealing due to retained B2 austenite. It showed the highest shape recovery of 2.5% under 45 MPa after annealing below 550°C.

The transformation sequence of $Ti_{50}Ni_{50-x}Cu_x$ shape memory alloys changed with Cu content. The reason is that Cu addition increases the driving force of $B2 \leftrightarrow B19$ transformation. The smaller transformation hysteresis of $B2 \leftrightarrow B19$ is due to its smaller transformation shear.

CHAPTER 1 INTRODUCTION

1.1 Background

Shape Memory Alloys (SMAs) have attracted much attention in recent years, since they are smart materials, as well as functional materials. The unique shape memory effect (SME) and superelasticity (SE) realized in these alloys, which are caused by the martensitic transformation, make SMAs potential materials for many applications such as actuators and medical devices [1, 2].

The first recorded observation of a thermoelastic martensitic transformation was in 1932 by Olander in an AuCd alloy. In 1951, Chang and Read observed the reversibility of the transformation in a bent bar of AuCd alloy which they termed a "rubber-like" behavior. Later, the behavior was also observed in an In-Ti alloy. However, it was not until 1962, when the shape memory effect was discovered in equiatomic Ni-Ti alloys by Buehler, Gilfich and Wiley of the U.S. Naval Ordnance Laboratory, that research into both the metallurgy and potential application became active. These Ni-Ti alloys, called Nitinol (Nickel Titanium Navy Ordnance Laboratory), are based on the intermetallic compound NiTi and have chemical compositions in the range from 53 to 57 (wt.%) nickel [2].

One of the most important aspects in Nitinol is its ability to experience large, reproducible shape recovery. The study of shape memory alloys has continued at an increasing pace, and understanding of the shape memory effect has advanced considerably [3]. In order to improve the shape memory properties of Ti-Ni SMAs, ternary addition was examined. It was found that adding Cu to NiTi effectively decreased the transformation hysteresis [4], reduced the composition sensitivity of martensitic transformation temperature, and lowered the martensite flow stress [5].

1.2 Motivation and logic of the work

Ti-Ni-Cu alloys, where Ni is replaced with Cu, have attracted considerable interest in recent years due to their narrow transformation hysteresis associated with B2→B19 transformation. The effect of Cu addition to Ti-Ni alloys on phase transformation characteristics has been systematically studied. In bulk Ti-Ni-Cu alloys, the transformation behavior was investigated by electrical resistivity measurements, internal friction, DSC, thermal cyclic testing under constant load and XRD analysis [4, 6-11]. The phase transformation sequence in Ti-Ni-Cu alloys changed with Cu contents: from B2→B19' (0-10 at.% Cu) to B2→B19→B19' (10-15 at.% Cu), and then to B2→B19 if Cu content was more than 15at.%. The transformation start temperatures for B2→B19' decreased with the addition of Cu. But the B2→B19 transformation start temperature increased slightly with the increase of Cu content [4, 7, 8]. The martensitic transformation hysteresis decreased from 37.1°C for 0 at.% Cu to 11.6°C for 13 at.% Cu [6].

Some models were proposed to explain the phenomenon, such as accommodation competition [12], shear modulus softening [13, 14], and the criterion of total electronic density of state at the Fermi energy $D(\epsilon_F)$ [15]. But they did not thoroughly explain why Cu addition changes the phase transformation temperatures, and narrows the transformation hysteresis.

Although some efforts were made on the characterization of microstructure of B19 phase in Ti-Ni-Cu alloys, the results were not in good agreement, twinning [16-18] or twinless [6, 19, 20]. Much work was also done in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy and results showed that B19 martensite is internally twinned [16-18].

Cu addition also changed the shape memory behavior and mechanical properties of Ti-Ni alloys. Ti-Ni-Cu alloy was found to have higher transformation temperatures, and smaller transformation hysteresis compared with Ti-Ni alloys. But the research was limited to alloys with Cu content less than 10 at.%. The bulk materials with high Cu content fabricated by conventional processing were brittle, which hindered the development of Ti-Ni-Cu alloys [21, 22].

Fabrication of Ti-Ni-Cu ribbon by melt-spinning technique proved suitable for producing alloys with controllable initial structures, such as amorphous or crystalline. Using this technique, Furuya et al. [23] successfully fabricated ribbons of the Ti-Ni-Cu alloys with Cu content above 10 at.%, which were too brittle for conventional hot rolling. Transformation hysteresis of the ribbons decreased with increasing Cu percentage, in agreement with the bulk materials. And Ti-Ni-10Cu (at.%) ribbons showed a much larger recoverable strain than the wires fabricated by the conventional method.

The deformation behavior of Ti-Ni-Cu ribbons was investigated by means of tensile tests and thermal cycling tests under constant stresses [24]. With the increase of Cu content, the recovery strain during phase transformation of as-spun $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ribbons reached a maximum value (4.8%) at 5 at.% Cu and then gradually decreased to 0 at 20 at.% Cu. It was found that melt-spun Ti-Ni-Cu ribbons with Cu-content over 10 at.% had good SME.

$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is the most widely studied Ti-Ni-Cu ribbon because it has one-stage transformation with small hysteresis and higher M_s . Some work has been done on the crystallization behavior of amorphous as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons and their transformation temperatures [25-33]. The transformation temperatures are also sensitive to the processing method, post heat treatments and external applied stress [34-36]. Aging

after solution-treatment lowered the M_s of B2→B19 in $Ti_{50}Ni_{25}Cu_{25}$ alloy [35]. Researchers reported different transformation behavior of $Ti_{50}Ni_{25}Cu_{25}$ ribbons after different heat treatment [16, 23, 37]. But the effect of heat treatment on the transformation behavior and microstructure change (such as grain size and texture development) has not been thoroughly studied in the Ti-Ni-Cu ribbons.

It was reported that the ribbon annealed at 500°C showed good SME, but the reason was not clear [38], and the shape memory properties of this ribbon have not been systematically studied. The effect of heat treatment on its shape memory properties needs further study. So far few reports have been found on how the initial structure affects the transformation behavior and shape memory properties.

In view of further application of the $Ti_{50}Ni_{25}Cu_{25}$ ribbon, controllability of shape memory property is very important. Hence a thorough understanding of the relationship between the thermo-mechanical properties and the microstructure of the ribbon is very important. The study of crystal structure and microstructural evolution of the ribbons will provide guidance for tailoring the material for specific applications.

This project was initiated to develop experiments which evaluate the effects of initial structure and post heat treatment on the transformation behavior and shape memory effect of $Ti_{50}Ni_{25}Cu_{25}$ ribbons, and Cu contents on the transformation characteristics of Ti-Ni-Cu bulk alloys. The objectives of the report are as follows:

1. To investigate the transformation behavior and crystal structure of Ti-Ni-Cu bulk shape memory alloys with different Cu contents and understand the mechanism behind these properties in view of thermodynamics,

2. To study the effect of initial structure, post-heat treatment on the crystal structure, microstructure, transformation behavior, and shape memory effect of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons, and explore the possibility of obtaining a suitable microstructure required to produce the optimum shape memory properties,
3. To obtain a better understanding of the twin morphology and twin elements in B19 martensite in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon by using TEM and selected area electron diffraction analysis.

The methodology of the project is as follows:

- a. Microstructural and texture analysis via XRD and TEM were valuable in elucidating the microstructural evolution. Shape memory properties include phase transformation behavior and shape memory effect. Results were analyzed to determine the heat treatment and initial structure required to produce the optimum properties.
- b. Adding ternary alloy Cu to the well-known shape memory alloy TiNi reduced the transformation hysteresis and sensitivity of M_s to composition. To understand the mechanism behind this unique property from a thermodynamic view is of fundamental importance and will contribute to the knowledge base in this area.
- c. In this report, the transformation behavior and structure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon with three initial structures (amorphous, crystalline, and partially-amorphous) under different post heat treatments were studied and compared by means of DSC and XRD. The microstructures of annealed ribbon and as-spun crystalline ribbon were observed by using TEM. The shape memory effect of the heat treated ribbons was studied by TMA. The transformation characteristics of Ti-Ni-Cu bulk materials with different Cu-content were also investigated.

1.3 Organization of the report

This thesis is organized into seven chapters. Chapter 1 is a brief introduction to the background, objectives and scope of this project. Chapter 2 gives a literature review of the fundamental aspects and recent progress in Ti-Ni-Cu shape memory alloys. Chapter 3 records the experimental procedures employed. Chapter 4 presents the results of Ti-Ni-Cu bulk materials and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons. Chapter 5 is the discussion on the results in Chapter 4. Chapter 6 provides the conclusions and recommendations for future work are proposed in Chapter 7.

CHAPTER 2 LITERATURE REVIEW

This chapter is an introduction to the basis of shape memory alloys and martensitic transformation, crystal structure of the phases and twinning in Ti-Ni alloys, and a review on Ti-Ni-Cu alloys and ribbons.

Shape Memory Alloys (SMAs) are metallic materials that demonstrate the ability to return to some previously defined shape or size when subjected to an appropriate thermal procedure [1]. The fundamental principle of these SMAs is the thermoelastic martensitic transformation. It is characterized by a small temperature hysteresis (a few to several tens of degrees), a mobile twin interface, and a crystallographically reversible transformation [2]. The characteristic transformation temperatures are defined as follows:

M_s : martensite start temperature upon cooling; M_f : martensite finish temperature upon cooling; A_s : reverse transformation (austenite) start temperature upon heating; A_f : reverse transformation (austenite) finish temperature upon heating.

In the Ti-Ni system, the high temperature austenite, an intermetallic compound B2 phase, undergoes a thermoelastic martensitic transformation into a low temperature martensite B19' phase with lower symmetry. Martensite can be induced thermally or mechanically. The former is referred to shape memory effect (SME). The latter is the cause of superelasticity (SE).

2.1 Martensitic transformation

The martensitic transformation is a diffusionless transformation described by a shear-like mechanism, as shown schematically in Figure 2.1. When the parent phase (a) is cooled to M_s , the structure changes into martensite (b). Since the parent phase has higher symmetry

than the martensitic phase, multiple formation of martensites with the same structure in different orientations is possible, as shown in (b). These are called *variants* (or domains) of martensite.

Figure 2.1 Illustration of martensitic transformation [3].

In fact, two or four variants of martensites are usually formed side by side, as shown in Figure 2.1(b), in order to accommodate elastic strains around the martensites. This is called *self-accommodation*. The two neighboring variants are twin-related to each other and may contribute to deformation if the interface is mobile under stress.

2.2 Mechanism of shape memory effect and superelasticity

SME is a unique property of certain alloys exhibiting martensitic transformations, as shown in Figure 2.2. The sample in martensitic state (A), whose shape is the same as that in the parent phase, is deformed at a temperature below M_f (B). The deformation will remain after unloading (C). However, it will revert to its original shape by means of the reverse transformation (D) if it is heated to a temperature above A_f .

Figure 2.2 Illustration of shape memory effect [39].

The mechanism of this phenomenon is explained in Figure 2.1 (a)–(c). When the parent phase in Figure 2.1 (a) is cooled below M_f , martensite variants are formed side by side, as shown in Figure 2.1 (b), as a result of self-accommodation. If stress is applied, deformation proceeds by twin boundary movement from Figure 2.1 (b) to (c). If, however, the sample is heated to a temperature above A_f , the martensite variants rearranged under stress revert to their original orientation in the parent phase.

Figure 2.3 Illustration of superelasticity [39]

SE is pseudoelasticity occurring at a temperature above A_f (Figure 2.3). The sample is strongly deformed at relatively low stresses (A to B) at a temperature above A_f . During subsequent unloading a complete shape recovery occurs (B to C).

The mechanism of superelasticity can be explained by using Figure 2.1 (a) and (c). Since the martensitic transformation occurs by a shear-like mechanism, it is possible to induce it even above M_s by stress. This is called a stress-induced martensitic transformation. However, the martensite is completely unstable at a temperature above A_f in the absence of stress. Thus, the reverse transformation must occur during unloading in this case, and the strain completely recovers in the thermoelastic transformation.

2.3 Crystal structures of the phases in Ti-Ni based alloys

Since Greninger and Mooradian first observed the shape memory effect in copper-zinc alloys (Cu-Zn) and copper-tin alloys (Cu-Sn) in 1938, many alloys have been known to exhibit the shape memory effect, such as Ni-Ti-based alloys, some copper based alloys, i.e. Cu-Zn and Cu-Al-Ni, and some others like Ag-Cd, and Fe-Pt [40]. The most widely used and well developed are Ni-Ti alloys because of their ability to experience large, reproducible shape recovery. The compositions of NiTi SMAs are generally between 48 and 52 at.% Ni [41]. Transformation temperatures of NiTi are extremely sensitive to composition, for example, an increase of 1 at.% in Ni can cause up to 150°C decrease in transformation temperature [42].

In Ti-Ni-based alloys, two major phases exist, high temperature austenite and low temperature martensite. Austenite is known to have a body-centered cubic B2 structure with the lattice parameter of $a_0 = 0.3010$ to 0.3020 nm [43, 44] (Figure 2.4). Its space group is $Pm\bar{3}m$ [45] with space group number No. 221.

There are three types of martensite transformations in Ti-Ni alloys depending on alloy composition and heat treatment. They are B19', R-phase, and B19 phase, respectively. The crystal structure of the B19' phase was determined to be monoclinic by X-ray

diffraction, neutron diffraction and electron diffraction methods [45-48]. R-phase has a rhombohedral structure [49, 50] and B19 phase orthorhombic [18, 51-53].

Figure 2.4 Structure of B2 phase [44]

2.3.1 B19' martensite

B19' phase is the most common martensite in Ni-Ti based alloys. B19' phase is universally agreed to have a monoclinic structure, which is observed in Ti-Ni binary alloys and in most of the ternary alloys. The crystal structure of the martensitic phase was first determined to be monoclinic in a polycrystalline Ti-49.75 at. %Ni alloy by Otsuka et al. using both X-ray diffraction measurements and transmission electron microscopy. The structure of B19' phase was further confirmed by Michal et al. [45] and Kudoh et al. [46] using single crystal electron and X-ray diffraction in TiNi alloy, respectively. The lattice parameters and atomic positions in the monoclinic martensitic crystal structure determined by the different authors are shown in Figure 2.5.

The lattice parameters reported by Michal et al. [45] have been widely recognized as the standard structure: $a = 2.898 \text{ \AA}$, $b = 4.108 \text{ \AA}$, $c = 4.648 \text{ \AA}$ and $\beta = 97.8^\circ$. The space group of B19' phase is $P2_1/m$ with space group number No.11.

Figure 2.5 Structure of B19' phase [47]

2.3.2 B19 martensite

B19 martensite often appears in $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ($x \geq 7.5$ at.%) alloys. Its structure is also often discussed as analogous to that of B19 phase in near equiatomic Au-Cd alloy [51]. It was reported to have an orthorhombic structure with $a = 2.87 \text{ \AA}$, $b = 4.23 \text{ \AA}$, $c = 4.48 \text{ \AA}$ by Potapov et al. [18, 52] using Rietveld method to refine the XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons. The B19 structure has Pmmn symmetry.

2.3.3 B11 TiCu precipitates

B11 TiCu phase always exists in TiNiCu alloys with higher Cu content when the alloy is heat treated. It has a tetragonal structure with $a = 3.11 \text{ \AA}$, $c = 5.91 \text{ \AA}$.

2.4 Twin in Ti-Ni shape memory alloys

In shape memory alloys twinning is an important characteristic of martensitic transformation. A description of twins is characterized by five crystallographic elements: K_1 = twinning plane; η_1 = twinning shear direction; K_2 = another undistorted plane; η_2 = intersection of K_2 and plane of shear; s = magnitude of twinning shear.

Twinning in martensites is very important with respect to martensite crystallography and deformation mode. The twinning modes in B19' martensite and crystallography of B2→B19' transformation in NiTi alloys were studied by many researchers [54-66]. Three types of twinning have been frequently observed using electron microscopy. They are $\langle 011 \rangle_m$ type II twins [57-60], $\{111\}_m$ type I twins [61-64] and $\{001\}_m$ compounds [57, 65, 66]. The crystallographic data of twins in NiTi alloys are compiled in Table 2.1. Among them, $\langle 011 \rangle$ type II twinning is the most important because it is the lattice invariant shear in the crystallography of B2→B19' transformation.

The twinning mode in B19 martensite was not clearly studied due to the uncertainty of its crystal structure, but two types of twinning were reported in Ti-Pd [65, 67] and Ti-Ni-Cu alloys [68], respectively, as type I (111) twin and (011) compound twin.

Table 2.1 Crystallographic data of twins observed in B19' Ti-Ni martensite [55, 56]

Twin	K_1	η_1	K_2	η_2	s
$\{111\}$ type I	$(\bar{1}\bar{1}1)$	$[0.54\ 0.46\ 1]$	$(0.25\ 0.51\ 1)$	$[\bar{2}\ 1\ 1]$	0.31
	$(1\ 1\ 1)$	$[\bar{1}.51\ 0.51\ 1]$	$(\bar{0}.67\ 0.34\ 1)$	$[2\ 1\ 1]$	0.14
$\langle 011 \rangle$ type II	$(\bar{0}.72\ 1\ 1)$	$[0\ 1\ \bar{1}]$	$(0\ 1\ \bar{1})$	$[\bar{1}.57\ 1\ 1]$	0.28
Compound	$(0\ 0\ 1)$	$[1\ 0\ 0]$	$(1\ 0\ 0)$	$[0\ 0\ 1]$	0.24

2.5 Ti-Ni-Cu shape memory alloys

The shape memory properties of Ni-Ti alloy can be readily modified by adding ternary elements, which are chemically similar to Ni or Ti. Ternary alloying element additions to near equi-atomic TiNi SMAs can provide a wide range of modification of their shape memory properties by affecting their transformation behavior, physical properties or

mechanical properties. Frequently used elements are Cu (to reduce the hysteresis) [4], Fe and Cr (to lower the transformation temperature) [69, 70], Zr, Hf, Pd, Pt and Au (to increase the transformation temperature) [70-75], and Nb (to raise the hysteresis) [76].

Among the alloying elements, Cu is unique since it can be substituted for Ni at up to 25 at.%, and the Ti-Ni-Cu alloys would still exhibit shape memory effect [6]. It narrows the transformation temperature hysteresis considerably [4], reduces the sensitivity of M_s to the Ni:Ti ratio, increases the strength difference between the parent and martensite phases [5], prevents the precipitation of the metastable Ti_3Ni_4 phases [77, 78], and improves the transformational cyclic behavior [4].

The factors, such as atomic size, relative ionic size, electron negativity and density of state at the Fermi energy can be correlated to the influence of the ternary additions on the transformation temperature and stability of crystal structure of Ti-Ni alloys [79]. Much research has been done on the phase transformation behavior, shape memory behavior and the structure of martensites in Ti-Ni-Cu alloys with different Cu contents, but it is unclear why Cu addition changes the phase transformation sequence and narrows the transformation hysteresis, and how it changes the crystallographic structure of B19 martensite.

2.5.1 Phase diagram of Ti-Ni-Cu alloys

The phase diagram is a basis to understand all kinds of phase transformations and is also very important for controlling the microstructure of an alloy, by which physical properties of the alloy are improved. According to the pseudo-binary phase diagram of TiCu and TiNi at high temperatures [80], the austenitic NiTi has a B2 cubic structure, while the TiCu is tetragonal. When Cu is substituted for Ni in Ti-Ni SMAs, the overall

Ti-content must remain close to 50 at.% in order to yield a single phase material desirable for shape memory applications [6]. It is seen in the diagram that the parent phase retains its B2 cubic structure for Cu contents up to 27 at.%.

The phase diagram of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ [17] at low temperatures is shown in Figure 2.6. The substitution of Cu for Ni changes the martensite start temperature M_s as well as the martensite structure and transformation sequence. When the Cu content is around 5%, the monoclinic martensite B19' is formed on cooling, similar to the transformation in the Ti-Ni compound. Upon increasing Cu content to 10 at.%, a two-step martensitic transformation occurs, the orthorhombic B19 martensite appears as an intermediate phase towards B19' formation ($\text{B2} \rightarrow \text{B19} \rightarrow \text{B19}'$). The width of the composition region in which B19 is stable increases with decreasing temperature. If the addition of Cu is more than 15 at.%, it leads to $\text{B2} \rightarrow \text{B19}$ only. Higher Cu levels inhibit the second step of this transformation and only B19 is retained [4, 7, 8].

Figure 2.6 Phase diagram of Ti-Ni-Cu alloys in the low temperature range [17]

The two-stage transformation in $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ alloy was reported by Lo et al. as the consequence of competition or accommodation between B19 and B19' martensite [12]. The transformation sequence may depend on other factors, such as thermo-mechanical treatments.

2.5.2 Transformation temperatures of Ti-Ni-Cu alloys

Substitution of Cu for Ni affects the transformation behavior of Ti-Ni alloy. The effect of Cu content on the martensitic transformation temperature in TiNiCu SMAs was shown in Figure 2.7 [4, 7]. M_s of B2→B19' decreased with the addition of Cu. But M_s of B2→B19 increased slightly with the increase of Cu content [7], while M_s of B19→B19' decreased. It does not occur even at liquid nitrogen temperature with Cu content exceeding 15 at.%.

Figure 2.7 Effect of Cu content on the martensitic transformations of $\text{Ti}-(50-x)\text{Ni}-x\text{Cu}$ alloys.

The solid line is the result for alloys cold-drawn and solution-treated at 800°C for 60 minutes [7]. The broken line is the result for alloys hot rolled and solution-treated at 850°C for 60 minutes [4].

Transformation temperatures also changed with applied stress in the measurement of the elongation-temperature curves under loads. The effect of applied stress on transformation

temperatures was studied in a $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ alloy [34]. M_s and A_f of $\text{B2} \leftrightarrow \text{B19}$ increased linearly with stress up to 90 MPa, above which a deviation from the linearity occurred. M_s of $\text{B19} \rightarrow \text{B19}'$ was not affected by applied stress below 30 MPa, but increased gradually for stresses more than 30 MPa. Nam et al. [34] proposed that the $\text{B19} \rightarrow \text{B19}'$ transformation was thermally induced under stress below 30 MPa, but stress-induced above 30 MPa.

The transformation hysteresis (defined as the difference between the peak temperatures of $\text{B2} \rightarrow \text{B19}'$ (B19) and $\text{B19}'$ (B19) $\rightarrow \text{B2}$) were also investigated by DSC and stress-strain curves [4, 7]. Tang et al. [7] reported that it decreased with the increase of Cu content, from 37.1°C for 0 at.% Cu to 11.6°C for 13 at.% Cu. Similar trend was also obtained from stress-strain curves by Nam et al. [4]. The small hysteresis is closely related to the ease of interface movement during the transformations [4, 34].

2.5.2.1 Effects of heat-treatment on transformation temperatures

The transformation temperatures are sensitive to the processing method, post heat treatment, and test conditions. Tsuji et al. [11] studied the effects of heat-treatment after cold working on phase transformation characteristics of Ti-Ni-Cu alloys. With the increase of heat treatment temperature from 450°C to 550°C, the phase transformation temperature increased at all compositions of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ($x = 6.1, 7.6$ and 9.2 at.% Cu). This is due to the removal of distortions during cold working by recovery (<500°C) and recrystallization (>550°C).

Shi et al. [35] reported that aging after solution-treatment lowered the M_s of $\text{B2} \rightarrow \text{B19}$ in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy by using internal frictions spectrum. The explanation was that a lot of

plate-shape precipitates formed during aging, which caused great internal stress in the matrix and the variations of chemical compositions in the regions near the precipitates. Thus the martensitic transformation was hindered, which agreed with the observation by Kajiwara et al. that the coherent precipitates strengthen the parent phase and thus hinder the martensite transformation [72].

The effect of aging time on the transformation temperature was studied by Fukuda et al. [36] in the hot-rolled and solution-treated Ti-40.5Ni-10Cu alloy. The start temperature of B2→B19 and B19→B19' increased with increasing aging time from 0s to 720Ks at 600°C. This increase was due to the formation of C11b-type Ti(NiCu)₂ precipitates. One cause was the increase of Ti content of the B2 phase near the precipitates. Another was the tensile stress on the matrix exerted by the precipitate, which was confirmed by in-situ TEM observation [78]. The precipitates acted as the nucleation sites of B19 martensite.

2.5.2.2 Thermal stability

Many applications of shape memory alloys involve repeated heating and cooling of the alloys, i.e. thermal cycling. The thermal cycling effect on the transformation temperature depends not only on whether a stress is applied, but also on the heat treatment conditions of the alloy. The thermal cycling effects on phase transformation temperature of Ti–Ni–Cu shape memory alloys was investigated by means of electrical resistivity measurements, thermal cycling tests under constant load, and transmission electron microscopy [81, 82]. Nam et al. [81] reported that thermal cycling without applied stress did not change the M_s of B2→B19 in solution treated Ti–35Ni–15Cu and Ti–30Ni–20Cu alloys. It was attributed to the improvement of the critical stress for slip deformation by Cu addition, while during thermal cycling with applied stress, M_s of B2→B19 increased irrespective of the amount of applied stress.

All changes in M_s during thermal cycling with applied stress in Ti–Ni–Cu alloys were explained by a combination of the thermal cycling effect and the structural refinement effect. The increase in M_s was ascribed to structural refinement where vestiges of martensite plates were in the form of dislocation tangles and local stress field developed during cycling. Dislocations introduced during thermal cycling without applied stress suppressed the martensitic transformation (TC effect), while those induced during thermal cycling with applied stress assisted martensitic transformation (SR effect). The change of M_s of B2→B19 under applied stress was due to the fact that SR effect dominates TC effect.

Jean et al. [82] reported that thermal cycling caused M_s' shift downward slightly for Ti-47Ni-3Cu samples solution-treated and aged at 400°C for 1 hour, but M_s' did not change in cold-worked specimens annealed at a temperature lower than recrystallization temperature. The explanation is that the thermal cycling reduced M_s by creating dislocation stress fields. In the annealed samples, the high density dislocations stabilized by intermediate annealing suppressed the effect of thermal cycling by inducing internal stress field.

2.5.2.3 Effects of Ti:Ni ratio on transformation temperatures

Composition sensitivity of M_s has been reported to be much reduced by Cu addition. Chemical changes in connection with the precipitation of TiCu have a minor influence on M_s compared to those in binary NiTi alloys since the Ti/(Ni+Cu)-ratio remains constant [5]. Moberly pointed out that in ternary TiNiCu SMAs M_s was found to be insensitive around (20-30 at.%) Cu [6].

Strnadel et al. [83] also reported that the transformation temperatures of Ti-Ni-10Cu alloy did not drop sharply as Ni content changed, while Tan et al. [84] reported that the transformation temperatures of B2→B19 in Ti-Ni-8Cu alloy decreased rapidly with reducing Ti content from 50.2 to 49.3 at.%.

2.5.3 Mechanical properties

Cu addition affects the mechanical behavior of Ti-Ni alloys in many aspects. However, Ti-Ni-Cu alloys with Cu more than 10 at.% have poor formability. The reported mechanical properties of Ti-Ni-Cu alloys were limited to the Cu content less than 10 at.%.

Es-souni et al. [21] used bending tests to investigate the mechanical properties of $\text{Ni}_{51}\text{Ti}_{42}\text{Cu}_7$ alloy in the temperature range from 6 to 60°C (Figure 2.8). The stress-strain curve was similar to that of the Ti-Ni alloys. Following the elastic deformation a stress plateau occurs, which was attributed to the movement of the martensitic variants with preferential orientation to the stress axis. Beyond that plateau, stress increased slightly and continuously with increasing deformation. With increase in the testing temperature, the plateau stress increased drastically due to the presence or thermal stabilization of the austenite phase. At 37°C where the alloy is austenite, it exhibited superelastic deformation behavior.

Figure 2.8 Stress/strain diagrams of the ternary NiTiCu alloy at different temperatures: 6°C (a), 22°C (b), 37°C (c) and 60°C (d) [21].

Because the shape memory and superelastic functions are often used under cyclic conditions, degradation of these functions and fatigue life are important. The addition of Cu to Ti-Ni alloys is an attractive option to increase fatigue life, because stress hysteresis and transformation strain decrease with increasing Cu-content.

Miyazaki et al. [22] studied the effects of strain amplitude and test temperature on the fatigue life of Ti-40Ni-10Cu (at.%) wires by rotary-bending fatigue tests. The fatigue life decreased with increasing strain amplitude. The fatigue lives under a constant strain amplitude of 2% decreased with increasing temperature in a temperature region below 95°C, while they were almost constant irrespective of temperature in a temperature region above 95°C. Deformation modes and applied stress during the fatigue testing were factors affecting fatigue life. In the highest temperature region, i.e. 95°C and 125°C (higher than A_f), the deformation mode was superelasticity associated with stress-induced transformation, which is most common among the deformation modes tested. In the second highest temperature region between 50°C and 65°C (between A_s and A_f), the

deformation mode included partially stress-induced transformation. In the lowest temperature region between 35°C and 50°C (lower than A_s), deformation modes were the twinning of martensite.

2.5.4 Shape memory properties

The maximum recovery strain due to B2→B19 transformation decreases with the increasing Cu content. It was 6.4% for Ti-50Ni and 5.2% for Ti-40Ni-10Cu alloy (Figure 2.9) [22]. This tendency was explained by the change of Bain strain with Cu content, which can be written as [8]:

$$B = \begin{pmatrix} \eta_1 & 0 & 0 \\ 0 & \eta_2 & 0 \\ 0 & 0 & \eta_3 \end{pmatrix}$$

Diagonal terms of η_1 , η_2 and η_3 in the Bain strain matrix are expressed by lattice parameters of the B2 phase (a_0) and B19 phase (a , b and c) as $\eta_1 = a/a_0$, $\eta_2 = b/(\sqrt{2}a_0)$, $\eta_3 = c/(\sqrt{2}a_0)$.

Figure 2.9 The effect of Cu on the recoverable strain of martensite [22]

The maximum elongation of B2→B19 in a single crystal is obtained along the $[110]_{B2}$. Because it corresponds to $[001]_{B19}$, the maximum elongation is given as $(\eta_3 - 1)$. Nam et al. [8] reported that the lattice parameter a_0 of B2 phase increased with the Cu-content. Therefore, the elongation showed a Cu dependence and was calculated to be 5.3% for 10 at.% Cu alloy.

The effect of aging time on elongation in the B2→B19 transformation region was determined by using strain-temperature curves for Ti-40.5Ni-10Cu under different aging time at 600°C [36]. It decreased with the increase of aging time from 0 Ks to 720 Ks in the whole stress range. Two factors affecting the elongation were associated with thermo-elastic martensitic transformation: the elongation of each grain due to the transformation, and the distribution of grains. The C11-type precipitates forced the variants to arrange preferentially around them to prevent the rearrangement of variants. The precipitates also increased the stress needed to deform the specimens below M_s [36, 68].

2.6 Melt-spun Ti-Ni-Cu ribbons

In the conventional process (i.e. melting followed by mechanically worked), it is difficult to produce Ti-Ni-Cu alloy of Cu contents over 10 at.% due to material embrittlement [23]. This difficulty can be alleviated by the melt spinning technique.

Fabrication of TiNiCu ribbon by a melt spinning technique was explored in the beginning of 1990. Using this technique, Furuya et al. [23] successfully fabricated ribbons of the Ti-Ni-Cu alloys with Cu content above 10 at.%. Transformation hysteresis of the ribbons decreased with increasing Cu percentage, in agreement with the bulk materials. The ribbons of Ti-Ni-10Cu (at.%) alloy showed a much larger recoverable

strain than the wires fabricated by the conventional method. This good quality was attributed to the texture and high resistance to yielding and plastic deformation due to the high dislocation density introduced during melt spinning.

2.6.1 Crystallization behavior of amorphous Ti-Ni-Cu ribbons

Because of the rapid solidification, as-spun ribbons may be amorphous or crystalline depending on the processing condition. The amorphous ribbons will crystallize when heated to a temperature above the crystallization temperature.

The crystallization behavior of amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons was studied by DSC, MDSC, X-ray diffraction and in-situ TEM observation [16, 25-33]. The amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons crystallized through a single stage exothermic reaction forming a Ti_2NiCu austenite phase with a cubic lattice of lattice parameter $a = 0.3047\text{nm}$ [25]. The crystallization temperature was determined around 450°C by DSC [16].

After annealing for more than 15 minutes above 500°C , plate-shaped γCuTi precipitated from Ti_2NiCu austenite. γCuTi has a tetragonal lattice with $a = 0.314\text{nm}$ and $c = 0.612\text{nm}$, in which 25 at.% Cu was replaced by Ni [25], which agrees well with the results of Rosner et al. [28]. Rosner et al. [28] also found higher density of plate-like precipitates in the melt-spun ribbons than in the bulk. It was related to a much higher amount of point defects quenched in by the rapid cooling in the melt-spinning process. The plate-like precipitates suppressed the martensitic transformation to a lower temperature. After such a long time annealing ($>15\text{minutes}$), Ti_2NiCu phase was gradually depleted in Ti and Cu. $\text{TiNi}_{0.8}\text{Cu}_{0.2}$ martensite phases formed after γCuTi and had a monoclinic structure of $a = 0.2896\text{nm}$, $b = 0.4239\text{nm}$, $c = 0.5887\text{nm}$ and $\beta = 90.016^\circ$ [25]. This was different from the results by Satto et al. [17], in which precipitates were identified as Cu_3Ti_2 and Ti_2Ni .

The reason may be that formation of a particular structure depended on the prior thermal and processing history of the specimen.

Rosner et al. [29] also studied the crystallization behavior of amorphous Ti–25Ni–25Cu (at.%) melt-spun ribbons annealed at temperatures lower than the crystallization temperature. It was found that after annealing at 410°C for 8 to 24 hours, well distributed amorphous-crystalline structures with average grain size around 4 μm were observed. The formation of subnanometric plate precipitates like the $L2_1$ -ordered structure (Heusler-type) on $\{100\}_{B2}$ -planes led to embrittlement of ribbons. Because annealing below the crystallization temperature results in unstable structures, heat treatment was performed above crystallization temperature. At 610°C, the crystallization in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons was completed after 90 seconds' annealing [29-31].

2.6.2 Structure of Ti-Ni-Cu ribbons

The ordering of the B2 phase in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons was studied by Morgiel [33] using ALCHEMI (atom location by channeling-enhanced microanalysis) technique. With the increase of annealing duration at 450°C from 1 minute to 90 minutes, the martensitic transformation peak shifted upward from 24 to 36°C. ALCHEMI measurements confirmed the occupancy of Ni-rich planes by Cu addition and showed that up to 16% of the Cu atoms might be located away from their proper positions. The heat treatment probably completed the ordering of B2 phase and thus shifted the transformation peak upward.

It was once believed that B19 was twinless [19, 20]. But recently it was reported that the martensite variants are internally twinned B19 with (011) or (111) twin relations in the annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons [16, 68, 85-88]. B19 martensite plates have an

orthorhombic lattice of $a = 0.287\text{nm}$, $b = 0.423\text{nm}$ and $c = 0.448\text{nm}$. When annealed at 750°C for 15 minutes, the ribbon recrystallized, and three self-accommodating variants of B19 martensite coexisted in one grain with both (011) and (111) twin relations [16].

2.6.3 Texture in Ti-Ni-Cu alloys

In a polycrystalline material, if the orientations of all grains clustered about some particular orientations, the material is said to have texture [89]. The measurement of recoverable strain in the rolled samples and melt-spun samples indicated that optimum shape memory properties can be obtained by optimizing the texture [90-95]. Textures in Ti-Ni SMAs were investigated by many researchers [96-104]. For example, Jee et al. [98] observed a high density of the $(11\bar{1})_m$ plane of martensite on the tension side and $(020)_m$ on the compression side of a Ti-49.6%Ni alloy bent sample. Li et al. [99] determined a $(111)[11\bar{2}]_p$ and $(111)[21\bar{3}]_p$ sheet texture in the rolled Ti-51.5%Ni alloy at two annealing conditions. Eucken et al. [100] found a $\langle 100 \rangle_p$ fiber texture and columnar grain structure in the NiTi ribbons produced at high cooling rate. Liu et al. [96] ascribed an asymmetry in the stress-strain response along the rolling and transverse direction to texture effects.

Thamburaja et al. [97] reported a larger transformation strain in the rolling direction compared to the transverse direction in a textured TiNi sheet by simulation. Inoue et al. [101, 102] analyzed the exact texture in the polycrystalline TiNi SMA quantitatively by ODF. Miyazaki et al. [103] reported that the transformation strain depended on direction in the TiNi rolled sample, while it was almost the same in all directions in the sputter-deposited TiNi thin films. The presence of texture facilitated the two way shape memory effect in Cu-Al-Ni melt-spun ribbons [105].

In Ti-Ni-Cu alloys, Willemse et al. [106] measured fiber texture in a cold-drawn Ti-44Ni-5Cu alloy with annealing treatment. Zhao et al. [107] studied the texture development and anisotropic shape memory behavior of a cold-rolled Ti-45Ni-5Cu alloy. For $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy, only Santamarta et al. [108, 109] reported $[011]_{\text{B19}}$ fiber texture in the crystallized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.

2.6.4 Transformation behavior of Ti-Ni-Cu ribbons

Transformation temperatures of ribbons were investigated by electrical resistivity measurements, internal friction, DSC, thermal cyclic testing under constant load, and XRD analysis [23, 24, 29, 32]. Furuya et al. [23] measured the transformation temperatures M_f , M_s , A_f and A_s of as-spun $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ribbons by strain-temperature curve under applied stress of 65 MPa. The results concurred with the trend in bulk materials. It was also found that the transformation temperatures of TiNiCu_{10} ribbons were lower than those of wires with the same composition, but the temperature hysteresis (A_f-M_f) was smaller. This was caused by the very fine-grains (smaller than $1\mu\text{m}$) in the rapidly solidified ribbons [24].

The effect of annealing temperature and duration on transformation temperatures of TiNiCu ribbons was also investigated by different researchers [16, 28, 37]. It can be seen that lower annealing temperature and shorter duration increased both the forward and reverse phase transformation temperatures of amorphous ribbons as shown in Table 2.2.

Khantachawana et al. [37] compared the transformation behavior of amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at 450 and 800°C by DSC and thermal cycling test. The transformation temperatures decreased with decreasing heat treatment temperature. Under an applied stress of 25 MPa, M_s of ribbon annealed at 800°C was about 40°C higher than

that of ribbon annealed at 450°C. But a small transformation hysteresis less than 10°C was obtained in all heat-treated ribbons.

Table 2.2 Transformation temperatures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons under different annealing conditions

Alloy	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	Annealing
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ [28]	57	47.5	60	68.5	2 hours at 460°C
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ [37]	51	45	57	62	1 hour at 800°C
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ [16]	73	59	61	78	15 minutes at 400°C

Although much work has been done on the crystallization behavior of amorphous as-spun ribbons and the effect of heat treatment on the transformation temperatures, a more systematic research on the heat treatment effect is needed. Moreover few have reported the effects of initial structure on the transformation behavior of the ribbons.

2.6.5 Mechanical behavior of Ti-Ni-Cu ribbons

The report on mechanical properties of ribbons was focused on two compositions: 50Ti-40Ni-10Cu and 50Ti-25Ni-25Cu. The transformation strain as a function of Cu content was studied by measuring strain-temperature curves under applied stress [23]. With the increase of Cu content, the strain range during phase transformation of as-spun $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ ribbons reaches a maximum value (4.8%) at 5 at.% Cu and then gradually decreases to 0 at 20 at.% Cu. It was found that melt-spun Ti-Ni-Cu ribbons with more than 10 at.% Cu had good SME. The transformation strains of Ti-Ni-10Cu ribbons from the strain-temperature curves under 65 MPa are 3-4 times larger than those of polycrystalline wires of Ti-Ni-10Cu and Ti50-Ni50, which are 5.1, 1.8 and 0.9%, respectively [24].

It was also found SME was stronger in the rapidly quenched $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ ribbons than in the high temperature annealed or recrystallized ribbons [23]. The transformation strain was larger and temperature hysteresis smaller in the former than those in the latter. It was attributed to the interactive effects of the strong anisotropy of crystals and the high resistance to yielding and the plastic deformation due to the high dislocation density in the as-spun ribbons. Grain size is not a predominant factor for the high SME, because as-spun ribbons have a larger grain size than the recrystallized.

Khantachawana et al. [37] found that $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons were brittle when annealing temperature was below 750°C . The ductility was improved by heat treatment above 750°C . A shape recovery strain of 2.5% was obtained under 600 MPa in ribbons annealed at 800°C .

Liu [38] studied the mechanical and thermo-mechanical properties of an initially amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt spun ribbon annealed at 500°C for 15 minutes. The crystallized ribbon exhibited a well-defined shape memory effect and a superelastic shape recovery of up to 10% strain with rather low hysteresis. During cyclic deformation with a strain lower than 10%, the stress-strain loop stabilizes, a stable superelasticity of about 7% with a stress hysteresis as low as 65 MPa was obtained (Figure 2.10). But the reason why the annealed ribbon exhibited good SME was not clear. The author also found that samples annealed at 500°C for 60 minutes and at 600°C for 15 minutes had poor mechanical properties, but did not give reasons.

Santamarta et al. [108,109] compared the shape recovery strain of Ti-Ni and $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons with those of the conventionally cast alloys with similar compositions and found

that they were of the same order. Therefore, melt spinning would be a good substitute for the conventional cast alloys.

Mechanical and shape memory properties are crucial for SMA's application. In order to control these properties, further systematic study of the effect of heat treatment and microstructure on the shape memory and mechanical properties of Ti-Ni-Cu ribbons is needed.

Figure 2.10 Cyclic deformation of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ melt spun ribbon at about 120°C.

(a) The strain amplitudes were increased to 3, 5, 7, 8, 9, 10, 11 and 12%, respectively. (b) Cyclic deformation within 10% strain. Inserts are the stress hysteresis and recovery strain as a function of cycling [38].

2.7 Thermodynamic description of martensitic transformation

2.7.1 Thermodynamics of martensitic transformation

According to thermodynamic description of the thermoelastic transformation behavior, it has been established that the equilibrium conditions for martensitic transformation within the volume of its parent phase can be expressed by means of the Gibbs free energy as the balance of chemical and non-chemical forces [110]:

$$\Delta G^{P-m} = \Delta G_{ch} + \Delta G_{nch} = \Delta G_{ch} + \Delta G_{el} + \Delta W_f = 0 \quad \text{Equation 2.1}$$

where ΔG_{ch} refers to the chemical contributions of the Gibbs free energy change between the parent and martensitic phase. ΔG_{el} is the change in elastic strain energy and ΔW_f is the frictional work term, both referring to the non-chemical forces ΔG_{nch} . The superscript p-m denotes the parent to martensite transformation. ΔG_{ch} arises from the difference in Gibbs free energy between austenite and martensite, and acts as a driving force promoting the phase with lower energy at each temperature.

ΔG_{el} is the need to accommodate the transformational shape and volume changes. If accommodation takes place elastically, the associated elastic energy is stored in the specimen during the transformation from austenite to martensite, and reversibly recovered during the reverse transformation. Therefore this contribution opposes the forward transformation and promotes the reverse one. Elastic accommodation of the transformational shape and volume changes is a necessary condition for thermo-elastic behavior [111, 112].

The frictional term can be written after Olson and Cohen [113-115] as $\Delta W_f = \pm \tau_0 \gamma_T$, where “+” denotes cooling and “−” heating. τ_0 is the shear stress required to initiate

and/or propagate the martensite interface, which accomplishes the transformation shear strain γ_T .

In a multiple-interface transformation, $\Delta W_f = \pm \tau_0 \gamma_T$ can be written as [116, 117]:

$$\Delta W_f = E_{fr}^{P-M} + E_{fr}^{M-P} = Q_A - Q_M \quad \text{Equation 2.2}$$

where, E_{fr}^{P-M} and E_{fr}^{M-P} are friction energy corresponding forward and reverse transformations, respectively. Q_M and Q_A denote the absolute values of the total heat measured in a forward and reverse thermoelastic martensitic transformation induced by temperature. ΔW_f is the energy dissipated in the specimen as internal work during the transformation, which is mainly devoted to overcome frictional barriers opposing interfacial motion. It is responsible for the thermal hysteresis.

The thermodynamic equilibrium temperature, T_0 , is defined for stress free conditions, where $\Delta G_{ch} = \Delta H - T\Delta S = 0$, i.e. $T_0 = \Delta H / \Delta S$. ΔH and ΔS are the changes in chemical enthalpy and entropy, respectively. The first plates form at M_s , which is associated with a certain driving force for the transformation of austenite into martensite as shown in Figure 2.11. The driving force for the nucleation of martensite at M_s is given by [111, 112, 118]:

$$\Delta G_{ch}^{P-M} = \Delta H^{P-M} - M_s \Delta S^{P-M} = \Delta H^{P-M} \frac{(T_0 - M_s)}{T_0} \quad \text{Equation 2.3}$$

Equation (2.1) and (2.3) lead to the following expression for the martensitic start temperature M_s :

$$M_s = T_0 + \frac{\Delta G_{el} + \tau_0 \gamma_T}{\Delta S} \quad \text{Equation 2.4}$$

Hornbogen [119] pointed out that T_0 depends on chemical composition, degree of order, and hydrostatic stress.

The second term, $\frac{\Delta G_{el} + \tau_0 \gamma_T}{\Delta S}$, in equation (2.4), describing the undercooling, $\Delta T = T_0 - M_s$, depends on nucleation and propagation of martensite inside the matrix. External shear stress and the resistance to shear, i. e. hardening mechanisms caused by point defects, dislocations, or particles in turn affected this.

Figure 2.11 The difference in Gibbs free energy between austenite and martensite in a thermoelastic martensite transformation.

2.7.2 Martensite nucleation and growth

The total increase in Gibbs free energy associated with the formation of the fully coherent martensite particle (oblate-spheroidal in shape, shown in Figure 2.12) of radius r and semi-thickness c in austenite can be expressed as [113]:

$$\Delta G = \frac{4}{3} \pi r^2 c \Delta G_{ch} + \frac{4}{3} \pi r c^2 A + 2 \pi r^2 \sigma \quad \text{Equation 2.5}$$

Figure 2.12 Formation of martensite particle

Where ΔG_{ch} is the chemical free energy change per unit volume; ΔG_{el} is the elastic strain energy per unit volume of the particle (ΔG_{el}), and σ is the interfacial energy per unit area.

In martensite transformation, the strain energy is much more important than the surface energy, since the shear component of the pure Bain strain is high and produces large strains in the surrounding austenite. On the other hand, the interfacial energy of a fully coherent nucleus is relatively small.

The rates of radial growth and thickening were related to the transformational forces in the corresponding directions as determined by the slopes of the free energy surface defined by equation (2.5). Once the radial growth of the particle is stopped by an obstacle,

the particle continues to thicken in response to the transformational force $(-\frac{\partial \Delta G}{\partial c})$ in the

c direction. It is found that this condition will occur when the strain energy, $\Delta G_{el} = A \frac{c}{r}$,

reaches a balance with the chemical driving force in the form:

$$\Delta G_{ch} + 2\Delta G_{el} = 0 \quad \text{Equation 2.6}$$

Increasing $|\Delta G_{ch}|$ relative to ΔG_{el} by further cooling results in thickening of the particle,

while a decrease in $|\Delta G_{ch}|$ relative to ΔG_{el} by heating results in shrinkage.

As a particle of fixed radius thins upon heating, a critical thickness will be reached (at $-\frac{\partial G}{\partial r} = 0$) for which the contribution of strain and surface energy is sufficient to render the particle unstable with respect to shrinkage in the radial direction, and then the particle will disappear. The chemical free energy difference at that condition is:

$$\Delta G_{ch} = -2\left(\frac{A\sigma}{r}\right)^{\frac{1}{2}} \quad \text{Equation 2.7}$$

Since A and σ are positive quantities, ΔG_{ch} must be negative. The earliest plates to form on cooling will tend to reach largest sizes and should be the last to revert on heating. Tong and Waymen [120] noted that A_s (the temperature on heating for the onset of reversion of the last-formed martensitic plate) could be below T_0 due to the effect of stored elastic strain energy.

CHAPTER 3 EXPERIMENTAL PROCEDURES

This chapter provides the materials used in this study, their heat treatment, and the characterization methods.

3.1 Materials

3.1.1 $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ as-spun ribbons

Three shape memory alloy ribbons with different initial structures provided by international cooperators (Institute of Metal Physics, Kiev, Ukraine) were used. The nominal chemical compositions were 50 at.% Ti, 25 at.% Ni and 25 at.% Cu. In this work, they were denoted as $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$. All as-spun ribbons were almost 40 μm thick but with different width. Table 3.1 shows the history and conditions of the as-received materials.

Table 3.1 The conditions and history of as-spun ribbons

Alloy	Width $\times$ thickness (mm $\times\mu\text{m}$)	Initial structure
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A	23 $\times$ 33	Fully amorphous
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B	15 $\times$ 39	Fully crystalline
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C	25 $\times$ 40	Partially amorphous

The compositions of the as-spun ribbons were examined by using an X-ray energy dispersive spectrometry (EDS) in three locations of each ribbon, shown in Table 3.2. There were differences between the measured compositions and the nominal ones. As the measurement error of EDS is $\pm 10\%$, these differences were within the measurement error. The differences among the three locations simply reflect the measurement errors.

Table 3.2 Chemical compositions of as-spun Ti-Ni-Cu ribbons

Alloy	$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$	$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$	0
Element	Ribbon A		

3.2 Heat treatment of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

The as-spun ribbons were heat treated at different temperatures in order to promote crystallization of the parent phase and to investigate the effect of heat treatment on the phase transformation characteristics and shape memory properties. The heat treatment conditions are summarized in Table 3.3. Because of oxidation, the surface of the ribbons was slightly ground to remove the oxide layer.

Table 3.3 Heat treatment conditions

Specimen	Annealing (°C)	Time (min.)	Cooling condition
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A, C	500, 550, 600, 650, 700, 750	15	
$\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B	300, 400, 450, 500, 550, 600, 650, 700, 750	15	Water quenched

3.3 Characterization techniques

3.3.1 X-ray diffraction

X-ray diffraction (XRD) techniques were used to characterize the crystal structure of Ti-Ni-Cu ribbons and bulk materials at room temperature (RT). X-ray diffraction patterns of the samples were recorded using a Rigaku DMAX 2200 diffractometer with CuK α radiation ($\lambda = 0.15405\text{nm}$, $U = 50\text{KV}$, $I = 20\text{mA}$). Measurements were made at room temperature with step intervals of 0.04° in 2θ and speed of $2^\circ/\text{min}$. Rectangular specimens of about $8 \times 18 \text{ mm}^2$ ribbons were glued onto a glass that was fixed to the sample holder.

Texture measurements were taken using a texture goniometer in a Rigaku DMAX 2200 diffractometer. Sample size was $18 \times 18 \text{ mm}^2$. Prior to the texture measurement, the Bragg diffraction angles, 2θ , of each pole were determined by θ - 2θ scans. Schultz method was used to measure pole figures within the range of rotation angle (β) from 0 to 360° and that of the tilt angle (α) from 0 to 60° . The definitions of rotation angle β and tilt angle α in pole figure are shown in Figure 3.1, in which RD is the spinning direction and TD is perpendicular to the spinning direction. Schulz formula was applied for correction of the pole figure intensity. Correction for background intensity was performed separately for each sample by off-Bragg angle measurements.

Figure 3.1 Definition of the rotation angle β and tilt angle α in a pole figure

The samples used in texture measurements were $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 450, 500, 550, 600, 650, 700°C and as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B. The texture components were qualitatively analyzed by comparing the measured pole figures with the standard stereographic projections. The stereographic projections of B19 orthorhombic lattice and B11 tetragonal lattice were calculated using CaRine Crystallography 3.1.

3.3.2 Transmission electron microscopy

Transmission electron microscopy (TEM) was used to investigate the microstructure and twin relationship. A JEOL TEM 2010 microscope equipped with a conventional double-tilt specimen stage was used. The operating voltage was 200 KV. Because the ribbon samples were around 40 μ m in thickness, disks with a diameter of 3 mm were directly punched from the ribbons. The disks were jet-polished in an electrolyte of 25% nitric acid and 75% methanol (in volume) at around -25°C in a twin-jet electro-polisher (FISCHIONE Instruments, model 110). The applied voltage for electro-polishing was around 20 V. Some TEM samples were prepared by ion-milling method.

3.3.3 Scanning electron microscopy

The compositions of as-received Ti₅₀Ni₂₅Cu₂₅ ribbon A, B and C and as-melt specimens after homogenization were examined by energy-dispersive X-ray analysis in a JSM-5410 scanning electron microscope (SEM). For every sample, 3 locations were randomly selected for analysis.

3.3.4 Differential scanning calorimetry

Phase transformations in the shape memory alloy in unstressed condition were investigated using differential scanning calorimetry (DSC). DSC is a technique in which the difference in heat flow into or out of a substance and a reference material is measured as a function of temperature [121, 122]. DSC is widely used for phase transformation studies because the quantity of heat flow at a particular temperature directly corresponds to the quantity of transformed material at that temperature.

Figure 3.2 shows the method used to determine the transformation temperatures. A_s , for instance, was determined from DSC peaks using a slope line extension method (the intersection of the tangents to each peak and the baseline). The transformation heats were

calculated from the integral of the area under the peak of the DSC curves in the temperature range M_s to M_f or A_s to A_f . The exothermic process was assigned to upward curves (positive direction), and the endothermic ones to downward curves (negative direction).

Figure 3.2 Description for determining transformation temperatures and transformation heat in a DSC curve

A TA instrument DSC 2920 (MDSC™ TA Instruments Inc., USA) modulated differential scanning calorimeter was used to determine the phase transformation of Ti-Ni-Cu ribbons and bulk materials. The samples with a weight of 8 to 50 mg were placed in aluminum pans with crimped lids. A matching empty pan with crimped lid was used as the reference. The heating or cooling rate was $\pm 10^\circ\text{C}/\text{min}$. The temperature in the DSC measurement was calibrated using a standard indium reference.

NETZSCH DSC-404C was used to determine the crystallization temperature of amorphous ribbons. The heating rate was $10^\circ\text{C}/\text{min}$. Sample weight was 10-20 mg. The reference was empty alumina crucible.

3.3.5 Thermo-mechanical testing

A thermo-mechanical analyzer (TMA) was used to determine the shape recovery strain under different constant biasing loads during thermal cycling from -40 to 120°C. Figure 3.3 shows the set-up of the thermal cycling test. Gauge length was 8.5mm. The specimens were mounted in the grips, which were connected to linear variable differential transformers (LVDTs) via quartz rods. They were then stressed under a tensile load along the spinning direction. Displacement of specimen was measured by LVDT with an accuracy of 0.1µm. The applied load was measured by a load cell with an accuracy of 1.0g. The maximum load was 1.8g. The specimen was kept in a chamber, in which the temperature was controlled by utilizing liquid nitrogen and an electric heater. The specimen was cut along the rolling direction (or spinning direction), at a width of 1mm and length of 15mm. The heating and cooling rate was 10°C/min.

Elongation-temperature curves of ribbons under tensile load were recorded through thermal cycling from -40 to 120°C. The shape recovery strain of the ribbon was determined by measuring the change of elongation versus the temperature under constant tensile load.

Figure 3.3 The thermo-mechanical testing set-up [123]

CHAPTER 4 RESULTS

In this chapter, the experimental results on the bulk Ti-Ni-Cu alloys and as-spun and heat treated $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons with three initial structures are presented. DSC was carried out to study the transformation characteristics of the above materials. XRD technique was used to study the crystal structure of the above materials and texture development. TEM was employed to study the microstructure of the as-spun and heat treated $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons. The shape recovery strain of the heat treated ribbons was studied using TMA.

4.1 Ti-Ni-Cu shape memory alloys

It is known that adding Cu to the Ti-Ni alloy changes the transformation behavior and the transformation hysteresis of $\text{B2} \leftrightarrow \text{B19}$ is much smaller than that of $\text{B2} \leftrightarrow \text{B19}'$. But the reason has still not been clarified. Because martensitic transformation temperatures in Ti-Ni alloys are extremely sensitive to their compositions, making accurate measurement difficult, it is important to set up a reference of M_s to the composition for our research. In this section, the transformation behavior and structure of $\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ bulk alloys were studied by DSC and XRD.

4.1.1 Ti-Ni-Cu alloy preparation

Most chemical analysis methods are inadequate in providing the accuracy needed to determine the composition of the NiTi-based SMAs [124]. Instead, it is customary to use transformation temperatures as an indication of composition because of the sensitivity of the transformation temperatures to the compositions. However, regardless of possible inaccuracy, data of the compositions were provided in this section as a reference for further study.

Ti₅₀Ni_{50-x}Cu_x bulk alloys with different Cu content, i.e., x = 0, 7.5, 10, 15, 20, 25 and 30, were fabricated by arc-melting technique, and then homogenized at 850°C for 40h in vacuum furnace. The compositions of three locations in the seven Ti-Ni-Cu alloys after homogenization were examined by EDS/SEM as listed in Table 4.1. It can be seen that the measured composition was slightly different from the nominal one. As the measurement error could be as high as $\pm 10\%$, there is no difference between them. And the differences of compositions among the three locations are within measurement error.

Table 4.1 Composition of arc-melt Ti₅₀Ni_{50-x}Cu_x alloys

Nominal composition	Element	Ti			Ni			Cu		
		1	2	3	1	2	3	1	2	3
	Ti ₅₀ Ni ₅₀	51.5	52.5	52.1	48.5	47.5	47.9	/	/	/
	Ti ₅₀ Ni _{42.5} Cu _{7.5}	51.3	51.1	52.6	41.4	41.5	40.6	7.3	7.4	6.8
	Ti ₅₀ Ni ₄₀ Cu ₁₀	51.1	50.6	52.1	39.2	38.8	38.5	9.7	10.6	9.4
	Ti ₅₀ Ni ₃₅ Cu ₁₅	52.1	51.8	51.1	34.5	35.6	34.8	13.4	12.6	14.1
	Ti ₅₀ Ni ₃₀ Cu ₂₀	51.5	50.9	54.0	29.9	30.9	28.4	18.6	18.2	17.6
	Ti ₅₀ Ni ₂₅ Cu ₂₅	51.4	51.8	52.3	24.5	23.7	23.9	24.1	24.5	23.8
	Ti ₅₀ Ni ₂₀ Cu ₃₀	50.5	50.8	51.1	19.4	20.2	19.6	30.1	29.0	29.3

4.1.2 XRD results

The crystal structures of arc-melt Ti-Ni-Cu alloys were investigated by XRD at room temperature (25°C). Figure 4.1 shows the XRD patterns of Ti-Ni-Cu alloys with different Cu content. For the XRD patterns of the alloy with Cu content of 0 and 7.5 at.%, the diffraction peak at 42 and 62° can be identified as the 110 and 200 reflection from B2

phase, respectively. For the XRD profile of alloy with 10 at.% Cu, the reflections from (020), (012), (022) and (103) plane of B19 phase occurred. The $(111)_{B19}$ peak and $(110)_{B2}$ overlapped. With the increase of Cu content from 15 to 30 at.%, the peak intensity of (012), (022) and (103) from B19 phase increased.

The XRD patterns showed the crystal structure in Ti-Ni-Cu alloys at RT with the Cu addition: $B2 \rightarrow B2+B19 \rightarrow B19$. Ti-Ni-Cu alloy with Cu at.% of 0, 5 and 7.5 exhibited a B2 structure, the alloy with 10 and 15 at.% Cu a mixture of B2+B19 and the alloy with more than 20 at.% Cu a B19 structure.

Since the reflections from (020), (002) and (111) of B19 partially overlapped, peak fitting was often used in order to get the accurate positions of these peaks. Three functions are widely used to refine peak shape in nonlinear least squares fitting, i.e., Gaussian, Lorentz and Pseudo-Voigt function (Appendix I) [125]. The fitting curves by using Gaussian, Lorentz and Pseudo-Voigt functions are shown in Figure 4.2. Gaussian and Pseudo-Voigt gave better accuracy. For simplicity, Gaussian function was used to determine the peak positions [124]. The error of peak fitting is $\pm 0.01^\circ$.

Figure 4.1 XRD patterns of Ti-Ni-Cu alloys

Figure 4.2 Peak fitting using Gaussian, Lorentz and Pseudo-Voigt functions

Lattice parameters of B2 austenite (a_c) and B19 martensite (a_o , b_o and c_o) are plotted against Cu-content in Figure 4.3. a_c was identical for the alloys with different Cu-content. The average lattice parameters of B19 phase, b_o and c_o , varied around 4.1 and 4.6 Å, respectively. And these variations are within measurement error. a_o was almost identical, around 3.0 Å. These results indicate that lattice parameters of B2 and B19 did not change with increasing Cu content. Ni-replaced with Cu in $\text{Ti}_{50}\text{Ni}_{50}$ binary alloys did not result in the change of lattice parameters because of their nearly equal atomic and ionic radius.

Figure 4.3 Lattice parameters of B2 and B19 phase in Ti-Ni-Cu alloys

Compared with monoclinic B19' martensite ($a = 2.898$, $b = 4.108$ and $c = 4.646$ Å, $\gamma = 96.8^\circ$) in Ti-Ni binary alloy [46], orthorhombic B19 martensite in Ti-Ni-Cu alloy was not only a change of lattice parameters, but a totally different lattice. a of B19 was larger, but b and c were almost the same. The γ angle of B19 phase was 90° .

4.1.3 Transformation results

Transformation temperature of shape memory alloy is a very important criterion for assessing its property. Normally it is expected to be higher than room temperature for practical application. Transformation temperatures of Ti-Ni-Cu alloys with different Cu contents were measured by DSC.

Typical DSC curves of $\text{Ti}_{50}\text{Ni}_{50}$, $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ and $\text{Ti}_{50}\text{Ni}_{30}\text{Cu}_{20}$ are shown in Figure 4.4. It can be seen that one-stage transformation of B2 (cubic) $\leftrightarrow$ B19' (monoclinic) (Figure 4.4 a) occurred in the equi-atomic Ti-Ni alloy (0 at.% Cu), whereas a two-stage transformation of B2 $\leftrightarrow$ B19 (orthorhombic) $\leftrightarrow$ B19' (Figure 4.4 b) occurred by substituting Cu for Ni by 10 at.%. Further substitution of Cu for Ni by 20 at.% changed

the transformation back to the one stage transformation of $B2 \leftrightarrow B19$ (Figure 4.4 c). This agrees well with the reports by Nam et al. [4, 8].

Figure 4.4 DSC curves for $Ti_{50}Ni_{50}$, $Ti_{50}Ni_{40}Cu_{10}$ and $Ti_{50}Ni_{30}Cu_{20}$ alloys

The transformation temperatures and hysteresis of Ti-Ni-Cu alloys with different Cu content are listed in Table 4.2 and shown in Figure 4.5 and Figure 4.6. The error of these temperatures mainly comes from peak picking, which is ± 0.2 °C. Table 4.2 and Figure 4.5 show that $B2 \leftrightarrow B19'$ (or $B19 \leftrightarrow B19'$) transformation temperatures (M_s' , M_f' , A_s' and A_f') decreased with increasing Cu content from 0 to 10 at.%. M_s' (or M_s) of the Ti-Ni-Cu

alloy with Cu content less than 10 at.% is lower than RT, indicating a B2 austenitic structure at RT. When Cu substitution is above 10 at.%, a two-stage transformation occurs. In the present experiment, this two-stage transformation was only observed in $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$ alloy. With further increase in Cu content from 15 to 30 at.%, the transformation temperatures of $\text{B2} \leftrightarrow \text{B19}$ (M_s , M_f , A_s and A_f) increased. $\text{Ti}_{50}\text{Ni}_{35}\text{Cu}_{15}$ alloy had a mixture of B19 and B2 phase at RT. Only when Cu substitution for Ni exceeded 20 at.%, did Ti-Ni-Cu alloy exhibit a B19 martensite structure at RT.

Table 4.2 Transformation temperatures for arc-melt Ti-Ni-Cu alloys

Cu at.%	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	A_p-M_p (°C)	M_s' (°C)	M_f' (°C)	A_s' (°C)	A_f' (°C)	$A_p'-M_p'$ (°C)
0						-2.6	-20.4	-0.6	44.4	37.8
7.5						-1.0	-21.1	-10.4	13.5	12.5
10	24.0	1.6	19.0	41.8	20.4	-3.7	-25.6	-17.1	13.3	16.8
15	42.9	-3.2	9.4	52.6	12.3					
20	56.3	24.6	29.5	62.2	7.3					
25	70.8	28.4	37.5	80.5	8.6					
30	67.0	36.8	45.1	74.5	8					

Note: M_s , M_f , A_s and A_f correspond to $\text{B2} \leftrightarrow \text{B19}$ transformation; M_s' , M_f' , A_s' and A_f' correspond to $\text{B2} \leftrightarrow \text{B19}'$ (0 and 7.5%Cu) or $\text{B19} \leftrightarrow \text{B19}'$ (15%Cu) transformation.

$\text{B2} \leftrightarrow \text{B19}'$ ($\text{B19} \leftrightarrow \text{B19}'$) transformation hysteresis decreased from 37.8 to 16.8°C with Cu addition, which was larger than that of $\text{B2} \leftrightarrow \text{B19}$ transformation (shown in Figure 4.6). $\text{B2} \leftrightarrow \text{B19}$ transformation hysteresis also decreased from 20.4 to 8.0°C with increasing Cu addition from 10 to 30 at.%. It is reported that the transformation hysteresis may be due

to energy-dissipation originated from specific volume changes, shape changes, and interfacial friction [4, 34]. The first two factors were found to have small effects. It was also reported by Nam et al. [4] that the introduction of dislocations was depressed with increasing Cu-content, indicating that the interfacial friction may decrease with the increase of Cu content, thus resulting in the decrease of the transformation hysteresis.

Figure 4.5 Dependence of transformation temperatures on Cu content

Figure 4.6 Dependence of transformation hysteresis on Cu content

Cu addition not only raises the martensitic transformation temperatures but also reduces the transformation hysteresis, both of which are beneficial to the application of Ti-Ni-Cu SMAs. 20 at.% Cu is a critical content, above which the alloy had a B19 structure at RT and transformation hysteresis was around 8°C. To obtain a stable structure in practical application, a Ti-Ni-Cu alloy with Cu content above 20 at.% was suggested.

4.2 Initially amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon (ribbon A)

Due to the high cooling rates during melt-spinning process, the melt-spun ribbons can be amorphous, partially amorphous and crystalline. In this study, $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ (at.%) as-spun ribbons with three initial structures were investigated in order to study the effect of initial structure, i.e. amorphous (ribbon A), fully crystalline (ribbon B), and partially amorphous (ribbon C).

In this section, the transformation behavior, the development of microstructure and crystal structure and shape memory properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A were studied under different annealing conditions, using DSC, XRD, TEM and TMA.

4.2.1 As-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A

The initial structure of as-spun ribbon A was characterized using both x-ray diffraction and electron diffraction. Figure 4.7 (a) is the x-ray diffraction pattern of the as-spun ribbon. The hump of very low intensity at around 42° (2 θ) in the XRD pattern indicates only some short-range order in the atomic arrangement. A similar phenomenon was also observed in electron diffraction pattern shown in Figure 4.8 (b), which indicates that as-spun ribbon is mainly amorphous. Its crystallization temperature was determined as 450°C as shown in Figure 4.7 (b), by heating the sample of as-spun ribbon to 800°C using DSC measurement.

Figure 4.7 (a) XRD pattern and (b) DSC curve of as-spun ribbon A

Figure 4.8 TEM micrograph (a) and corresponding electron diffraction pattern (b) of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A showing amorphous microstructure

The microstructure of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is mainly amorphous as shown in Figure 4.8 (a).

4.2.2 Annealed ribbon A

In order to study the effect of annealing temperature on the shape memory properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon, annealing was carried out from 450 to 750 $^{\circ}\text{C}$. It was found that

annealing played a crucial role in structure evolution and shifting shape memory properties.

4.2.2.1 Structure analysis

Figure 4.9 shows the XRD patterns of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 450°C for 5 and 15 minutes, respectively. The 5minute-annealed ribbon consisted of a mixture of amorphous and B19 structure (Figure 4.9 (a)), while the 15minute-annealed ribbon had a fully crystalline B19 structure (Figure 4.9 (b)).

Figure 4.9 XRD patterns of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 450°C

The lattice parameters of B19 were found to be: $a = 2.93\text{\AA}$, $b = 4.29\text{\AA}$ and $c = 4.53\text{\AA}$, which are similar to the values reported by other researchers [8, 18]. The high intensity ratio of 111/002, 111/022 and 111/131 revealed the preferred orientation developed in this crystallized ribbon [126].

Figure 4.10 shows the XRD pattern of the ribbon annealed at 500°C for 15 minutes. Only diffraction peaks of B19 martensite with preferred (111)-B19 orientation were observed.

Figure 4.10 XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15 minutes

The XRD pattern of annealed ribbons changed with the increase of annealing temperature, for example, samples annealed above 550°C showed a mixture of B19 martensite and B11-TiCu phase. Figure 4.11 shows a typical XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 550°C for 15 minutes. In addition to the diffraction peaks of B19 martensite, peaks corresponding to a tetragonal B11-TiCu phase occurred. Some peaks of B19 and B11-TiCu overlapped, such as $(111)_{\text{B19}}$ and $(102)_{\text{B11-TiCu}}$ at 42.3° , as well as $(022)_{\text{B19}}$ and $(200)_{\text{B11-TiCu}}$ at 59.4° . The lattice parameters of the B11-TiCu were determined to be: $a = 3.11 \text{ \AA}$ and $c = 5.91 \text{ \AA}$, which are similar to those reported by Rosner et al. [29]. From the relative intensity ratio of the B19 diffraction peaks, we can see that the preferred orientation of (111) -B19 still existed in the 550°C -annealed ribbon. The standard XRD data of B11 and B19 phase are listed in Appendix II.

Figure 4.11 XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 550°C for 15 minutes

The evolution of crystal structure with annealing temperature can be seen clearly from Figure 4.9, Figure 4.10, Figure 4.11 and Figure 4.12. The position of diffraction peaks did not change with annealing temperature, which means the lattice parameters of B19 and B11-TiCu phase are identical for all the annealed ribbons. This was because the precipitation of B11 phase did not change the ratio of Ti/Ni(Cu) in B19 phase. However, the relative intensity of diffraction peaks changed with the increase of annealing temperature, indicating the change of texture developed in the ribbon. The intensity of (110) peak of B11-TiCu increased when annealing temperature increased, and $(110)_{\text{B11}}$ became the strongest peak at annealing temperature above 700°C , suggesting the increase of volume fraction of B11-TiCu with the annealing temperature. In addition, (011) of B2 phase appeared in the XRD patterns of ribbon A annealed above 650°C (Figure 4.12).

Figure 4.12 XRD patterns of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at different temperatures

The crystal structure evolution of ribbon A is: B19 structure with preferred orientation annealed below 550°C, a mixture of B19 + B11 annealed from 550 to 650°C and B19 + B11 + B2 with further annealing.

Since SMAs used for practical purpose are polycrystalline, it is important to know the anisotropy of the grains. Specific texture developed in materials causes anisotropic characteristics to appear in mechanical and electrical behavior [127, 128]. It has been reported that strain induced by the martensitic transformation showed strong orientation dependence in Ti-Ni alloys [101, 103]. The rapid quenching in melt-spinning technique causes grain refinement and changes grain morphology from equi-axial to columnar [105], resulting in the formation of texture and affects the mechanical properties. Santamarta et

al. [108,109] compared shape recovery strain of Ti-Ni alloys with that of Ti-Ni-Cu ribbons and found that textures affected SME.

4.2.2.2 Texture analysis

Texture, also known as preferred orientation, is the distribution of grain or particle orientation of a sample in space and can be classified into macrotexture and microtexture. In a macrotexture, the grains in a polycrystal are regarded as constituting a single statistical population without regard to the spatial location of any particular grain or its relation to its neighbors. In contrast, a microtexture describes the nature and degree of the misorientation of a grain with respect to its immediate neighbors [93]. Macrotexture is further classified into fiber texture, sheet texture, or rolling texture. A fiber texture is described by a crystal vector $[uvw]$, which indicates the unique direction such as fiber or wire axis. In materials with fiber texture, a set of planes belonging to the zone $[uvw]$ tend to align along $[uvw]$. Rolling texture is denoted by a notion $(hkl)[uvw]$, where (hkl) refers to planes parallel to the sheet surface and $[uvw]$ is the direction parallel to the rolling direction. In materials with rolling texture, most grains are oriented with their $\{hkl\}$ planes roughly parallel to the sheet surface and their $[uvw]$ direction in that plane parallel to the rolling direction.

A texture is conventionally described in two dimensions by means of pole figures, which record the intensity variation and location of a specific family of planes (poles) with respect to the sample. They show the axis density distribution in the specimen coordinate system RD (rolling direction)-TD (transverse direction)-ND (normal direction of the rolling plane), where the center of the pole figures corresponds to ND.

Texture development in B19 martensite in the annealed ribbon A was investigated by pole figure measurement. Pole figures of $\{002\}$, $\{111\}$, $\{012\}$, $\{022\}$, $\{200\}$ or $\{131\}$ were measured at RT. The maximum relative pole intensity is indicated in each of the figures. The texture component was qualitatively analyzed by comparing the measured pole figures with standard stereographic projections of B19 phase.

In Figure 4.13 the pole figures of $\{002\}$, $\{012\}$, $\{022\}$ and $\{200\}$ exhibited a considerably uniform pole density distribution, revealing a random texture. Only $\{111\}$ pole figure showed a strong texture with two pole density peaks symmetrically located within 5° from ND and maximum relative intensity of 31.7, indicating that $\{111\}$ planes of B19 were very close to the ribbon surface (about 5° away). The angle between (111) and $[211]$ is 4.5° . By comparing the measured pole figures with the standard stereographic projection of the B19 lattice shown in Figure A3.1 of Appendix III, the pole peaks of $\{111\}$ formed the center of $[211]$ fiber texture. It indicates that a strong $[211]$ fiber texture was present in the ribbon plane. This indicated that B19 grains were grown column-like in the ribbon annealed at 450°C for 15 minutes [105]. And the columnar B19 grains were distributed more or less rotationally about the $[211]$ direction, which was nearly parallel to ND, while (111) of B19 phase was nearly parallel to the ribbon surface.

Pole figures of $\{002\}$, $\{111\}$, $\{012\}$ and $\{131\}$ of B19 phase as a function of annealing temperature are shown in Figure 4.14, Figure 4.15, Figure 4.16, Figure 4.17 and Figure 4.18, respectively.

Figure 4.13 Pole figures of 450°C-annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A for 15 minutes

Figure 4.14 shows pole figures of $\{002\}$, $\{111\}$, $\{012\}$ and $\{131\}$ in ribbon A annealed at 500°C. Only $\{111\}$ pole figure showed a clustered distribution around ND. Compared with the pole figures of 450°C-annealed ribbon, the position of the maximum pole density of $\{111\}$ in Figure 4.14 did not change, but the maximum relative intensity of the $\{111\}$ pole decreased from 31.7 to 9.5, indicating a $[211]$ fiber texture weaker than that of the 450°C -annealed ribbon.

Figure 4.14 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15 minutes

Figure 4.15 is a set of pole figures of $\{002\}$, $\{111\}$, $\{012\}$ and $\{131\}$ in the ribbon annealed at 550°C . The clustered distribution of $\{111\}$ was the same as that of the 450°C -annealed sample. In addition, the pole figure of $\{012\}$ showed obvious clustered density distribution. One pole density peak was located at 50° from ND along RD, whose maximum relative intensity was 36.9. The pole figures of $\{002\}$ and $\{131\}$ showed a random distribution. $\{111\}$ pole peaks distributed around ND and the angle between (111) and (012) is 50° , indicating that (111) is the rolling plane. Compared with the standard stereographic projection of B19 structure, as shown in Figure A3.2, clusters of $\{111\}$ and $\{012\}$ poles appeared at the positions that correspond to $(111)[\bar{2}11]$ sheet texture. This indicates that a $(111)[\bar{2}11]$ sheet texture existed in this ribbon. The (111) plane of B19 phase was also the ribbon surface as in the 450°C -annealed sample. Therefore, increasing

the annealing temperature did not change the orientation of (111) plane of B19 phase, but it changed the texture component from fiber to sheet texture, in which the rolling direction (RD), as well as the spinning direction of the ribbon was $[\bar{2} 11]$.

Figure 4.15 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 550°C for 15 minutes

Figure 4.16 displays pole figures of $\{002\}$, $\{111\}$, $\{012\}$ and $\{131\}$ in the ribbon annealed at 600°C . The pole figures all demonstrated clustered distribution except for the $\{002\}$ pole figure. The distribution of $\{111\}$ and $\{012\}$ pole figures was similar to that in the 550°C -annealed ribbon. In addition, the $\{131\}$ pole figure had two maximum pole densities covering the region at around 20° from ND, respectively. But the texture component derived from these pole figures was still a $(111)[\bar{2} 11]$ sheet texture, meaning (111) was still parallel to the ribbon surface.

Figure 4.16 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 600°C for 15 minutes

Figure 4.17 and Figure 4.18 present the pole figures of $\{002\}$, $\{111\}$, $\{012\}$ and $\{131\}$ in the ribbon annealed at 650°C and 700°C , respectively. They shared similar distribution of pole densities to those of the 600°C -annealed samples. The maximum intensity of $\{111\}$, $\{012\}$ and $\{131\}$ pole in the 650°C -annealed ribbon was 4.8, 2.6 and 3.6, respectively, while the maximum intensity of these poles in the 700°C -annealed ribbon was 4.3, 2.1 and 3.1, respectively. Therefore, the texture component was still $(111)[\bar{2}11]$ sheet texture.

Figure 4.17 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 650°C for 15 minutes

The texture type and relative intensity of (111) pole as a function of annealing temperature were tabulated in Table 4.3. It was seen that texture components and intensity changed with the annealing temperature. With the increase of annealing temperatures, texture component changed from [211] fiber to $(111)[\bar{2}11]$ sheet texture, but $\{111\}$ plane of B19 phase was always nearly parallel to the ribbon surface in all the annealed ribbons. The relative intensity of (111) pole decreased with annealing temperature, which indicated the preferred orientation of (111) plane weakened. Ribbon with fiber texture consists of column-like grains distributing rotationally along [211]. For sheet texture, $[\bar{2}11]$ direction is parallel to the spinning direction. Ribbon with sheet texture aligns its grains with $[\bar{2}11]$ direction along spinning direction and (111) plane parallel to the ribbon surface.

Figure 4.18 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 700°C for 15 minutes

Table 4.3 Texture type of B19 phase and its relative intensity in annealed ribbon A

Texture	Annealing temperature (°C)					
	450	500	550	600	650	700
[211] fiber	31.7	9.5				
$(111)[\bar{2}11]$			7.3	5.1	4.8	4.3

Pole figures of $\{110\}_{\text{B11-TiCu}}$ in the annealed ribbons are displayed in Figure 4.19. Only 700°C-annealed ribbon showed an obvious preferred orientation. The $\{110\}$ pole figure had a maximum pole density at around 5° from ND, indicating that the volume of B11

precipitate was high enough for measuring the preferred orientation. The texture component was determined to be [110] fiber texture by comparing with the stereographic projection of B11 TiCu (appendix IV). This means that the (110) plane of B11 phase was preferentially arrayed along the ribbon surface. The sheet texture of B19 phase and fiber texture of B11 phase in this ribbon suggests that the orientation relation between B11 and B19 is: $(110)_{B11} // (111)_{B19}$.

Figure 4.19 $\{110\}_{B11}$ pole figures of ribbon A annealed at different temperatures

4.2.2.3 Microstructural analysis

Figure 4.20 shows the microstructure of the amorphous ribbon annealed at 450°C for 5 minutes. Austenite started to form in the amorphous matrix even when heat treated below the crystallization temperature. Apart from the amorphous area, big crystalline grains in

micro-scale were observed in Figure 4.20 (a). This was confirmed by the corresponding selected area diffraction pattern in Figure 4.20 (b) and (c). The amorphous ribbon was fully crystallized after annealing at the same temperature (450°C) for 15 minutes, as shown in Figure 4.21. In most grains, only a pair of variants was observed. According to the electron diffraction analysis, the parallel martensite plates were internally twinned with $\{111\}$ type I twin relation, as shown in Figure 4.21 (b).

Figure 4.20 (a) TEM micrograph of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 450°C for 5 minutes. (b) and (c) are SAD patterns taken from the region A and B in (a), respectively.

Figure 4.22 and Figure 4.23 show the microstructure of the ribbons annealed at 500°C for 15 min.. In most areas, black granular particles (around 200 nm) were observed in the white matrix (Figure 4.22 (a)). Electron diffraction patterns in Figure 4.22 (b) and (c) indicated that both the matrix and black particles were polycrystalline B19 martensite. A high-resolution TEM observation (Figure 4.23) further reveals that the grain size of the polycrystalline white matrix was only about 10 nm, while no martensite twin was observed. The larger grains may form during fast solidification in the process of melt

spinning, or it may be due to the earlier nucleation or unstable growth of the smaller matrix.

Figure 4.21 TEM micrograph and corresponding electron diffraction pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 450°C for 15 minutes.

Figure 4.22 (a) TEM micrograph of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 500°C for 15 minutes (b) and (c) SAD patterns corresponded to the white area and the black particle in (a), respectively.

Figure 4.23 High-resolution TEM micrograph of the white matrix in Fig. 4.22 (a) showing nanocrystalline B19 martensite

Larger martensite grains were also observed in some areas of the sample annealed at 500°C, as shown in Figure 4.24. Figure 4.22 to Figure 4.24, indicating that the microstructure in the ribbon annealed just above the crystallization temperature was not uniform. The inhomogeneous structure in thickness was also reported by Dalle et al. in Ti-Hf-Ni-Re SMA [129].

In the ribbons annealed at higher temperatures, mainly B19 martensite with strong preferential orientation was observed as shown in the TEM micrographs in Figure 4.25 to Figure 4.27, but grain size of B19 martensite did not change drastically, remaining around 0.5 μm . In the ribbon annealed at 550°C, B19 martensite variants were observed to accommodate each other by a twinned structure, as shown in Figure 4.25. Only one pair of twinned martensite variants was observed in most of the grains. B11-TiCu precipitates were observed in some of the B19 martensite grains in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at higher temperatures.

Figure 4.24 TEM micrograph of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15min.

Figure 4.25 TEM micrograph and corresponding electron diffraction pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 550°C for 15min.

Figure 4.26 TEM micrographs (a, c, d) and corresponding electron diffraction pattern (b) of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 550 °C for 15min. showing B11-TiCu precipitates.

Figure 4.26 shows one example of bright field images of B11-TiCu precipitates in B19 martensite in the ribbon annealed at 550°C. Two sets of very thin plate-like precipitates can be seen along the beam direction of $[100]_{B19}$. The precipitated thin plates formed a cell structure on a nanometer scale as shown in Figure 4.26 (a). Faint streaks due to these

thin precipitates can be seen in the $\{011\}$ planes of B19 (Figure 4.26 (b)), showing that the thin plate-like precipitates were lying along the $\{011\}$ planes of B19 martensite, indicating that the habit planes of these precipitates were $\{011\}_{B19}$. Internal strain fields were visible with a strong strain contrast around the plate-like precipitates in Figure 4.26 (c) because of the lattice misfit between the surrounding martensite and the precipitate, which agrees well with the observations of Rosner et al. [29].

In particular, the thin nature of the precipitates is shown in Figure 4.26 (d) by high-resolution TEM as fully coherent and consisting of single or only a few atomic layers marked by the arrow head. No misfit dislocations were found, which indicates that a kind of elastic accommodation exists in the martensite. The length of the precipitates was around 100 nm. A similar phenomenon was also observed in Ti-rich Ti-Ni thin films by Kikuchi et al. [130].

With the increase of annealing temperature, the martensite grain with strong preferred orientation grew slightly. Parallel martensite plates were observed extending through the whole grain in the ribbon annealed at 750°C (Figure 4.27 (a)). The mirror symmetry with (111) plane in the diffraction pattern of (b) revealed that these parallel plates were related to each other by type I $\{111\}$ twin. Compound twin $\{011\}$ in B19 martensite was reported by Youichi et al. [68], but was not observed in this ribbon, suggesting that (111) type I twin is a frequently observed twinning mode of the martensite variants in B19 martensite of this initially amorphous ribbon.

Figure 4.27 TEM micrograph and corresponding electron diffraction pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 750°C for 15min.

4.2.2.4 Transformation results

Transformation temperatures are important shape memory properties of SMAs. They were studied by means of DSC measurement. Figure 4.28 shows the DSC curve of amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 450°C for 15 minutes. A sharp peak during heating and cooling revealed a reversible martensitic single-step transformation. Upon cooling, B2 austenite started to transform to B19 martensite phase at 67.6°C and finished transformation at 50.7°C . During heating B19 started to transform back to B2 at 57.3°C and finished at 72°C , indicating a B19 martensite at RT, which agrees well with the XRD results.

Figure 4.28 DSC curve of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 450°C for 15min.

The transformation behavior of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 500°C for 15 minutes was shown in Figure 4.29. The two-stage transformation was seen during heating and cooling process. The observed two-stage transformation in Figure 4.29 cannot be attributed to $\text{B2} \rightarrow \text{B19} \rightarrow \text{B19}'$ phase transformation. This is because $\text{B19} \rightarrow \text{B19}'$ transformation in Ti-Ni-Cu alloy was suppressed to very low temperature when Cu content is above 15 at.%, and the transformation peak of $\text{B19} \rightarrow \text{B19}'$ in DSC curve was very low and diffuse [4]. Similar phenomenon observed by Rosner et al. [30] in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons was ascribed to the influence of the precipitates. This is not our case, because XRD results confirmed that B11 precipitates did not form until annealing above 550°C .

Figure 4.29 DSC curve of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15min.

TEM observation in the present study (Figure 4.22) indicates that it should be the grain size difference that causes the observed two-stage phase transformation. The first transformation peak in DSC curve during cooling may be due to $\text{B2} \rightarrow \text{B19}$ transformation of the larger size particle. The second one may be due to the same transformation in the nano-crystallites of the white matrix. Because the volume fraction of black grains is much less than that of the nanograins, the exothermic heat of the first transformation is less than that of the second. That is why the first peak on DSC curve of cooling process is observed to be lower than the second one in Figure 4.29. Using the same extrapolation, we can see that the austenitic transformation also occurred at a lower temperature in the nanoscaled grains during heating [131].

DSC curves of ribbons annealed at different temperatures ($550, 600, 650, 700, 750^{\circ}\text{C}$) are shown in Figure 4.30. All the samples show a one-stage transformation during heating and cooling. This one-stage transformation corresponds to $\text{B2} \leftrightarrow \text{B19}$. With the increase of annealing temperature from 550°C to 700°C , DSC peaks did not change. Annealing

above 700°C shifted DSC peak toward lower transformation temperatures, and DSC peak height decreased with annealing temperature. However, all the transformation temperatures were above RT, indicating that the ribbons at RT had B19 structure.

Figure 4.30 DSC curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons annealed at different temperatures

Table 4.4 Phase transformation temperatures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A at different annealing temperatures

Annealing temperature (°C)	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	M_p (°C)	A_p (°C)	A_p-M_p (°C)
450	67.6	50.7	57.3	72.0	59.0	65.6	6.6
500	66.4	53.3	60.2	70.8	58.2	65.8	7.6
550	66.3	53.4	60.5	74.2	60.8	66.3	5.5
600	64.8	52.5	58.2	74.4	59.3	67.9	8.6
650	64.5	52.8	58.7	73.3	59.0	67.6	8.6
700	63.8	46.8	53.9	70.9	55.3	63.4	8.1
750	54.4	42.2	49.1	60.1	48.6	54.6	6.0

The transformation temperatures are listed in Table 4.4, in which M_p and A_p refer to the peak temperatures of $B2 \rightarrow B19$ and $B19 \rightarrow B2$ transformations. The measurement errors of these temperatures are $\pm 0.2^\circ\text{C}$, which were mainly caused by peak picking of DSC curves. Figure 4.31 (a) shows the dependence of transformation temperatures (M_s , M_f , A_s and A_f) on the annealing temperature. All the four transformation temperatures showed a similar tendency that were identical with increasing annealing temperatures from 450°C to 650°C , followed by a slight decrease with annealing above 700°C .

Figure 4.31 Dependence of transformation temperatures (a) and hysteresis (b) on annealing temperatures

The transformation hysteresis between $B2 \rightarrow B19$ and $B19 \rightarrow B2$ of the annealed ribbons is defined as the difference between A_p and M_p . In Figure 4.31 (b) we can see that the transformation hysteresis had an average value of 8°C . The measurement error of the hysteresis is $\pm 0.4^\circ\text{C}$, which is around $\pm 5\%$.

4.2.2.5 Thermo-mechanical testing results

Shape recovery strain is an important criterion to evaluate shape memory property of SMAS. It was measured by thermal cycling tests using TMA. Thermal cycling tests on annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons were carried out under different tensile loads: 6.3, 11.3, 25, 37.5 and 45 MPa. Strain-temperature curves were measured under various constant stresses during a thermal cycle from below M_f (-40°C) to above A_f (120°C). Figure 4.32 shows the strain – temperature curves of the 500°C -annealed ribbon under different loads. The elongation on cooling and shrinkage on heating indicated that the annealed ribbon exhibited a well-defined shape memory effect. Under a constant stress, the specimen started to elongate at M_s and finished the deformation at M_f upon cooling, while it started to recover the deformation and shrink at A_s and finished the recovery at A_f upon heating.

The shape recovery strain was calculated as a difference between the elongation in martensitic and austenite phase. The 500°C -annealed ribbon showed a very small recovery strain under lower applied load (0.2% under 6.3 MPa). With the increase of applied load, the shape recovery strain increased. Under 45 MPa, a recoverable strain of 1.4% was obtained.

Figure 4.32 TMA curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15min. under different stresses

Figure 4.33 shows the effect of thermal cycling on the strain-temperature behavior of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 500°C under 45MPa. After 10 cycles of thermal cycling, the strain-temperature curves did not change significantly. It may be due to the low stress or small number of cycles, suggesting that under such a stress there is no formation or rearrangement of lattice defects.

Figure 4.33 TMA curves of thermo-cycled $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at 500°C for 15min.

Thermal cycling is always an easy way to induce two-way shape memory effect (TWSME). The strain-temperature was re-measured under load-free condition after the sample was cycled 10 times. No obvious shape recovery was observed, revealing there was no TWSME induced in the ribbon annealed at 500°C.

The strain-temperature curves under 45 MPa of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different temperatures are shown in Figure 4.34. All the annealed ribbons showed perfect shape memory effect. With the increase of annealing temperature, strain-temperature loop became smaller, indicating the decrease of recovery strain.

Figure 4.34 TMA curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at various temperatures under 45MPa

Figure 4.35 provides the shape recovery strain as a function of annealing temperatures under different loads. Under a lower load (6.3 and 11.3 MPa), the recovery strain decreased slowly with the annealing temperature, which may be due to the small volume of reoriented martensite under low stress. When stressed under higher load (>11.3 MPa), a sharp decrease of recovery strain was observed when annealing temperature increased from 500 to 550°C, while recovery strain increased slightly with further increasing

annealing temperature to 750°C. For the ribbon annealed at 450°C, the recoverable strain was 1.5% under 45 MPa. It decreased drastically to 0.38% with the increase of annealing temperature to 750°C. This may be due to the strengthening of large amounts of precipitates in this ribbon. Therefore, the stress of 45 MPa was not enough to initiate the movement of twin boundaries and reorientation of B19 martensite. In this study, due to limitation of the TMA equipment, 45 MPa was the maximum stress achievable.

Figure 4.35 Shape recovery strain under different stress for $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A annealed at different temperatures

At all the annealing temperatures in this study, the shape recoverable strain of annealed ribbons increased with the increase of applied stress. It is interesting to find that under lower stress the 450°C-annealed ribbon showed much higher recoverable strain than the rest of the annealed ribbons. It had a shape recovery of 0.7% even under 6.3 MPa, indicating that twins reoriented easily in this ribbon.

4.3 Initially crystalline $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon (ribbon B)

In order to study the effect of initial structure on the transformation behavior and shape memory properties, initially crystalline $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon was selected and its results were compared with those of initially amorphous ribbon. It was found that initially crystalline ribbon showed a higher recovery strain and lower transformation temperatures than initially amorphous ribbon after annealing.

4.3.1 As-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B

The as-spun ribbon B was fully crystalline as shown in Figure 4.36. It consists of B2 and B19 phases. From the relative intensity ratio of B2 and B19 phase, a strong texture in the ribbon was observed.

Figure 4.36 XRD pattern of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B (a) and its enlargement (b)

Figure 4.37 shows the bright field image and SAD pattern of B19 martensite plates in the as-spun ribbon B. B19 martensite was above 1 μm (Figure 4.37(a)) and demonstrated a different twinning morphology from those of annealed ribbon A. The parallel bands did not cross the whole grain and the accommodation of martensite variants was observed. In

some areas of the sample, B2 austenite of $0.2\mu\text{m}$ was also observed as shown in Figure 4.37 (c).

(a) Martensite

(b) $\mathbf{B}/[100]_{\text{B19}}$

(c) Austenite

Figure 4.37 Bright field image of B19 martensite (a) and austenite (c) in as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B and SAD pattern of the martensite plates (b)

The texture of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B was also investigated. The pole figures of $\{002\}$ and $\{022\}$ and $\{111\}$ from B19 phase and $\{011\}$ and $\{200\}$ from B2 phase were measured at RT (shown in Figure 4.38). Only pole figures of $\{111\}$ and $\{022\}$ from B19 phase showed an obvious texture. For example, four $\{111\}_{\text{B19}}$ pole density peaks in Figure 4.38 (b) covered a region within 0 to 10° from ND with maximum relative intensity of 3.2, while in $\{022\}_{\text{B19}}$ pole figure, the pole density peaks formed a ring at 50° from ND with maximum relative intensity of 6.8. These two pole figures were interpreted as a $[001]$ fiber texture of B19 phase, indicating that $\{002\}$ plane was located preferentially along ribbon surface in this as-spun ribbon, unlike the texture in annealed ribbon A. Santamarta et al. [108] reported a different $[011]$ fiber texture in the crystallized as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon.

Figure 4.38 Pole figures of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ as-spun ribbon B

A one-stage $B2 \leftrightarrow B19$ transformation was observed in this as-spun ribbon with transformation temperatures of: $M_s = 32.5$, $M_f = 12.0$, $A_s = 17.4$ and $A_f = 43.8$ °C, indicating the as-spun ribbon B had a mixture structure of B2 and B19 phase at RT, agreeing well with the XRD result.

Shape recovery strain of as-spun ribbon B was measured by thermo-mechanical test under 45 MPa, as shown in Figure 4.39. It was about 2.5%, much higher than those of annealed ribbon A.

Figure 4.39 TMA curve of as-spun $Ti_{50}Ni_{25}Cu_{25}$ ribbon B under 45 MPa

4.3.2 Annealed ribbon B

4.3.2.1 Structure analysis

Figure 4.40 is the XRD pattern of ribbon B annealed at 300°C. It shows the coexistence of B2 and B19 phase, as in the as-spun ribbon. However, the relative peak intensity is different, indicating a different texture in this annealed ribbon.

Figure 4.40 XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B annealed at 300°C for 15min.

Figure 4.41 shows the XRD patterns of ribbon B annealed at 300°C to 550°C. It can be seen that ribbon B annealed up to 550°C had a coexistence of B2 and B19 structure and the lattice parameters of B19 and B2 phase did not change. However, the relative intensity of diffraction peaks changed with the increase of annealing temperature. The $(200)_{\text{B2}}$ peak intensity decreased and $(110)_{\text{B2}}$ peak disappeared after annealing above 300°C. This means that the volume fraction of B2 phase decreased with further annealing. The position of the strongest peak changed from 42° (annealed at 300 and 400°C) to 61° (450°C annealing), 42° (500°C annealing), and 60° (550 °C annealing). Compared with the XRD pattern of the as-spun ribbon B, the variation of the strongest peak indicates the evolution of texture in the sample.

The XRD patterns of ribbon B annealed at higher temperatures (600-750°C) are presented in Figure 4.42. In addition to B2 and B19 phase, the precipitation of TiCu phase was observed, but the lattice parameters of B19 and TiCu phase did not change with annealing. However, the intensity of the peaks from TiCu phase increased, indicating that the

volume fraction of precipitates increased with the annealing temperature. The change in intensity ratio reveals the reorientation of B19 martensite and B11-TiCu phase. The formation of B11 precipitates in turn stabilized B2 austenite.

Figure 4.41 XRD patterns of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B annealed at 300-550°C for 15min.

(a)

(b)

(c)

(d)

Figure 4.42 XRD patterns of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B

Annealing resulted in the formation of TiCu phase, the reorientation of B19 martensite, and the orientation of B11 TiCu phase. Compared with annealed ribbon A, the main difference is that B2 existed in all the annealed ribbon B and the texture evolution was different.

4.3.2.2 Microstructural analysis

Figure 4.43 shows the microstructure and corresponding diffraction pattern of the 300°C -annealed sample. Figure 4.43 (a) shows that the crystal grain size is about 200 nm. The ring diffraction pattern in Figure 4.43 (b) was indexed to be a B2 austenite. Strong texture was also shown in this ring pattern.

Similar microstructure features were also observed in the ribbon annealed up to 450°C . Figure 4.44 and Figure 4.45 show essentially the same microstructure as those in the 300°C -annealed sample. Diffraction analysis showed that these grains were also retained

B2 austenite, while the grain size did not change significantly with the increase of annealing temperature from 300 to 450°C. Lower temperature annealing resulted in the formation of large areas of submicron equiaxed grains.

Figure 4.43 Microstructure (a) and corresponding diffraction pattern (b) of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B at 300°C for 15min.

Figure 4.44 Microstructure of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B at 400°C for 15min.

Figure 4.45 Microstructure of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B at 450°C for 15min.

Figure 4.46 Microstructure of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B at 500°C for 15min.

Increasing annealing temperature leads to the increase of volume fraction of B19 martensite. In the sample annealed at 500°C twinned martensite was observed as parallel plates crossing the whole grain in Figure 4.46. The grain size of B19 martensite was

significantly larger than those of B2 in the lower temperature-annealed samples. Diffraction analysis revealed that the martensite plates were related to each other by type I (111) twin. This can be proved by the simulated diffraction pattern in Figure 5.4 (a).

(a)

(b)

(c)

(d) $B // [1\bar{2}1]_M // [\bar{1}2\bar{1}]_T$

Figure 4.47 Microstructure of annealed $Ti_{50}Ni_{25}Cu_{25}$ ribbon B at 600°C for 15min.

Annealing at 600°C caused the formation of precipitate at the grain boundaries of B2 austenite (shown Figure 4.47 (a)). In other areas, twinned morphology of martensite grains was observed (Figure 4.47 (c)). SAD patterns corresponding to the $[1\bar{2}1]$ orientation revealed it was type I (111) twin (Figure 4.47 (d)). Annealing up to 700°C caused the formation of TiCu particles inside the grains of B2 phase (shown in Figure 4.48). Kajiwara [132] also reported particle-like precipitates produced by higher temperature annealing.

Figure 4.48 Microstructure of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B at 700°C for 15min.

Compared with annealed ribbon A, the main difference of microstructure of ribbon B is that submicron-sized B2 austenite existed in all the annealed ribbons and the twin morphology in as-spun ribbon B was different. B11 precipitates formed as particles inside or at the boundary of B19 martensite, suggesting that the B2 and B19 in the as-spun ribbon favored the formation of particle-like precipitates.

4.3.2.3 Transformation results

All the annealed ribbons exhibited a one-stage $B2 \leftrightarrow B19$ transformation during heating and cooling. As shown in Figure 4.49, M_f and A_s of all the samples annealed below 650°C were lower than room temperature (25°C), which means that the annealed ribbons had a mixture of B19 martensite and B2 austenite at RT. The measurement error of these temperatures is $\pm 0.2^\circ\text{C}$. This was also confirmed by XRD and TEM observation. Different from the annealed ribbon A, all the transformation temperatures increased with the increase of annealing temperature from 300°C to 600°C . A_s and M_f were more sensitive to the annealing temperature than M_s and A_f . Like ribbon A, further annealing up to 750°C led to a slight decrease in the transformation temperatures.

Figure 4.49 Dependence of transformation temperatures on the annealing temperatures

Figure 4.50 shows the effect of annealing temperature on the transformation hysteresis. The transformation hysteresis remained unchanged with annealing. It varied around 8.5°C , which is almost the same as that of the annealed ribbon A. The measurement error of the hysteresis is $\pm 5\%$.

Figure 4.50 Dependence of transformation hysteresis on the annealing temperatures

4.3.2.4 Thermo-mechanical testing results

Thermal cycling tests on annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B were carried out under a tensile load of 45 MPa. Figure 4.51 and Figure 4.52 show the strain – temperature curves of the annealed ribbon under 45 MPa, indicating that all the annealed ribbons exhibited a similar strain-temperature curve and a well-defined shape memory effect. The annealed ribbon showed an identical temperature-strain curve when annealed below 500°C (Figure 4.51). However, annealing above 550°C significantly changed the temperature-strain curve and decreased the shape recovery strain, as shown in Figure 4.51 and Figure 4.52. The 700°C and 750°C-annealed samples showed a negligible shape recovery.

Figure 4.51 TMA curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B annealed at 300-550°C for 15min.

Figure 4.52 TMA curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B annealed at 550-750°C for 15min. under 45MPa

Figure 4.53 shows the plot of shape recovery strain against annealing temperature. Different from ribbon A, the shape recovery strain first remained constant and then decreased sharply with the increase of annealing temperature. For the ribbon annealed below 550°C, the recoverable strain was around 2.5%, which is equal to the value of as-spun ribbon. It was much higher than that of ribbon A at the same annealing temperature.

It decreased drastically with further annealing above 550°C. Annealed at 750°C, the ribbon showed a recoverable strain of 0.11%.

Figure 4.53 Shape recovery strain of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B vs. annealing temperature

M_s and A_s determined from the strain-temperature loop (shown in Figure 4.54) were almost the same as those determined by DSC (Figure 4.49) under stress-free condition. They showed the same variation trend against annealing temperatures.

Thermal cycling under a constant stress is a common way to induce the two-way shape memory effect (TWSME) [133-135]. The strain-temperature curve was re-measured under load-free condition after the as-spun sample was thermally cycled. As shown in the strain-temperature curve (Figure 4.55), a shape recovery of 3% was obtained, showing that TWSME can be induced in the as-spun ribbon B.

Figure 4.54 Transformation temperatures of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon B under 45MPa

Figure 4.55 Two-way shape memory effect of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ as-spun ribbon B

TESME is related to the anisotropy dislocation structure developed in the matrix, which creates an anisotropic stress in the matrix. This stress guides the formation of martensite into variants of preferential orientations related to the deformation in the cycling, thus

resulting in a macroscopic shape change during subsequent thermal transformation cycles [136, 137].

4.4 Initially partial amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon (ribbon C)

Practically, it is common to obtain ribbon which is not purely amorphous or crystalline, but with a mixture structure of amorphous and crystalline. Partially amorphous ribbon was also selected to study which part is more important in determining the properties. And it was found that this ribbon shared similar transformation behavior and shape recovery strain with the initially amorphous ribbon at the same annealing condition.

4.4.1 As-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C

The XRD pattern of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C is shown in Figure 4.56. A broad hump at 41° (2θ) and sharp peaks of B2 and B19 were both observed, suggesting that the as-spun ribbon C had a mixture of amorphous and crystalline structure.

Figure 4.56 XRD pattern of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C

By heating as-spun ribbon to 800°C at a heating rate of 10°C/min in DSC measurement, the crystallization temperature was determined to be 460.9°C and recrystallization temperature 687°C, as shown in Figure 4.57. It is 10°C higher than that of the fully amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon A in the previous section.

Figure 4.57 DSC curve of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C

Figure 4.58 TEM micrograph (a) and corresponding electron diffraction patterns (b) and (c) of as-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C $\mathbf{B} // [\bar{0}11]_{\text{B19}}$

Figure 4.59 Simulated diffraction pattern of $\mathbf{B} // [0\bar{1}1]_M // [01\bar{1}]_T$

TEM observation revealed that the as-spun was mainly amorphous, with crystalline grains embedded in the amorphous matrix, as shown in Figure 4.58(a). The volume fraction of crystalline phase was around 10%. Electron diffraction analysis in the region A (Figure 4.58 (b)) in Figure 4.58 (a) shows that the parallel bands in the grain were martensite related to each other by (111) type I twin, which agreed well with the simulated diffraction pattern of type I (111) twin (Figure 4.59). And a dispersive amorphous halo in Figure 4.58 (c) was observed from the region B in Figure 4.58 (a).

4.4.2 Annealed ribbon C

4.4.2.1 Structure analysis

Figure 4.60 to Figure 4.65 are the XRD patterns of the ribbon C annealed at different temperatures, showing the change of crystal structure with annealing temperatures similar to that of annealed ribbon A. The 500°C-annealed ribbon C consisted of B19 martensite. Annealing above 550°C caused the precipitation of B11-TiCu phase, while a peak at 41.9° (denoted with 'Δ') from retained austenite B2 appeared in the samples annealed above 650°C (Figure 4.63 to Figure 4.65). The lattice parameters of B19 martensite and B11-TiCu were similar to those of annealed ribbon A. The variation of peak intensity in annealed ribbon C shared the same tendency with annealing temperature as that of

annealed ribbon A. This phenomenon indicates that B2 and B19 phase in the amorphous matrix of as-spun ribbon C did not affect its crystallization behavior and may have no effect on the final structure of the annealed ribbon.

Figure 4.60 XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C annealed at 500 °C for 15 min.

Figure 4.61 XRD pattern of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C annealed at 550 °C for 15 min.

Figure 4.62 XRD pattern of ribbon C annealed at 600°C for 15min.

Figure 4.63 XRD pattern of ribbon C annealed at 650°C for 15min. showing the occurrence of B2

Figure 4.64 XRD pattern of ribbon C annealed at 700°C for 15min.

Figure 4.65 XRD pattern of ribbon C annealed at 750°C for 15min.

4.4.2.2 Microstructural analysis

Figure 4.66 shows the microstructure of the ribbon C annealed at 700°C, the grain size of B19 martensite was around 0.5μm, and diffraction analysis (Figure 4.66 (b)) showed the parallel bands were internally twinned by (111) type I twin. Particles of B11-TiCu precipitates were found inside as well as at the grain boundary of B19 martensite in some areas. Because of the small size of these particles, they were not analyzed by selected area diffraction method. These precipitate particles may pin the grain boundaries and suppress the grain growth, resulting in the submicron order grain size.

Figure 4.66 TEM micrograph of B19 martensite (a) and its corresponding diffraction pattern (b) in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C annealed at 700°C for 15min.

Figure 4.67 presents the microstructure and corresponding diffraction pattern of the ribbon annealed at 750°C. Results show that the grain size, martensite morphology, and B11-TiCu precipitates were similar to the 700°C-annealed sample and the parallel plates in Figure 4.67 (a) were also related to each other by (111) type I twin (Figure 4.67 (b)). In

addition, nano-sized B2 grains were also observed occasionally in some areas of the sample annealed at 750°C (Figure 4.67 (c)), which confirms the XRD results.

(a)

(b) $\mathbf{B} // [11\bar{2}]_{\mathbf{M}} // [\bar{1}12]_{\mathbf{T}}$

(c)

Figure 4.67 Bright field images of B19 martensite and B2 austenite (a, c) and diffraction pattern taken from a grain in (a) of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C annealed at 750°C for 15min.

Similar to annealed ribbon A, B19 martensite plates were related each other by type I (111) in the annealed ribbon C. Different with annealed ribbon A, particles of B11-TiCu precipitates instead of B11 plates were found inside or at the boundary of B19 martensite.

4.4.2.3 Transformation results

Similar to the annealed ribbon A, a one-stage $B2 \leftrightarrow B19$ transformation was observed in all the annealed ribbon C. The phase transformation temperatures of ribbon C at different annealing temperatures are shown in Figure 4.68. M_f and A_s were all above room temperature, which indicates that annealed ribbon C had a B19 structure at room temperature. With the increase of annealing temperature to 700°C, all the transformation temperatures M_s , M_f , A_s and A_f remained unchanged, while above 700°C, the transformation temperatures decreased slightly. Although the trend is similar to that of annealed ribbon A, the decrease in transformation temperatures of ribbon C was smaller than that of annealed ribbon A.

Figure 4.68 Dependence of transformation temperatures of annealed $Ti_{50}Ni_{25}Cu_{25}$ ribbon C on annealing temperatures

The transformation hysteresis was almost identical at all annealing temperatures (Figure 4.69). The average hysteresis was around 8°C, almost the same as that of the annealed ribbon A, indicating that annealing did not change the friction energy accounting for the transformation hysteresis. The measurement error of the hysteresis is $\pm 5\%$.

Figure 4.69 Dependence of transformation hysteresis of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C on annealing temperatures

4.4.2.4 Thermo-mechanical testing results

The shape memory effect of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C was measured by thermal cycling tests under a tensile load of 45 MPa. The strain-temperature curves of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at different temperatures are shown in Figure 4.70. The annealed ribbon C showed an excellent shape memory effect like the annealed ribbon A. With the increase of annealing temperature, the strain-temperature loop became smaller.

Figure 4.71 presents the measured shape recoverable strain of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C as a function of annealing temperatures under 45 MPa. The 500°C-annealed ribbon C showed the maximum recoverable strain of 1.3%, but it dropped sharply when

the annealing temperature was above 600°C. Annealed at 750°C, the ribbon showed a recoverable strain of 0.14%. In comparison, the shape recovery strain of annealed ribbon C was slightly smaller than that of the annealed ribbon A under the same condition.

Figure 4.70 TMA curves of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon C under 45Mpa

Figure 4.71 Shape recovery strain of annealed ribbon C under 45MPa

Figure 4.72 Plot of transformation temperatures of annealed ribbon C vs. annealing temperature under 45MPa

Transformation temperatures M_s , M_f , A_s and A_f determined from the strain-temperature loop under 45 MPa are plotted vs. annealing temperature in Figure 4.72. They showed the same trend against annealing temperature as those determined by DSC under stress-free conditions. However, under 45 MPa, the values of M_s and M_f were higher while A_s and A_f were lower than those under stress-free conditions. This was due to the stress inducing martensite and austenite transformation.

CHAPTER 5 DISCUSSION

In this chapter, the effects of Cu content on the transformation behavior of Ti-Ni-Cu alloys will be discussed in terms of thermodynamics in order to understand the mechanism of the change of transformation sequence and hysteresis due to Cu addition. Twin elements in B19 martensite of Ti-Ni-Cu alloys will be calculated and simulated to understand its effect on shape memory effect. Finally, the effects of initial structure and heat treatment will be evaluated in terms of structure evolution, transformation behavior and shape memory property to establish a structure-property relationship.

5.1 Effects of Cu on the transformation characteristics of Ti-Ni-Cu alloys

As shown in the results in Figure 4.5 and Figure 4.6, the substitution of Cu for Ni affects the transformation behavior of Ti-Ni alloy, changes the martensite start temperature M_s as well as the martensite structure, transformation hysteresis and the transformation sequence. When Cu content is less than 7.5 at.%, Ti-Ni-Cu alloys transform directly from B2 austenite to monoclinic B19' martensite upon cooling. When Cu content is more than 7.5 at.%, B2 transforms first to orthorhombic B19 and then to monoclinic B19' upon cooling. M_s of B2→B19' decreases with the addition of Cu. But M_s of B2→B19 increases slightly with the increase of Cu content. And when Cu content is above 20% at.%, B19→B19' transformation is suppressed, and only B2↔B19 is observed. A small transformation hysteresis of 8°C is obtained in the alloy with more than 20 at.% Cu.

5.1.1 Effects of Cu on the transformation behavior

The difference in Gibbs free energy between two phases gives the driving force for the transformation from one phase to another. The equilibrium transformation temperature T_{B2-B19} ($T_{B2-B19'}$ and $T_{B19-B19'}$) is defined at the point where the difference of chemical free energy between two phases equals zero for stress-free conditions.

In Ti50-Ni(50-x)-Cux system, B2 phase can be considered as an ordered b.c.c. phase: Ni and Cu fill the corners while Ti fills the body center (shown in Figure 5.1). Tang's model [7, 47, 138] was adopted to describe this lattice, i.e., $(\text{Cu, Ni})_{0.5}\text{Ti}_{0.5}$. The molar Gibbs energy of B2 can be expressed by [138]:

$$G_{B2} = G_{ord}(y_i^a, y_i^b) - G_{ord}(x_i) \quad \text{Equation 5.1}$$

where $G_{ord}(y_i^a, y_i^b)$ and $G_{ord}(x_i)$ are the molar Gibbs energy of the ordered b.c.c. phase with site fractions y_i^a, y_i^b and mole fraction x_i , respectively. y_i^a, y_i^b are site fractions of species i (Ti, Ni or Cu) in the corner and center, respectively; the mole fraction x_i and y_i^a, y_i^b are related according to $x_i = 0.5y_i^a + 0.5y_i^b$.

Figure 5.1 Structure of austenite B2 [139]

The condition for the transformation of $B2 \rightarrow B19'$ ($B19$) is: $G_{B19'} - G_{B2} < 0$ ($G_{B19} - G_{B2} < 0$).

$G_{B19'}$ and G_{B19} are molar Gibbs energy of $B19'$ and $B19$, respectively, which are given in

Appendix V. The driving force for the transformation is: $G_{B2}-G_{B19'}$ ($G_{B2}-G_{B19}$). In Ti50-Ni(50-x)-Cu_x system, the driving force of B2→B19' and B2→B19 can be written as follows (Appendix V):

$$G_{B2} - G_{B19'} = \Delta G_{B2-B19'} = (1-2x)({}^0G_{Ni,Ti}^{B2} - {}^0G_{Ni,Ti}^{B19'}) + 2x({}^0G_{Cu,Ti}^{B2} - {}^0G_{Cu,Ti}^{B19'}) - 0.5RT[(0.5-x)\ln(0.5-x) + x\ln x + 0.5\ln 0.5]$$

Equation 5.2

$$G_{B2} - G_{B19} = \Delta G_{B2-B19} = (1-2x)({}^0G_{Ni,Ti}^{B2} - {}^0G_{Ni,Ti}^{B19}) + 2x({}^0G_{Cu,Ti}^{B2} - {}^0G_{Cu,Ti}^{B19}) - 0.5RT[(0.5-x)\ln(0.5-x) + x\ln x + 0.5\ln 0.5]$$

Equation 5.3

Where ${}^0G_{i,j}^{B2}$ is related to the bond energy referred to the element in the b.c.c. state. ${}^0G_{i,j}^{B19'}$ and ${}^0G_{i,j}^{B19}$ are the Gibbs energy of the hypothetical compounds with the same structure of the B19' and B19 phase, respectively. R is the gas constant; and T is the temperature in Kelvin. The difference between the driving force of B2→B19' and B2→B19 transformation is:

$$\Delta G_{B2-B19} - \Delta G_{B2-B19'} = -154 + (10.86T - 92)x$$

Equation 5.4

In Ti50-Ni50 alloy, $x = 0$, $\Delta G_{B2-B19} < \Delta G_{B2-B19'}$ at any temperature. B2→B19' occurs.

At temperatures above 8.5K, where $10.86T-92>0$, the difference between ΔG_{B2-B19} and $\Delta G_{B2-B19'}$ increases with the increase of Cu content. The driving force for B2→B19 increases with the increase of Cu content. At room temperature (20°C), when Cu content is higher than 5 at.%, $\Delta G_{B2-B19} > \Delta G_{B2-B19'}$. Therefore, B2 transforms to B19 and then to

B19'. Tang [7] obtained this critical Cu content of 7.7 at.% by thermodynamic calculation, which is in good agreement with our results in Figure 4.5.

In martensitic transformation, T_0 (T_0') was used to evaluate the transformation temperature under the condition of B2 and B19 (B19') equilibrium. T_0 (T_0') is derived by setting $G_{B2} = G_{B19}$ and $G_{B2} = G_{B19'}$:

$$T_0' = \frac{(0.5-x)^0 G_{Ni}^{bcc} + 0.5^0 G_{Ti}^{bcc} + x^0 G_{Cu}^{bcc} + 6203x - 5819}{13.311 - 44.422x - 8.31[(0.5-x)\ln(0.5-x) + x\ln x]} \quad \text{Equation 5.5}$$

$$T_0 = \frac{(0.5-x)^0 G_{Ni}^{bcc} + 0.5^0 G_{Ti}^{bcc} + x^0 G_{Cu}^{bcc} + 6295x - 5565}{13.311 - 33.562x - 8.31[(0.5-x)\ln(0.5-x) + x\ln x]}$$

Where $^0 G_{Ti}^{b.c.c}$, $^0 G_{Ni}^{b.c.c}$ and $^0 G_{Cu}^{b.c.c}$ are Gibbs energies of pure elements Ti, Ni and Cu in b.c.c. structure, respectively. It can be seen that T_0 and T_0' are functions of Cu content x . Tang [7] has proved that T_0' decreased, while T_0 increased with the increase of Cu content x . Therefore, equation (5.5) can explain why the transformation temperatures of B2→B19' decreased while those of B2→B19 increased with the increase of Cu content.

By setting $G_{B19} = G_{B19'}$, the equilibrium transformation temperature of B19→B19' (T_0'') can be obtained.

$$T_0'' = \frac{154 + 92x}{10.86x} = \frac{14.2}{x} + 8.5 \quad \text{Equation 5.6}$$

The relation of T_0'' and x was plotted in Figure 5.2. It can be seen from that T_0'' decreases with the increase of Cu content x . It means that B19→B19' transformation will be suppressed to lower temperature, thus causing an one-stage transformation of B2↔B19 observed in the alloy with higher Cu content.

Figure 5.2 Calculated transformation temperature of B19→B19' in Ti-Ni-Cu alloys

5.1.2 Effects of Cu on transformation hysteresis

Martensitic transformation would start at T_0 if there were no energy barriers for nucleation. In reality, there are always some non-chemical forces to resist the transformation. The non-chemical forces come from the reversible elastic strain energy and the irreversible frictional energy. It is known that the thermoelastic transformation is due to local balance between chemical and non-chemical forces.

The chemical force is the difference between Gibbs free energy of the austenite and martensite. It acts as the driving force to promote the phase at lower energy. The non-chemical force arises from two major contributions. The first is the elastic free energy accommodating the shape and volume change during transformation. It is responsible for the temperature interval between the transformation start and finish temperatures. The second contribution is the frictional energy required to propagate the martensite-austenite phase interface during transformation. This energy dissipation is irreversible and

responsible for the thermal hysteresis observed in many thermoelastic transformations [111-115].

For the forward transformation on cooling, an undercooling is required to overcome the frictional energy barrier; whilst on heating superheating is needed. These energy barriers shift the transformation temperatures to either side of the equilibrium temperature, i.e. T_{p-m} or T_{m-p} , resulting in a transformation hysteresis. P and M represent austenite and martensite.

The balance conditions for the forward and reverse martensitic transformations may be expressed as [111, 112]:

$$\Delta G^{p-m} = \Delta H^{p-m} - T\Delta S^{p-m} + \Delta E_e^{p-m} + \Delta E_i^{p-m} = 0 \quad \text{Equation 5.7}$$

$$\Delta G^{m-p} = \Delta H^{m-p} - T\Delta S^{m-p} + \Delta E_e^{m-p} + \Delta E_i^{m-p} = 0 \quad \text{Equation 5.8}$$

Where ΔG is the total free energy change, ΔH and ΔS are the changes in chemical enthalpy and entropy, respectively, T is temperature in Kelvin, ΔE_e is the change in elastic energy and ΔE_i is the irreversible frictional energy associated with the transformation. The superscripts p-m and m-p refer to austenite to martensite (forward) and martensite to austenite (reverse) transformations, respectively.

The transformation hysteresis is written as:

$$T_{p-m} - T_{m-p} = 2\Delta E_i / \Delta S \quad \text{Equation 5.9}$$

The frictional energy can be written after Olson and Cohen [113, 114] as $\Delta E_i = \tau_0 \gamma$, where τ_0 is the shear stress required to initiate and/ or propagate the martensite interface

which accomplishes the transformation shear strain γ . Anything that raises τ_0 and γ will proportionately increase the transformation hysteresis. Shear stress can be written as $\tau_0 = G\gamma$ according to Hooke's Law, where G is the shear modulus. Therefore, the transformation hysteresis is:

$$T_{p-m} - T_{m-p} = 2G\gamma^2 / \Delta S \quad \text{Equation 5.10}$$

According to Sehitoglu et al. [19] the transformation shear direction of B2→B19 in Ti₅₀Ni₄₀Cu₁₀ alloy is <0.0648, 0.0499, 0.0500>. The magnitude of shear is 0.0959. While the transformation shear direction of B2→B19' in TiNi alloy is <0.0135, 0.0433, 0.0320> and the magnitude of shear is 0.1451. Therefore, the transformation shear in B19 martensite is smaller than that of B19' martensite. Ren et al. [13] found that the shear modulus of Ti₅₀Ni₃₀Cu₂₀ was lower than that of the Ti₅₀Ni₅₀ alloy. According to Xu et al. [140], the shear modulus of Ti₅₀Ni₄₀Cu₁₀ is 60% of that of Ti₅₀Ni₅₀ alloy. So the dissipated energy ΔE_i of B2→B19' transformation is larger than that of B2→B19 transformation. Since ΔS for these two transformation is very small and independent of the Cu content [7], the B2→B19' transformation hysteresis is larger than that of the B2→B19 transformation. The decrease of B2→B19 hysteresis with Cu content may be due to the decrease of modulus G .

Based on the above discussion, the reason why the transformation hysteresis of B2→B19 is smaller than that of B2→B19' is probably due to their smaller shear modulus and transformation shear strain.

James et al [141] gave the relationship between the hysteresis and middle eigenvalue of the transformation stretch tensor, using geometric nonlinear theory of martensite which is

based on crystal symmetry and geometric compatibilities between martensite and austenite. $\lambda_2 = \frac{b}{\sqrt{2}a_0}$, where b and a_0 are lattice parameters of B19 martensite and austenite, respectively. The closer to one λ_2 is, the more compatible the austenite and martensite are. The hysteresis decreases with increasing middle eigenvalue. The middle eigenvalue λ_2 of Ti-Ni-Cu alloys was calculated and tabulated in Table 5.1. It can be seen that λ_2 increased with Cu content, indicating that transformation hysteresis decreased with Cu content. This explains why hysteresis decreases with the increase of Cu content from a different point of view.

Table 5.1 Middle eigenvalue λ_2 of Ti-Ni-Cu alloys with different Cu contents

Cu (at.%)	10	15	20	25
λ_2	0.94015	0.96059	0.94704	0.97677

5.2 Twin elements in B19 martensite

Twinning and detwinning are important microstructural processes responsible for the shape memory effect in shape memory alloys. In order to predict the shape recovery process, the details in twinning should be considered. Therefore, a complete understanding of the twinning mechanism is a prerequisite. In Ti-Ni-Cu alloys with Cu content more than 7.5 at.%, B2 transforms to B19 martensite and then to B19'. B19 is a totally different crystal structure from B19'. Twinning modes in B19 martensite are different from those of B19' martensite. In the following parts, the construction of twin and twin elements in B19 martensite will be discussed.

5.2.1 Determination of twin elements

Twinned crystals are usually characterized by four crystallographic elements symbolized by K_1 , K_2 , η_1 and η_2 (shown in Figure 5.3). The crystallography of twinning is described by either the K_1 plane (twinning plane) and η_2 direction (the intersection of the K_2 plane and the plane of shear) or by the K_2 plane (another undistorted plane) and η_1 direction (twinning shear direction). Type I twinning has the rational K_1 plane and η_2 direction. Type II twinning has the rational K_2 plane and η_1 direction. The two twinned crystals in type I twinning are related by mirror symmetry with respect to the K_1 plane. While in type II twinning they are related by a rotation of 180° around the η_1 axis. All the indices of the four elements are rational in compound twinning [142, 143].

On the macroscopic scale, the deformation consists of homogeneous simple shear displacements parallel to the plane K_1 in the direction η_1 , of shear magnitude defined by $s = 2\tan\alpha$.

To any given twin mode

$$K_1 = (h_1 \ k_1 \ l_1), K_2 = (h_2 \ k_2 \ l_2), \eta_1 = [u_1 \ v_1 \ w_1] \text{ and } \eta_2 = [u_2 \ v_2 \ w_2] \quad \text{Equation 5.11}$$

There corresponds theoretically a reciprocal mode [143]

$$K_1' = (h_2 \ k_2 \ l_2), K_2' = (h_1 \ k_1 \ l_1), \eta_1' = [u_2 \ v_2 \ w_2] \text{ and } \eta_2' = [u_1 \ v_1 \ w_1] \quad \text{Equation 5.12}$$

involving the same s . Accordingly, apart from compound twins, the reciprocal of a reflection twin (type I) is a rotation twin (type II), and vice versa.

Figure 5.3 Schematic of twin relation

In Ti-Ni-Cu alloys, twinning modes of B19 martensite were reported by Watanabe et al [68] as type I (111) and compound twin (011). Lattice parameters of B19 phase: $a = 2.93$, $b = 4.29$ and $c = 4.53 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. Type I twin has twinning elements $K_1 = (111)$ and $\eta_2 = [211]$ [68, 144]. Its corresponding reciprocal mode which involves the same s is type II twin with elements: $K_2' = (111)$ and $\eta_1' = [211]$.

According to Jaswon and Dove's theory [145] (Appendix VI), the type I twin elements were calculated as follows:

$$\mathbf{K}_1 = (1, 1, 1), \mathbf{K}_2 = (0.5199, -0.0399, -1), \eta_1 = [1, -0.0823, -0.9177], \eta_2 = [2, 1, 1], s = 0.15$$

Where the irrational shear direction η_1 is about 4° away from $[10\bar{1}]$.

For compound twin (011)[011], its twinning elements are $K_1 = (011)$ and $\eta_2 = [011]$.

Using the same method, the following twinning elements are obtained:

$$\mathbf{K}_1 = (0, 1, 1), \mathbf{K}_2 = (0, 1, -1), \boldsymbol{\eta}_1 = [0, 1, -1], \boldsymbol{\eta}_2 = [0, 1, 1], s = 0.11$$

These results agree well with that reported by Watanabe et al [68].

In B19' martensite, the most frequently observed twinning are $\langle 011 \rangle$ type II, $\{111\}$ type I and $\{001\}$ compound twin [57-60]. According to Miyazaki [55, 56], the predominant twinning mode is $\langle 011 \rangle$ type II twin. Its twinning shear s is 0.28. Compared with the twinning shear of B19' martensite, B19 martensite has a smaller twinning shear. Because the mechanism of shape memory effect is detwinning, smaller twinning shear indicates smaller recovery strain due to detwinning, thus resulting in the inferior SME of B19 martensite to B19' martensite.

5.2.2 Type I (111) twin observed in B19 martensite

According to TEM observations in Chapter 4, the most frequently observed twinning in B19 martensite is type I twin (111)[211]. The orientation relationship of two martensite variants, A and B, having (111) type I relationship, is determined by the transformation equations [143]:

$$\begin{aligned} u' &= 2U(Hu + Kv + Lw) - u(UH + VK + WL) \\ v' &= 2V(Hu + Kv + Lw) - v(UH + VK + WL) \\ w' &= 2W(Hu + Kv + Lw) - w(UH + VK + WL) \end{aligned} \quad \text{Equation 5.13}$$

Where $[uvw]$ are the indices of the direction before twinning and $[u'v'w']$ are the indices after twinning. If the twin is type I, (HKL) are the indices of $\mathbf{K}_1$ and $[UVW]$ the indices of $\boldsymbol{\eta}_2$. For type II twin, (HKL) are the indices of $\mathbf{K}_2$ and $[UVW]$ the indices of $\boldsymbol{\eta}_1$.

Thus we have:

$$\begin{aligned}
 u' &= 4v + 4w \\
 v' &= 2u - 2v + 2w \\
 w' &= 2u + 2v - 2w
 \end{aligned}
 \quad \text{Equation 5.14}$$

It can be written as a transformation matrix as follows:

$$\begin{pmatrix} u' \\ v' \\ w' \end{pmatrix} = \begin{pmatrix} 0 & 2 & 2 \\ 1 & -1 & 1 \\ 1 & 1 & -1 \end{pmatrix} \begin{pmatrix} u \\ v \\ w \end{pmatrix}
 \quad \text{Equation 5.15}$$

The directions in the two variants that are parallel to each other and lying in (111) plane are listed in Table 5.2, where the subscripts A and B refer to the neighboring variants A and B, respectively. $[10\bar{1}]$ is a direction 4° away from the shear direction.

Table 5.2 Direction pairs of (111) type I twin that lie in the (111) plane

Zone axes in (111) plane	Angular difference ($^\circ$)	Angle away from $[10\bar{1}]$ ($^\circ$)
$[\bar{3}21]_A // [\bar{3}2\bar{1}]_B$	0	49
$[\bar{4}31]_A // [\bar{4}3\bar{1}]_B$	0	56
$[\bar{1}10]_A // [\bar{1}1\bar{0}]_B$	0	72
$[2\bar{3}1]_A // [\bar{2}3\bar{1}]_B$	0	88
$[1\bar{2}1]_A // [\bar{1}2\bar{1}]_B$	0	77
$[0\bar{1}1]_A // [01\bar{1}]_B$	0	52
$[1\bar{1}2]_A // [\bar{1}1\bar{2}]_B$	0	28
$[21\bar{3}]_A // [\bar{2}1\bar{3}]_B$	0	19
$[10\bar{1}]_A // [\bar{1}01]_B$	0	0
$[\bar{4}13]_A // [\bar{4}1\bar{3}]_B$	0	16
$[\bar{3}12]_A // [\bar{3}1\bar{2}]_B$	0	22
$[\bar{2}11]_A // [\bar{2}1\bar{1}]_B$	0	35

In order to clearly observe the twin boundary, it is preferable to observe it along a zone axis that lies in (111) plane and has the lowest index. Among the zones listed in Table 5.2, $[10\bar{1}]_A // [\bar{1}01]_B$ direction pair is the best choice for obtaining clear atomic image of twin boundary.

Figure 5.4 shows the simulated electron diffraction patterns along some direction pairs listed in Table 5.2. The corresponding experimentally observed patterns are shown in Figure 5.5. It is obvious that the patterns observed in Figure 5.5 agree well with the simulated patterns in Figure 5.4. They confirm the twin observed is (111) type I twin, which is the most frequently observed twin in the present study.

The atomic arrangement of the twinned plates was studied by high resolution TEM. Figure 5.6 (a) is a HRTEM image of a pair of parallel bands and (b) is the corresponding diffraction pattern taken from the parallel bands. The observation direction is that electron beam is parallel to $[1\bar{2}1]_M // [\bar{1}2\bar{1}]_T$. It is obvious that the domain M and T in Figure 5.6 (a) are in a (111) twinning relationship. $(10\bar{1})_M$ and $(10\bar{1})_T$ are symmetric with respect to (111) plane. Because the beam direction is in the (111) plane, atomic arrangement in (111) plane was not seen. (111) plane is a line in TEM graph, as shown in Figure 5.6 (a). Thus (111) planes are not resolved. Their directions are along the parallel lines in Figure 5.6 (a). The twin boundary (parallel lines) is sharp and straight, showing a clear and smooth twin boundary. Atomic planes were connected coherently across the boundary. No high strain contrast was observed.

Figure 5.4 Simulated electron diffraction patterns of $\{111\}$ type I twin in B19 martensite

(a) $\mathbf{B} // [1\bar{2}1]_A // [\bar{1}2\bar{1}]_B$

(b) $\mathbf{B} // [\bar{3}4\bar{1}]_A // [\bar{3}4\bar{1}]_B$

(c) $\mathbf{B} // [12\bar{3}]_A // [\bar{1}2\bar{3}]_B$

(d) $\mathbf{B} // [13\bar{4}]_A // [\bar{1}3\bar{4}]_B$

Figure 5.5 Observed electron diffraction patterns showing twin relationship in B19 martensite

Figure 5.6 High resolution TEM micrograph showing type I (111) twin in B19 martensite

5.3 Effects of initial structure and post heat treat in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

The most important shape memory related properties that have been the focus of this work are the transformation temperatures and shape recovery strain. It has been shown that it is possible to change these properties of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ (at.%) ribbon by processing and post heat treatment. Due to the high cooling rates during melt-spinning process, the melt-spun ribbons can be amorphous, partially amorphous and crystalline. Because of the variation in structure and microstructure, it is possible to identify which characteristic is important to shape memory behavior.

Three $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons with different as-spun structures were investigated in this study to find the effect of initial structure on the shape memory properties. They are initially amorphous, crystalline, and mixture of amorphous and crystalline structures.

5.3.1 Structure evolution of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

Crystal structures of the three ribbons were studied by XRD. They were dependent on the annealing temperatures. The initially amorphous and partially amorphous ribbon showed a B19 structure annealed below 550°C, a mixture of B19 + B11 annealed from 550 to 650°C and B19 + B11 + B2 with further annealing. Crystal structure of initially crystalline ribbon is a mixture of B2 and B19 phase. It did not change with increasing annealing temperature up to 550°C except that the volume fraction of B19 martensite increased. Above 550°C, B11 precipitates formed as was observed in the ribbon with initial amorphous structure.

The initially amorphous and partially amorphous ribbon shared similar structure dependence on annealing temperature, which indicates that B2 and B19 phase in the amorphous matrix of as-spun ribbon did not affect its crystallization behavior. They may have no effect on the final structure of the annealed ribbon.

The crystal structure and lattice parameters of the phases existing in the annealed ribbons are tabulated in Table 5.3.

Table 5.3 Crystal structure and lattice parameters of the phases in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

Phase	Austenite	Martensite	Precipitate
Crystal structure	Cubic B2	Orthorhombic B19	Tetragonal B11
Lattice parameters	$a = 0.305\text{nm}$	$a = 0.287\text{nm}$ $b = 0.423\text{nm}$ $c = 0.448\text{nm}$	$a = 0.311\text{nm}$ $c = 0.591\text{nm}$

Strong textures developed in the annealed and crystallized ribbons with initially amorphous structure, and the texture changed with the annealing temperature. In the as-spun crystalline ribbon, a [001] fiber texture developed in B19 martensite, which is different from the texture developed in the annealed ribbons with initially amorphous structure. The textures observed suggest that the fully crystalline as-spun ribbon had a different orientation distribution of crystal grains from the ribbon with initial amorphous structure. The different structure of initially amorphous and crystalline ribbon will result in the different shape memory properties as observed in Chapter 4. Therefore, the structure evolution will be discussed in terms of the formation of B11, and B2 austenite, and texture development in B19 martensite.

Formation of B11 TiCu precipitates

It is identical for all the ribbons that precipitates formed with annealing above 550°C. Using XRD techniques, the precipitate is confirmed to have crystal lattice similar to B11 TiCu having a tetragonal structure, which agrees well with Rosner's [31] results.

Ti₅₀Ni₂₅Cu₂₅ crystallizes through a single stage polymorphic reaction forming a B2 austenite phase. According to in-situ TEM observation by Satto [17] and Louzguine [25], precipitates formed after the crystallization of B2. In this study, the starting composition of B2 phase is Ti₅₀Ni₂₅Cu₂₅, which can be written as Ti₂NiCu. The formation of B11 phase can be regarded as the decomposition of B2, because Ti₂NiCu is metastable. B11 TiCu appears as a ternary compound with chemical composition of about 51 at.% Ti, 42 at.% Cu and 7 at.% Ni [31]. It can be written as Ti₅₀Ni₁₀Cu₄₀. As a result of Cu depletion in the matrix, the austenite has a composition close to Ti₅₀Ni₄₀Cu₁₀. The precipitation process can be written as follows:

As a result of this decomposition, the composition of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ will change to $\text{Ti}_{50}\text{Ni}_{40}\text{Cu}_{10}$.

As pointed out by Louzguine [25], the process of the decomposition is relatively slow even at around 700°C . At lower annealing temperature, i.e. below 500°C , the diffusion of Cu is not sufficiently rapid to form B11 TiCu phase. Thus, the volume fraction of TiCu will increase with the annealing temperature because of the increase of Cu diffusion. As observed from XRD patterns, at higher annealing temperature, the amount of B11-TiCu precipitates increased.

The volume fraction of a phase is proportional to the integrated intensity of its XRD pattern. 110 peak of TiCu was selected. Its integrated intensity in the three ribbons at different annealing temperatures is listed in Table 5.4. The increase of the integrated intensity of 110_{B11} with annealing temperature indicates the increase of the volume fraction of B11 TiCu, which may cause the change of transformation temperatures and shape recovery strain, and also the evolution of texture component in initially amorphous ribbon.

Satto et al. [17] reported a different precipitate of Cu_3Ti_2 by annealing amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon up to 700°C through in-situ TEM study, which was not observed in our study. Cu_3Ti_2 has a tetragonal structure with $a = b = 0.313\text{nm}$ and $c = 1.395\text{nm}$. In fact, the chemical composition of this precipitate in their report is similar to that of TiCu phase reported by Rosner [31]. But Satto et al. [17] did not confirm the Cu_3Ti_2 phase using XRD. The observed different precipitates by these two authors may belong to the same phase TiCu.

Table 5.4 The integral of 110_{B11} of $Ti_{50}Ni_{25}Cu_{25}$ ribbons at different annealing temperatures

	Annealing temperature (°C)				
	550	600	650	700	750
Initially amorphous ribbon	368	474	637	987	1238
Initially crystalline ribbon	/	251	1049	1894	2715
Initially partial amorphous ribbon	51	59	64	72	76

Evolution of texture

A strong $[211]$ fiber texture existed in the 450 and 500°C-annealed initially amorphous ribbon and $(111)[\bar{2}11]$ sheet texture in the samples annealed above 550°C. However, both these two textures suggest that (111) plane of B19 phase was always parallel to the ribbon surface in all the annealed ribbons. Therefore, increasing annealing temperature did not change the orientation of (111) plane of B19 phase, but changed the texture component from fiber to sheet texture.

$[211]$ fiber texture has its fiber axis perpendicular to the ribbon surface. Its schematic illustration is shown in Figure 5.7. In fiber texture the grains are often column-like. Column grains were also observed by Goryczka [105] in Cu-Al-Ni melt spun ribbons with fiber texture. Crystalline orientation distribution is uniform and rotational on the ribbon surface so that the transformation anisotropy is weak.

$(111)[\bar{2}11]$ sheet texture is schematically drawn in Figure 5.8. In fact, $[211]$ is not exactly perpendicular to (111) , but 4° away from the normal of (111) which is irrational, and the angle between $[\bar{2}11]$ and $[01\bar{1}]$ is 92° . Therefore, this result is the closest interpretation of the sheet texture components. In this sheet texture, grains are arranged

with their (111) parallel to the ribbon surface, $[\bar{2}11]$ parallel to RD, and $[01\bar{1}]$ parallel to TD. On the ribbon surface, crystalline orientation distribution is anisotropic, which will result in orientation dependence of shape recovery strain.

Figure 5.7 Schematic of $[211]$ fiber texture

Figure 5.8 Schematic of $(111)[\bar{2}11]$ sheet texture

Kim et al. [146] reported the texture development in the annealed cold-rolled Ti-Nb-Ta alloy due to recrystallization. In our study, recrystallization temperature is above 700°C. The change of texture with annealing temperature type may be due to the grain growth and restrained orientation of martensite by the formation of B11 TiCu precipitates. From TEM observation, it is known that the grain size of B19 martensite did not change significantly, which suggests that the effect of grain size is negligible. The stress field near precipitates favors the orientation of martensite along the precipitates $[11]$. And B11 TiCu precipitates formed above 550°C. Thus, the change of texture in this study is due to

the formation of B11 TiCu precipitates. Because these precipitates formed in austenite, during cooling the stress field around them may direct the growth and propagation of martensite plates, resulting in the formation of sheet texture.

(111)_{B19} plane was the ribbon surface both in fiber and sheet texture. This is due to fact that the grain tends to minimize its surface energy during crystallization and grain growth [147]. This process was achieved by selecting preferential crystallographic plane on the surface. (110)_{B2} plane is the close-packed plane which has the lowest surface energy. According to the transformation correspondence between B2 and B19 lattice, (111)_{B19} corresponds to (011)_{B2}. Therefore, it is easy to form (110)_{B2} austenite texture, which will transform to (111)_{B19} texture during the followed cooling.

In addition, B11 precipitates were found reoriented around its [110] direction in the 700°C-annealed ribbon. The oriented precipitates were also observed by TEM in TiNi alloys [130, 132]. These precipitates act as obstacles to the orientation of martensite, which deteriorates shape recovery strain and hinders martensite transformation.

Formation of B2 austenite

B2 austenite was found in the initially amorphous and partially amorphous ribbon annealed above 650°C. One reason is the high amount of B11 precipitates. Austenite was stabilized and retained at RT by the stress field around B11 precipitates [12]. Another reason is that the composition of B2 changed to Ti₅₀Ni₄₀Cu₁₀ due to the formation of B11 TiCu, whose M_s is lower than that of Ti₅₀Ni₂₅Cu₂₅ alloy.

B2 in the initially crystalline ribbon annealed at lower temperature is due to the stabilization of austenite by the stress from melt-spinning process. At higher annealing

temperature, the reason of the existence of B2 is similar to that in initially amorphous ribbon.

B2 retained austenite is not stable because it will transform to martensite when the environment temperature is low enough, which is not good for application of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy.

5.3.2 Transformation behavior of annealed $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

The martensitic transformation behaviors of the three annealed ribbons were studied by DSC measurement. All the annealed ribbons showed a one stage B2→B19 transformation. Transformation temperatures of initially amorphous ribbon and partially amorphous ribbon did not change with annealing below 650°C, but decreased with further annealing to 750°C. In initially crystalline ribbon, they increased with the increase of annealing temperature from 300°C to 600°C followed by a decrease with further annealing to 750°C.

Comparison of M_s

The comparison of M_s of the annealed ribbons is plotted in Figure 5.9. The difference is that annealing at lower temperature significantly increased M_s of initially crystalline ribbon while it did not change those of the two ribbons with initial amorphous structure. And M_s of the former ribbon is much lower (10-20°C) than that of the latter. The similarity is that M_s of the three annealed ribbons decreased with further annealing above 600°C. The variation in M_s of the annealed initially crystalline ribbon is more significant than that of the other two ribbons. M_s of initially partially amorphous ribbon is 5°C lower than that of initially amorphous ribbon. Since the difference is within the error range, we may say that there is no difference between M_s of these two annealed ribbons. Similar

dependence of M_s on the annealing temperature was also reported in Ti-Ni-Hf [148], Ti-Ni-Zr [149] and Ti-Ni [150-153] SMAs.

Figure 5.9 Comparison of dependence of M_s on the annealing temperatures

Thermodynamic description of M_s

According to thermodynamic description of the thermoelastic transformation behavior, martensitic start temperature M_s was written as:

$$M_s = T_0 + \frac{\Delta G_{el} + \tau_0 \gamma_T}{\Delta S} \quad \text{Equation 5.16}$$

Where ΔG_{el} is the elastic strain energy, and τ_0 is the shear stress required to initiate or propagate the martensite interface which accomplishes the transformation shear strain γ_T . Hornbogen [119] pointed out that T_0 depends on chemical composition, degree of order, and hydrostatic stress. The effect of hydrostatic stress on T_0 can be immediately excluded since in all of our experiments no external stresses were applied. The change in the degree of order of B2 phase is also negligible. The change of chemical

composition/decomposition due to precipitation of a chemically different phase will be discussed later.

$\frac{\Delta G_{el} + \tau_0 \gamma_T}{\Delta S}$, describing the undercooling, $\Delta T = T_0 - M_s$, depends on nucleation and propagation of martensite inside the matrix. External shear stress and the resistance to shear, i. e. hardening mechanisms caused by point defects, dislocations, or particles in turn affected this [154]. Since ΔS is always negative, it is evident that strengthening raises τ_0 , and leads to a decrease of M_s . The contribution of ΔG_{el} is due to the nucleation and growth of the martensitic phase within the volume of its parent phase. The sign of ΔG_{el} was evaluated positive by Rosner et al. [31] and Liu [118] et al., which results in lowering M_s . Ortin et al. [116] reported that the elastic energy in single crystal is much smaller than polycrystals, suggesting that grain boundary is an obstacle to martensite transformation.

It is concluded that the factors that affect the transformation temperatures in this study are B11 precipitates, stress in retained B2 austenite and grain size.

Effects of B11 precipitates

Precipitates, plate-like or particle-like, have two major effects on M_s , composition and stress field [148]. First, the composition of the matrix changed to $Ti_{50}Ni_{40}Cu_{10}$ after the formation of B11 TiCu phase, which has a lower M_s than $Ti_{50}Ni_{25}Cu_{25}$ alloy. Thus, the chemical contributions represented by T_0 have a considerable influence. Secondly, these widely dispersed precipitates which are often semi-coherent with the parent phase will strengthen the matrix. The strengthening leads to the increase of τ_0 and will lower M_s .

From the XRD and TEM observation in this study, it is known that the volume fraction of precipitate increased with the annealing temperature. At higher annealing temperature, B11-TiCu precipitates play an important role in shifting the transformation temperatures to lower values.

Effects of stress in B2 retained austenite

The initially crystalline ribbon consists of B2 and B19. B2 austenite is stabilized by the stress from melt-spinning process. The stress field acts as an obstacle to martensite transformation and raises τ_0 , which will decrease M_s . This is the reason why its M_s is much lower than that of the initially amorphous and partially amorphous ribbon.

This stress in B2 can be relieved by annealing through recovery or recrystallization [11, 155]. With the increase of annealing temperature, the influence of this stress field will diminish. And thus M_s of initially crystalline ribbon increases with the annealing temperature, resulting in the increase of B19 percentage in the annealed ribbons.

Effects of grain size

The grain boundary acts as obstacles to prevent propagation of the martensite. Therefore, the smaller grain size contributes to the increase of the elastic energy and τ_0 . Thus it will decrease M_s . Several researchers also reported a decrease in the transformation temperatures when the grain size reduced [156-159]. For instance, the transformation temperatures for several Cu-based melt-spun SMAs were experimentally fitted to the following expression [157, 159]: $\Delta M_s \propto d^{-\frac{1}{2}}$. Where ΔM_s is the difference between the M_s of bulk alloy and ribbon with the same composition, and d is grain size.

In the initially amorphous and partially amorphous ribbon, grain size of B19 martensite did not change significantly with annealing temperature. Since martensitic transformation is diffusionless, the grain size of martensite can represent that of austenite. Therefore, grain size is not a dominant factor that changes M_s of these two ribbons.

In the initially crystalline ribbon, the grain size of B2 is around 0.2 μm as observed in TEM, which is much smaller than that observed in annealed initially fully and partially amorphous ribbons. Fine size of B2 grains is a considerable contribution to a lower M_s of this ribbon.

Therefore, B11 TiCu precipitates at higher temperature annealing resulted in lowering M_s of the three ribbons. In initially crystalline ribbon, stress-relief acts to raise M_s of this ribbon annealed at lower temperature. Smaller grain size and stress in B2 retained austenite result in lower M_s of this ribbon than those of the other two ribbons.

5.3.3 Shape recovery strain of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons

The dependence of shape recovery strain on the annealing temperature and initial structure of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons was studied using TMA under different tensile loads. Figure 5.10 showed the shape recovery strain of the three $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons under 45 MPa. The shape recovery strain of three annealed ribbons showed similar tendency with the increase of annealing temperature. Higher temperature annealing deteriorated the recovery strain. The recovery strain decreased sharply when annealed above 550°C. The three annealed ribbons had identical recovery strain of around 0.5% after annealing above 600°C, at which precipitates B11 formed. Initially amorphous ribbon and partially amorphous ribbon shared almost the same shape recovery strain after annealing. This indicates that small amount of B2+B19 crystal in the amorphous matrix of the latter has

little effect on the shape memory property. Initially crystalline ribbon showed a higher recovery strain than the initially amorphous and partially amorphous ribbon at annealing temperatures below 500°C.

Figure 5.10 Comparison of shape recovery strain of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons under 45MPa

According to Miyazaki, the maximum recovery strain depends on the chemical composition and heat treatment in Ni-rich TiNi thin films [160]. In this study, the change of shape recovery strain with annealing temperature and initial structure can be attributed to several factors such as B11 TiCu precipitates, texture in B19 martensite, B2 retained austenite and grain size.

Recovery strain

Recovery strain was calculated as a difference between the elongation in martensitic and austenite phase. Under a constant stress, the volume fraction of martensite can be split into self-accommodating martensite (pure thermal effect) and oriented martensite (thermo-mechanical effect). The self-accommodating martensite does not produce any

macroscopic strain because the local transformation strains of the martensite variants cancel each other. However, the oriented martensite whose orientation is the most consistent with the stress tensor will induce macroscopic transition strain [19, 161]. In the case of thermo-mechanical loading, two types of martensite may be created and the self-accommodating martensite can be reoriented to the most favorable martensite variants. Since recoverable deformation in shape memory alloys is generally accomplished by means of reorientation of martensite variants, the recoverable elongation decreases with decreasing volume fraction of favorably oriented variants [83]. The recovery strain (ε_r) is proportional to the volume fraction of oriented martensite. It can be written as [83]:

$$\varepsilon_r = kZ_{ori} \quad \text{Equation 5.17}$$

Where k is a constant and Z_{ori} is the total volume fraction of oriented martensite. Z_{ori} depends on the amount of reoriented thermally induced martensite (Z_T) and stress-induced martensite (Z_σ) according to

$$Z_{ori} = Z_T + Z_\sigma \quad \text{Equation 5.18}$$

Therefore, the recovery strain is the sum of the pseudoelastic strain and the shape memory effect strain. The increase in recoverable strain with increasing stress is attributed to an increase in volume ratio of the favorably reoriented martensites [159, 161, 162].

The theoretical recovery strain is based on several models, i.e. Phenomenological Theory of Martensite Transformation, the Lattice Deformation Theory and the Energy Minimization Theory [19]. The last two are often used. Lattice deformation model assumes that B2 austenite transforms into a single crystal of martensite and calculates recovery strain by directly considering the lattice correspondence between martensite and

austenite. It does not account for the existence of internal twin structure. In energy minimization model, the recovery strain consists of two parts: the transformation strain (ε_{tr}) corresponding to the formation of a correspondent variant pair (CVP), and the detwinning strain (ε_{de}) referring to the growth of one of the variants in a CVP with respect to the other. According to Sehitoglu et al. [19], ε_{tr} is related to the transformation shear and habit plane normal, and ε_{de} is related to the twinning shear and twin plane normal. ε_{tr} is the major contribution to recovery strain and is much larger than ε_{de} . Using these two models, Sehitoglu et al. [19] calculated the recovery strain of B2→B19' and obtained the same results.

In this work, the lattice deformation model was used to calculate the recovery strain that was related to the transformation matrix. Since any vector x in austenite phase is transformed to x' due to martensite transformation using the following equation

$$x' = Tx \quad \text{Equation 5.19}$$

Where T is the lattice distortion matrix with respect to the coordinates of austenite phase.

The recovery strain ε_r^i in each grain can be calculated as follows [159]:

$$\varepsilon_r^i = \frac{|x'| - |x|}{|x|} \quad \text{Equation 5.20}$$

This equation indicates that recovery strain is orientation dependent. Strong orientation-dependent behavior of recovery strain for B2↔B19 in Ti-Ni-Cu alloys was also predicted by Sehitoglu et al. [19] and Nam et al. [8]. The maximum recovery strain of 5.3% was obtained along $[001]_{B19}$. It decreased with changing direction from $[001]$ to $[100]$ or $[010]$. It is noted that the maximum recovery strain of B2↔B19 is much smaller than that for the B2↔B19' transformation in Ti-Ni alloys which is 10% [159].

The recovery strain for a polycrystal with randomly distributed grains can be estimated by averaging the representative 36 orientations which are located in the [001]-[011]-[111] standard stereographic triangle. If there is a texture, it is necessary to consider the orientation density I^i which can be determined from inverse pole figure. The recovery strain is estimated as follows [159]:

$$\bar{\varepsilon}_r = \left(\sum_{i=1}^{36} \varepsilon_r^i I^i \right) / 36 \quad \text{Equation 5.21}$$

Effect of texture

Texture affects the shape memory and superelastic behavior of shape memory alloys. In particular, the transformation strain is dependent on the texture [103, 105]. Therefore, it is very important to carry out texture studies in order to obtain the maximum transformation strain in a desired direction in shape memory alloys. Because of the relation between detwinning and shape recovery [147], in order to have good shape memory effect a ribbon with a texture favorable to martensite detwinning is desired.

As it has been found in the texture analysis, the 450°C-annealed initially amorphous ribbon has a pure sharp [211] fiber texture, which indicates strong orientation of B19 martensite. In this texture, most of the B19 martensite variants oriented their (111) twin plane nearly parallel to the ribbon surface and their shear direction randomly within (111) plane. In this case, the detwinning of (111) type I twin is isotropic along different directions. Therefore, the detwinning strain is isotropic, which means that the recovery strain is the same for all directions on the ribbon surface. This is not favorable for optimized properties in a particular direction, but good for designing microactuators. The calculated recovery strain is the average for all directions on the ribbon surface, which is parallel to (111)_{B19}.

With the increase of annealing temperature, a sheet texture component $(111)[\bar{2}11]$ developed in the B19 martensite, which means the orientation distribution is not uniform on the ribbon surface. In this sheet texture, most of the martensite variants oriented their (111) plane nearly parallel to the ribbon surface as in the $[211]$ fiber texture, and their shear direction is 35° from RD. This sheet texture is not favorable to the detwinning of (111) type I twin when tensioned along the spinning direction.

For sheet texture, it is known that the recovery strain along RD is different from that along TD. In TMA test, loading was along spinning direction (RD), which is $[\bar{2}11]$ in the ribbon annealed above 550°C . TD is $[0\bar{1}1]$. According to the transformation matrix of Nam et al. [8], the calculated recovery strain along $[\bar{2}11]$ and $[0\bar{1}1]$ of B19 martensite is 2.3% and 2.2%, respectively. In addition, (111) is also the twinning plane of type I (111) twin. Its twinning shear direction is very close to $[10\bar{1}]$, along which the calculated recovery strain is 0.3%. Therefore, transformation strain on the ribbon surface of this sheet texture is anisotropic, orientation density should be considered in the calculated recovery strain, which was not obtained in this study. This sheet texture is not favorable for achieving high recovery strain, since the direction $[001]$ for inducing maximum recovery strain is not in the ribbon surface which indicates that the maximum strain can not be obtained on the ribbon surface,.

With the increase of annealing temperature, the intensity of texture decreased. It is known that the anisotropy of mechanical properties increases with the strength of texture [61]. This means that the volume fraction of oriented martensite decreased, although crystals in sheet texture are more orderly arranged than in fiber texture. Therefore, pure strong $[211]$

texture is beneficial to shape memory effect in this study. The isotropic transformation strain in the ribbon surface is convenient for designing micro-actuators.

Effect of precipitates

Plate-like precipitates also played an important role in the orientation of martensite. According to TEM observation, they were lying on the $\{011\}$ planes of B19 martensite. From the texture results in the initially amorphous ribbon, it is known that (111) plane of B19 is parallel to the ribbon surface, $[0\bar{1}1]_{B19}$ is TD and $[\bar{2}11]_{B19}$ is RD for the ribbon annealed above 550°C. Therefore, the distribution of B11 precipitates can be schematically shown in Figure 5.11. $[0\bar{1}1]$ is the intersection of (111) and (011). $[\bar{2}11]$ is the intersection of (111) and $(0\bar{1}1)$. Twin shear direction of type I (111) twin is $[10\bar{1}]$, which is 145° from RD. B11 precipitates were arranged along RD or TD direction of the ribbon. These precipitates have two effects. First, the stress field around the precipitates will force B19 martensite to orientate around them. Those along RD will favor the reorientation of martensite to the stress direction during TMA testing, while those along TD will restrain the reorientation of martensite to the stress direction. Second, the precipitates, plate-like or particle-like, will strengthen martensite and thus increase the stress for reorientating martensite. The overall effect of precipitates is an obstacle to the reorientation of martensite toward the stress direction.

Figure 5.11 Relationship between B11 precipitates and B19 martensite corresponding to the dimension of ribbon

Effect of B2 retained austenite

Initially crystalline ribbon annealed below 550°C showed the highest shape recovery of around 2.5%, much larger than those of the initially amorphous ribbons. The reason is due to the retained B2 austenite. During thermo-mechanical test, these austenites undergo stress-induced martensite transformation which preferentially arrays along the applied stress. It was reported that stress for inducing martensite increased with the increase of testing temperature [38, 163]. Compared with initially amorphous and partially amorphous ribbons, the retained austenite in initially crystalline ribbon is easily stress-induced because its M_s and A_s were around 25°C lower (and Figure 5.12), which indicates that stress for inducing martensite transformation in this ribbon is lower. Under a constant stress, the contribution of stress-induced martensite (Z_σ in Equation 5.18) to the recovery strain in this ribbon is larger than that in initially amorphous and partially amorphous ribbons, resulting in the highest recovery strain of 2.5% obtained in this ribbon annealed below 550°C.

Figure 5.12 Comparison of A_s of the three annealed ribbons

In this study, texture, precipitates and B2 austenite are the main factors affecting the shape recovery strain of annealed ribbons. At lower annealing temperature, strong texture in martensite favors the recovery strain. While at higher annealing temperature B11 TiCu precipitate is a dominant factor to reduce the recovery strain. B2 retained austenite in initially crystalline ribbon contributes to the higher recovery strain. Grain size is not a dominant factor because the grain size of martensite did not change significantly with annealing temperature.

5.3.4 Structure-property relation of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

The structure-property relation of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon is shown in Figure 5.13 and Figure 5.14. Among the three ribbons, initially crystalline ribbon in as-spun state or annealed below 500°C had the highest recovery strain around 2.5% under 45 MPa. However, this structure was not stable for application due to the coexistence of B2 and B19 martensite.

Figure 5.13 Structure-property relationship of initially amorphous ribbon (hollow and solid rectangle) and initially partially amorphous (hollow and solid circle)

Figure 5.14 Structure-property relationship of initially crystalline ribbon

Higher temperature annealing not only decreased M_s , but deteriorated the shape recovery strain due to the formation of B11 TiCu precipitates. So it is better to keep the annealing

temperature below 550°C for a good combination of shape memory properties (high M_s and recovery strain).

For a good combination of shape recovery strain and M_s , it is recommended that initially amorphous or partially amorphous ribbon be used and annealing temperature be kept below 550°C. For application of superelasticity, it is recommended that initially crystalline ribbon be used and annealing temperature be kept below 500°C.

The conclusions obtained in this thesis offer a possibility for controlling the shape memory properties for particular applications by controlling texture development during heat treatment. For example, for applications under multi-axial loading where the behavior of the material should be isotropic, initially amorphous ribbon annealed below 550°C is preferred.

Compared with Ti-Ni-Cu ribbons with respect to shape recovery strain and transformation hysteresis, the shape recovery strain of $B2 \leftrightarrow B19'$ and $B2 \leftrightarrow R$ transformation in Ti-Ni alloys under nearly the same stress (50.5MPa) are 3.4% and 0.4%, respectively. The transformation hysteresis for $B2 \leftrightarrow B19'$ and $B2 \leftrightarrow R$ are 35 and 2°C, respectively [21]. The $B2 \leftrightarrow B19$ transformation has equivalent shape recovery strain to $B2 \leftrightarrow B19'$ but with much smaller hysteresis. It fills the gap between $B2 \leftrightarrow B19'$ and $B2 \leftrightarrow R$ transformation.

CHAPTER 6 CONCLUSIONS

The objective of this work was to study the effects of initial structure and heat treatment on the crystal structure, microstructure, transformation behavior and shape memory effect of the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons, to establish a relationship between the internal structure and shape memory properties, and to understand the effect of Cu content on the transformation behavior of Ti-Ni-Cu alloys in a thermodynamic view.

The microstructure and twin morphology of B19 martensite and B11 TiCu precipitate, texture development in the initially amorphous ribbon, transformation behavior and shape recoverable strain of heat treated ribbons with different initial structures were studied. DSC and TMA measurements were performed to study the transformation behavior and shape recovery effect of the heat treated ribbons. The morphology of B19 martensite and twin relationship in B19 martensite were studied by TEM, electron diffraction analysis and simulation method. The evolution of crystal structure and texture development was examined by using XRD techniques.

Based on the experimental results obtained, the following conclusions are drawn.

Initially amorphous $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon

1. As-spun ribbon is amorphous. Its crystallization temperature is 450°C.
2. XRD results shows that ribbons annealed below 550°C has a B19 structure with a pure [211] texture at RT, while annealing above 550°C causes the formation of B11 TiCu precipitates and increases its volume fraction, thus resulting in the change of texture type to $(111)[\bar{2}11]$ and reorientation of B11 precipitates.

3. TEM observations reveal that the most frequently observed twin is (111) type I twin. Grain size of B19 martensite does not change significantly. Only one pair of twinned martensite plates extends the whole grain. Thin plate-like TiCu precipitates lies along the {011} planes of B19 martensite.
4. DSC results show that all the annealed ribbons except the 500°C-annealed one show a one-stage B2 $\leftrightarrow$ B19 transformation. M_s of the annealed ribbons is in the range of 55 to 68°C. Due to the formation of B11 TiCu, annealing above 550°C decreases M_s , M_f , A_s and A_f . Transformation hysteresis is around 8°C, regardless of annealing temperature.
5. TMA measurements show that all the ribbons annealed between 450 and 750°C exhibit a well-defined shape memory effect. Annealing above 550°C deteriorates the shape recovery strain of the annealed ribbons. The maximum recovery of 1.5% is obtained in the 450°C-annealed ribbon under 45 MPa. Pure strong fiber texture is beneficial to shape recovery strain, while B11 TiCu precipitates hinder the reorientation of martensite and diminish recovery strain.

Initially crystalline Ti₅₀Ni₂₅Cu₂₅ ribbon

1. As-spun ribbon has a crystalline structure consisting of B2 and B19 martensite with a [001]_{B19} fiber texture.
2. Annealed ribbons demonstrate the coexistence of B2 and B19 at RT. Annealing above 550°C induces the precipitation of TiCu phase.
3. Submicron austenite grains and twinned B19 martensite with type I (111) twin are observed. Particles of B11 distribute inside grains as well as at grain boundary.
4. Similar to the initially amorphous ribbon, all the ribbons annealed between 300 and 750°C show a one stage B2 $\leftrightarrow$ B19 transformation. M_s , M_f , A_s and A_f

increase with the increase of annealing temperature followed by a decrease. The increase is due to stress relief and decrease due to presence of B11 TiCu. M_s of the annealed ribbons is in the range of 30 to 50°C. Transformation hysteresis is similar to that of annealed initially amorphous ribbons.

5. The maximum recovery of 2.5% is obtained in the as-spun ribbon under 45 MPa. It does not change with annealing up to 500°C, but is deteriorated by annealing above 550°C due to the formation of B11 TiCu. Shape recovery strain of ribbons annealed below 550°C is higher than that of annealed initially amorphous ribbons. This is ascribed to B2 retained austenite. Two-way shape memory effect is observed in the as-spun ribbon.

Initially partial amorphous $Ti_{50}Ni_{25}Cu_{25}$ ribbon

1. As-spun ribbon has a mixture of amorphous and crystalline structure. Its crystallization temperature is 461°C.
2. The B19 martensites in the amorphous matrix of the as-spun ribbon have no effect on the structure of annealed ribbons. The annealed ribbons share similar crystal structure dependence on annealing temperature as that of annealed initially amorphous ribbons.
3. Type I (111) twin is observed. Particles instead of plate-like of B11 TiCu precipitates are found inside B19 martensite grains.
4. M_s , M_f , A_s and A_f , transformation hysteresis and shape recovery strain of annealed ribbons show similar tendency with annealing temperature to those of the annealed ribbons with initially amorphous structure.

Comparison of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons with different initial structures

1. After annealing, the initially amorphous ribbon and partially amorphous ribbon share similar structure, transformation behavior and shape recovery strain.
2. Compared with the initially amorphous ribbon, the initially crystalline ribbon shows different structure evolution, microstructure, transformation temperatures and recovery strain. And it shows higher recovery strain but lower transformation temperatures because of the existence of B2 austenite.
3. Three phases exist in the annealed ribbons: B19 martensite, B11 TiCu precipitate and B2 austenite. Ribbon with B2+B19+B11 shows the lowest recovery strain and M_s . The ribbon with B2+B19 structure has a higher recovery strain but lower M_s than those containing B19 phase.
4. Higher temperature annealing not only decreases M_s , but deteriorates the shape recovery strain. So it is better to keep the annealing temperature below 550°C for a good combination of shape memory properties (high M_s and recovery strain).

Ti-Ni-Cu bulk materials

1. The transformation sequence of Ti-Ni-Cu alloys changes with Cu content from $\text{B2} \leftrightarrow \text{B19}'$ (0-7.5 at.% Cu) to $\text{B2} \leftrightarrow \text{B19} \leftrightarrow \text{B19}'$ (10 at.% Cu) to $\text{B2} \leftrightarrow \text{B19}$ (more than 15 at.% Cu). With the increase of Cu content, $\text{B2} \leftrightarrow \text{B19}'$ (or $\text{B19} \leftrightarrow \text{B19}'$) transformation temperatures decrease, while $\text{B2} \leftrightarrow \text{B19}$ transformation temperatures increase. This is due to the alteration of the driving force of $\text{B2} \leftrightarrow \text{B19}$ by Cu addition.
2. The transformation hysteresis of $\text{B2} \leftrightarrow \text{B19}'$ is much larger than that of $\text{B2} \leftrightarrow \text{B19}$. The reason is that $\text{B2} \leftrightarrow \text{B19}$ has a smaller transformation shear, which is 0.0959

for $B2 \leftrightarrow B19$ and 0.1451 for $B2 \leftrightarrow B19'$. Transformation hysteresis decreases with Cu-content.

3. Ti-Ni-Cu alloy with Cu less than 10 at.% exhibits a B2 structure at RT, alloy with 15 at.% Cu a mixture of B2 and B19 and alloy with Cu more than 15 at.% a B19 structure. The lattice parameters of B2 and B19 change slightly with increasing Cu content. a of B2 is in the range of 3.02 to 3.04 Å. For B19, lattice parameters are: $a = 2.95\text{-}3.03$, $b = 4.0\text{-}4.12$ and $c = 4.55\text{-}4.70$ Å.

CHAPTER 7 RECOMMENDATIONS FOR FUTURE WORK

The crystal structure, microstructure, transformation behavior and shape memory effect of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons were studied in this thesis. Further research can be carried out in the following areas to have a better understanding of this ribbon:

1. Study of shape memory effect under higher applied stress

The maximum applied stress in TMA test was 45 MPa. It is not enough to evaluate the shape memory properties because it is a little low for initializing detwinning in some alloys. A Microforce tester equipped with higher load is a better choice.

2. ODF analysis of texture

In this thesis, the texture components were qualitatively analyzed because of the lack of quantitative analyzing method. But it is not possible to derive accurate relationships between materials properties and information obtained from pole figures or inverse pole figures [90]. It is important to obtain quantitative analysis in order to study how texture affects the shape memory properties.

3. Fabrication of melt-spun ribbons with controllable structure

Up to now the optimum condition of fabricating melt-spun Ti-Ni-Cu ribbon has not been known. And the fabrication of this ribbon is still conducted in laboratory. In order to get uniformly distributed nano-crystalline grains, more work must be carried out to determine the optimal processing parameters.

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Appendix I Peak Fitting Functions

1. Gaussian function [125]

The Gaussian function can be written as: $y = y_0 + \frac{A\sqrt{4\ln 2}}{\sqrt{\pi}W} e^{\frac{-4\ln 2(x-x_c)^2}{W^2}}$ Equation A1

Where y_0 is baseline offset, A is the total area under the curve from the baseline, x_c is the center of the peak, W is approximately 0.849 of the width of the peak at half height. This model describes a bell-shaped curve like the normal (Gaussian) probability distribution function.

2. Lorentz function [125]

The equation of Lorentz function is: $y = y_0 + \frac{2AW}{\pi[4(x-x_c)^2 + W^2]}$ Equation A2

Where y_0 is baseline offset, A is total area under the curve from the baseline, x_c is the center of the peak, W is full width of the peak at half height. The parameters in the Lorentz model are similar to the parameters defined for the Gaussian model.

3. Pseudo-Voigt function [125]

The equation of Pseudo-Voigt function is:

$$y = y_0 + A \left\{ \frac{2WM}{\pi[4(x-x_c)^2 + W^2]} + \frac{(1-M)\sqrt{4\ln 2}}{W\sqrt{\pi}} e^{\frac{-4\ln 2(x-x_c)^2}{W^2}} \right\} \quad \text{Equation A3}$$

Where y_0 , x_c , A , W , M are offset, the center of peak, amplitude, peak width and profile shape factor respectively.

Appendix II Standard XRD Data of B19 and B11-TiCu Phase

XRD data - B19

2 θ	36.6	39.8	42.1	42.4	45.2	57	59.3	63.7
Intensity	7	23	28	100	14	3	12	6
Plane	101	002	020	111	012	121	022	200

2 θ	70.1	74	77.2	77.8	79.4	81.6	85.3	89.41
Intensity	5	6	12	4	6	3	5	4
Plane	103	113	131	202	220	212	123	014

XRD data - B11 TiCu

2 θ	41.1	42.3	44	55.3	59.4	63.1	75.6	78.1	88.9
Intensity	60	100	5	5	25	10	40	10	5
Plane	110	102	111	103	200	113	212	203	220

Appendix III Stereographic Projections of B19 Phase

Figure A3.1 Stereographic projection of $[211]$

Figure A3.2 Stereographic projection of $(111)[\bar{2}11]$

Appendix IV Stereographic Projections of TiCu Phase

Figure A4.1 Stereographic projection of $[110]$

Appendix V Thermodynamic Calculation

In the equation (5.16), the first term is calculated by the following equation.

$$G_{odr} = \sum_i \sum_j y_i^a y_j^b {}^0G_{i,j}^{B2} + 0.5RT \left(\sum_i y_i^a \ln y_i^a + \sum_j y_j^b \ln y_j^b \right. \\ \left. + \sum_i \sum_{k>i} y_j^a y_k^a \sum_j y_j^b L_{i,k;j}^{B2} + \sum_j \sum_{k>j} y_j^b y_k^b \sum_i y_i^a L_{i,j,k}^{B2} \right) \quad \text{Equation A4}$$

$i = \text{Ni, Cu}$ and $j = \text{Ti}$

${}^0G_{i,j}^{B2}$ is related to the bond energy referred to the element in the b.c.c. state. It can be determined from experimental information, because the Ni (Cu) atoms mainly occupy the corner (a), whereas the Ti atoms mainly occupy the center (b) [140,141]. y_{Cu}^b , y_{Ni}^b and y_{Ti}^a are very small and set to zero for simplification. The above equation can be rewritten as:

$$G_{odr}(y_i^a, y_j^b) = y_{Ni}^a y_{Ti}^b {}^0G_{Ni,Ti}^{B2} + y_{Cu}^a y_{Ti}^b {}^0G_{Cu,Ti}^{B2} + 0.5RT(y_{Ni}^a \ln y_{Ni}^a + y_{Cu}^a \ln y_{Cu}^a + y_{Ti}^b \ln y_{Ti}^b)$$

Equation A5

where ${}^0G_{i,j}^{B2}$ is given as [140]:

$${}^0G_{Ni,Ti}^{B2} = -11450 + 3.8T$$

$${}^0G_{Cu,Ti}^{B2} = -50100 + 30T$$

$G_{odr}(x_i)$ can be determined by replacing y_i^a, y_i^b with molar fraction x_i .

$$G_{odr}(x_i) = x_{Ti} x_{Ni} {}^0G_{Ni,Ti}^{B2} + x_{Ti} x_{Cu} {}^0G_{Cu,Ti}^{B2} + 0.5RT(x_{Ni} \ln x_{Ni} + x_{Cu} \ln x_{Cu} + x_{Ti} \ln x_{Ti})$$

Equation A6

In Ti50-Ni(50-x)-Cux system, $y_{Ni}^a = 1 - 2x$, $y_{Cu}^a = 2x$ and $y_{Ti}^b = 1$. $x_{Ti} = 0.5$, $x_{Cu} = x$ and $x_{Ni} = 0.5 - x$.

The martensitic transformation is a first-order transition associated with latent heat, i.e. transformation enthalpy. It is a diffusionless transition. The Gibbs free energy of B19' and B19 martensite will be evaluated by the following equations [140]:

$$G_{B19'} = \sum_i \sum_j y_i^a y_j^b {}^0G_{i,j}^{B19'} + 0.5RT(\sum_i y_i^a \ln y_i^a + \sum_j y_j^b \ln y_j^b) + \sum_i \sum_{k>i} y_i^a y_k^a \sum_j y_j^b L_{i,k;j}^{B19'} + \sum_j \sum_{k>j} y_j^b y_k^b \sum_i y_i^a L_{i,j,k}^{B19'}$$

Equation A7

$$G_{B19} = \sum_i \sum_j y_i^a y_j^b {}^0G_{i,j}^{B19} + 0.5RT(\sum_i y_i^a \ln y_i^a + \sum_j y_j^b \ln y_j^b) + \sum_i \sum_{k>i} y_i^a y_k^a \sum_j y_j^b L_{i,k;j}^{B19} + \sum_j \sum_{k>j} y_j^b y_k^b \sum_i y_i^a L_{i,j,k}^{B19}$$

Equation A8

$i = Ti, Ni$, and $j = Ti$

Where G_{B19} and $G_{B19'}$ are the molar Gibbs energy of B19 and B19', respectively. The subscript comma separates components in the same atomic position, and the colon separates those in different atomic positions. ${}^0G_{i,j}^{B19'}$ and ${}^0G_{i,j}^{B19}$ are the Gibbs energy of the hypothetical compounds with the same structure of the B19' and B19 phase, respectively. R is the gas constant; and T is the temperature in Kelvin. The parameters $L_{i,k;j}$ or $L_{i:j,k}$ represent interaction between atoms in the same position under different circumstances giving an excess contribution to the Gibbs energy.

The above two equations can be simplified as follows:

$$G_{B19'} = y_{Ni}^a y_{Ti}^b {}^0G_{Ni:Ti}^{B19'} + y_{Cu}^a y_{Ti}^b {}^0G_{Cu:Ti}^{B19'} + 0.5RT(y_{Ti}^b \ln y_{Ti}^b + y_{Ni}^a \ln y_{Ni}^a + y_{Cu}^a \ln y_{Cu}^a)$$

Equation A9

$$G_{B19} = y_{Ni}^a y_{Ti}^b {}^0G_{Ni:Ti}^{B19} + y_{Cu}^a y_{Ti}^b {}^0G_{Cu:Ti}^{B19} + 0.5RT(y_{Ti}^b \ln y_{Ti}^b + y_{Ni}^a \ln y_{Ni}^a + y_{Cu}^a \ln y_{Cu}^a)$$

Equation A10

Where

$$\begin{aligned} {}^0G_{Ni:Ti}^{B19'} &= 0.5 {}^0G_{Ni}^{bcc} + 0.5 {}^0G_{Ti}^{bcc} - 43394 + 12.069T \\ {}^0G_{Cu:Ti}^{B19'} &= 0.5 {}^0G_{Cu}^{bcc} + 0.5 {}^0G_{Ti}^{bcc} - 11305 + 14.63T \end{aligned}$$

Equation A11

$$\begin{aligned} {}^0G_{Ni:Ti}^{B19} &= 0.5 {}^0G_{Ni}^{bcc} + 0.5 {}^0G_{Ti}^{bcc} - 43240 + 12.069T \\ {}^0G_{Cu:Ti}^{B19} &= 0.5 {}^0G_{Cu}^{bcc} + 0.5 {}^0G_{Ti}^{bcc} - 11105 + 9.2T \end{aligned} \quad \text{Equation A12}$$

Here ${}^0G_{Ti}^{b.c.c}$, ${}^0G_{Ni}^{b.c.c}$ and ${}^0G_{Cu}^{b.c.c}$ are Gibbs energies of pure elements Ti, Ni and Cu in b.c.c. structure, respectively.

Appendix VI Calculation of Twin Elements

According Jaswon and Dove's theory [145], $h_2u_1 + k_2v_1 + l_2w_1 = 4$

Then the indices of K_1' plane is:

$$h_1' = h_2 - N[100] \cdot [211] / [211]^2 = 1 - 4 \cdot 2a^2 / (4a^2 + b^2 + c^2) = 0.0626$$

$$k_1' = k_2 - N[010] \cdot [211] / [211]^2 = 1 - 4 \cdot b^2 / (4a^2 + b^2 + c^2) = -0.0048$$

$$l_1' = l_2 - N[001] \cdot [211] / [211]^2 = 1 - 4c^2 / (4a^2 + b^2 + c^2) = -0.1204$$

So

$$\begin{pmatrix} h_1' \\ k_1' \\ l_1' \end{pmatrix} = \begin{pmatrix} 0.0626 \\ -0.0048 \\ -0.1204 \end{pmatrix} = \begin{pmatrix} 0.5199 \\ -0.0399 \\ -1 \end{pmatrix} \quad \text{Equation A13}$$

The normal direction of $K_{\perp}'$ plane is $[211]$. Then the indices of $K_{\perp}'$ plane is:

$$\begin{pmatrix} h_{\perp} \\ k_{\perp} \\ l_{\perp} \end{pmatrix} = \begin{pmatrix} 2a^2 \\ b^2 \\ c^2 \end{pmatrix} = \begin{pmatrix} 17.1698 \\ 18.4041 \\ 20.5209 \end{pmatrix} = \begin{pmatrix} 0.8367 \\ 0.8968 \\ 1 \end{pmatrix} \quad \text{Equation A14}$$

Thus the indices of direction η_s' is:

$$\eta_s' = \begin{pmatrix} u_s \\ v_s \\ w_s \end{pmatrix} = (K_2) \times (K_1) = \begin{pmatrix} i & j & k \\ 0.5199 & -0.0399 & -1 \\ 1 & 1 & 1 \end{pmatrix} = \begin{pmatrix} 0.9601 \\ -1.5199 \\ 0.5598 \end{pmatrix} = \begin{pmatrix} 0.6317 \\ -1 \\ 0.3684 \end{pmatrix} \quad \text{Equation A15}$$

η_s' is the normal direction of the shear plane S' . Thus the indices of S' plane can be written:

$$(S') = \begin{pmatrix} h_s \\ k_s \\ l_s \end{pmatrix} = \begin{pmatrix} 0.6317a^2 \\ -b^2 \\ 0.3684c^2 \end{pmatrix} = \begin{pmatrix} 5.4231 \\ -18.4041 \\ 7.5599 \end{pmatrix} = \begin{pmatrix} 0.2947 \\ -1 \\ 0.4108 \end{pmatrix} \quad \text{Equation A16}$$

η_2' is a vector in S' plane and the intersect of K_2' and S' plane. So the indices of η_2' are:

$$[\eta_2'] = \begin{pmatrix} u_1 \\ v_1 \\ w_1 \end{pmatrix} = (K_2') \times (S') = \begin{pmatrix} i & j & k \\ 1 & 1 & 1 \\ 0.2947 & -1 & 0.4108 \end{pmatrix} = \begin{pmatrix} 1.4108 \\ -0.1161 \\ -1.2947 \end{pmatrix} = \begin{pmatrix} 1 \\ -0.0823 \\ -0.9177 \end{pmatrix}$$

Equation A17

$$\theta = (K_1') \wedge (K_2') = 85.83^\circ, \quad s = 2 \tan \alpha = 2 \tan(90 - 85.83) = 0.15$$

Therefore, the type I twin elements are:

$$\mathbf{K}_1 = (1, 1, 1), \mathbf{K}_2 = (0.5199, -0.0399, -1), \eta_1 = [1, -0.0823, -0.9177], \eta_2 = [2, 1, 1], s = 0.15$$

Appendix VII List of Publications

1. Cheng, G.P. and Xie, Z.L. "Some results on shape memory properties of Ti50Ni25Cu25 melt spun Ribbons" J. Alloy & Comp., 2005 (396), 128-132.
2. Cheng, G.P., Xie, Z.L., and Liu, Y. "Transformation characteristics of annealed Ti50Ni25Cu25 melt spun ribbon", J. Alloy & Comp., 2006 (415), 182-187.
3. Cheng, G.P., Xie, Z.L., and Liu, Y. "Texture and Shape Memory Property of Annealed Ti50Ni25Cu25 Ribbons", Materials Science and Engineering A, 2006 (425), 268-271.
4. Xie, Z.L., Cheng, G.P., and Liu, Y. "Microstructure and Texture Development in Ti50Ni25Cu25 Melt-spun Ribbon", Acta Materialia 2007 (55), 361-369.
5. Cheng, G.P., and Xie, Z.L. "Effects of Initial Structure on the Shape Memory Properties of Ti50Ni25Cu25 Ribbons", Materials Letters (accepted)
6. Cheng, G.P., Xie Z.L., and Liu, Y. "The Effect of Heat Treatment on the Transformation Characteristics of Ti50Ni25Cu25 Melt Spun Ribbons", The 3rd International Conference on Materials Processing for Properties and Performance (MP3), Nov. 2004, Singapore.
7. Xie, Z.L., Cheng, G.P., and Liu, Y. "Transformation characteristics and shape memory properties of Ti50Ni25Cu25 melt-spun ribbons". Presented on the International Conference on Martensitic Transformations 2005 (ICOMAT'05), Shanghai, China, June 2005.