

SPECIAL ISSUE: A TRIBUTE TO PROF. SHUICHI MIYAZAKI - FROM FUNDAMENTALS TO APPLICATIONS, INVITED REVIEW PAPER

My Experience with Ti–Ni-Based and Ti-Based Shape Memory Alloys

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Abstract The present author has been studying shape memory alloys including Cu-Al-Ni, Ti-Ni-based, and Nifree Ti-based alloys since 1979. This paper reviews the present author's research results for the latter two materials since 1981. The topics on the Ti-Ni-based alloys include the achievement of superelasticity in Ti-Ni alloys through understanding of the role of microstructures consisting of dislocations and precipitates, followed by the contribution to the development of application market of shape memory effect and superelasticity, characterization of the R-phase and monoclinic martensitic transformations, clarification of the basic characteristics of fatigue properties, development of sputter-deposited shape memory thin films and fabrication of prototypes of microactuators utilizing thin films, development of high temperature shape memory alloys, and so on. The topics of Ni-free Ti-based shape memory alloys include the characterization of the orthorhombic phase martensitic transformation and related shape memory effect and superelasticity, the effects of texture, omega phase and adding elements on the martensitic transformation and shape memory properties, clarification of the unique effects of oxygen addition to induce non-linear large elasticity, Invar effect and heating-induced martensitic transformation, and so on.

Shuichi Miyazaki miyazaki@ims.tsukuba.ac.jp **Keywords** Shape memory · Superelasticity · Transformation strain · NiTi < materials · Martensite · Ti-based shape memory alloy · Shape memory films

Introduction

The shape memory effect in Ti–Ni was first reported as dramatic demonstration of temperature-sensitive dimensional changes in plastically deformed Ti–Ni specimens by Dr. William J. Buehler's group of the U.S. Naval Ordnance Laboratory in 1963 [1], though the shape memory phenomenon was first found as serendipitous discovery at the laboratory management meeting to review ongoing projects in 1961 [2].

Since the discovery of the shape memory effect in the Ti-Ni, this alloy has attracted many scientists and engineers. However, there had been many difficult phenomena unsolved until 1981 when the present author achieved the superelasticity in the Ti-Ni by utilizing microstructures consisting of dislocations and/or precipitates [3, 4] which were formed by heat treatment at an intermediate temperature region. Table 1 shows research topics on Ti-Ni-based alloys investigated by the present author since 1980 [3-60]. The mechanism to achieve the superelasticity and quite stable shape memory effect utilizing such microstructures of the Ti-Ni was clearly explained in 1982 [4]. By this finding of the effect of microstructures, the equilibrium phase diagram of Ti-Ni was needed to be modified so as to extend the B2 single phase region down to room temperature. After understanding the relationship between microstructures versus functions and phenomena, the present author tried to clarify a variety of aspects of the Ti-Nibased alloys. These include basic properties such as Lüders-like deformation [5], the effect of texture on

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Table 1 Findings in Ti–Ni-based alloys

Category	Finding	Year	Reference		
A	(Basic properties)				
	Achievement of SE	1981-	[3, 4]		
	Lüders-like deformation	1981	[5]		
	Texture	2000	[<mark>6</mark>]		
	Aging treatment, Ti ₃ Ni ₄ , and R-phase	1982–	[4, 7–11]		
В	(Single crystals)				
	Crystal structure of M	1985	[12]		
	Crystallography of M transformation	1984–	[13, 14]		
	Orientation dependence of deformation behavior (M)	1983	[15, 16]		
	Mechanism of SME associated with M	1989	[17, 18]		
	Crystal structure of R-phase	1988	[19, 20]		
	Orientation dependence of deformation behavior (R)	1988	[19, 20]		
	Mechanism of SME associated with R-phase	1988	[19, 20]		
С	(Fatigue properties)				
	Thermal cycling	1986	[21]		
	Stress cycling	1986	[22]		
	Fatigue life	1988–	[23-25]		
	Crack nucleation	1988	[26]		
	Crack propagation	1988	[27]		
D	(Ti-Ni-X ternary alloys)				
	Ti–Ni–Cu	1997	[28-31]		
	Ti–Ni–Nb	1992	[32, 33]		
	Ti–Ni–Fe	1984	[34]		
Е	(High-temperature SMAs)				
	Ti–Ni–Hf–Nb	2011	[35]		
	Ti–Ni–Pd–Cu	2012-	[36–38]		
F	(Sputter-deposited thin films)				
	SME, SE	1992-	[39–41]		
	Microstructure	1996–	[42-44]		
	Ti–Ni–Cu thin films	1996–	[45-49]		
	Ti–Ni–Pd thin films	2004-	[50]		
	Ti–Ni–Zr thin films	2009	[51]		
	Microactuators	2002-	[49, 52, 53]		
	Microtubes	2008	[54]		
	Multilayer thin films	2005-	[55, 56]		
G	(Melt-spun ribbons)				
	Ti–Ni	2007	[57]		
	Ti–Ni–Pt	2006	[58]		
Н	(Reviews)		-		
	TiNi-based alloys	1989	[59]		
	Thin films	1999	[60]		
	High-temperature alloys	2015	[38]		

M martensite, R Rhombohedral-phase (R-phase)

deformation behavior [6], formation of Ti_3Ni_4 precipitates by aging treatment [4, 7–11]. More basic properties were characterized by using Ti–Ni single crystals which were made by the strain-anneal method in order to prevent contamination of oxygen and elements of crucibles. It was successful in making several large grains of 50 mm length and 20–30 mm width, with which systematic researches were possible to clarify the crystal structures of the martensite [12] and R-phase [19, 20], the crystallography of the martensitic transformation [13, 14] and R-phase transformation [19, 20], the orientation dependence of deformation behavior associated with the martensitic transformation [15, 16] and R-phase transformation [19, 20], and the mechanisms of shape memory effects due to both the transformations [17–20]. The Ti–Ni alloys revealed unique fatigue properties including functional degradation such as thermal cycling [21] and stress cycling [22], fatigue life [23–25], fatigue crack nucleation [26], and fatigue crack propagation [27] which could be understood systematically by clarifying the effects of the martensitic transformation start temperature M_s , test temperature, and alloy composition. The basic properties of Ti-Ni-X ternary alloys were characterized for Ti-Ni-Cu [28-31], Ti-Ni-Nb [32, 33], and Ti-Ni-Fe [34]. High temperature shape memory alloys such as Ti-Ni-Hf-Nb [35] and Ti-Ni-Pd-Cu [36–38] were developed; these alloys presented deformable nature and stability at high temperatures, respectively. Due to keen demands for the applications of MEMS (Micro Electro Mechanical Systems), Ti-Ni thin films with micron meter thickness were fabricated by sputter-deposition method. These thin films revealed perfect shape memory effect and superelasticity [39-41] and specific microstructures were found useful for achieving stable shape memory behavior [42-44]. Ti-Ni-X ternary alloy thin films were also developed to reveal narrow stress hysteresis in Ti-Ni-Cu [45-49] and high transformation temperatures in Ti-Ni-Pd [52, 50] and Ti-Ni-Zr [51]. Diaphragm-type microactuators were fabricated utilizing these thin films and they revealed fast actuation with even 100 Hz by the joule heating method [49, 53]. Ti-Ni superelastic microtubes were also fabricated by the sputterdeposition method [54]. Multilayer thin films consisting of sputter-deposited Ni and Ti thin layers were successfully alloyed by following heat treatment revealing shape memory effect and specific microstructures [55, 56]. Ribbons of Ti-Ni and Ti-Ni-Pt with 10-30 µm thickness were also fabricated by the melt-spinning method [57, 58]. Reviews on Ti-Ni [59], sputter-deposited thin films [60], and high-temperature shape memory alloys [38] were published to summarize some of the above results.

Since the success of applications utilizing Ti–Ni-based shape memory and superelastic alloys in medical fields, developing Ni-free Ti-based shape memory and superelastic alloys was considered to be important and attractive research topics. The present author's group has investigated and developed such Ni-free Ti-based alloys since 2002 as shown in Table 2 [61–102]. The developed Ti-based alloys which reveal shape memory effect and superelasticity are Ti–Nb binary alloys [61–65], many ternary alloys such as Ti–Nb–Al [66–70], Ti–Mo–Ga [71, 72], Ti–Nb–Ga [73], Ti–Nb–O [74], Ti–Nb–Zr [75, 76, 95, 102], Ti–Nb–Mo [77, 78], and Ti–Nb–Ta [79, 80, 95, 102] and quaternary alloys [84, 93, 94]. Basics

of crystallography and microstructures were characterized. including the martensitic transformation [62, 65, 69, 80, 81], textures [68, 80], microstructures [63, 65, 81, 82], and ω phase [62, 63]. Unique properties achieved by the addition of interstitial elements such as O [83-88], N [89, 90] and B [91] were characterized. Such unique properties are non-linear and large elastic deformation [83, 92], Invar effect [84, 86, 88], large shape recovery [93-95], cyclic deformation [64, 94], unique twinning systems in metastable β phase [96], and heatinginduced martensitic transformation [85]. Attractive hightemperature shape memory alloys were developed such as Ti-Ta [97, 98], Ti-Ta-Al [99], and Ti-Ta-Sn [100], because they do not have any problems of brittleness. Review papers including some of the above topics were published for Ti-Nb binary alloys [92, 101] and Ti-Nb-(Zr or Ta) ternary alloys [95, 102].

This paper is a short summery instead of a full review, presenting a short historical flow of the present author's researches using some of the above results and their contribution to the basic understanding of Ti–Ni-based and Nifree Ti-based shape memory alloys and the great progress of the applications using shape memory effect and superelasticity on the market. Thus, the readers may refer to each of the references about the details of the experimental information and results of each topic if necessary.

Ti–Ni-Based Alloys

Achievement of Superelasticity in Ti-Ni

The present author started studying Ti–Ni alloys in 1980. The commonly used heat treatment condition for achieving martensitic transformation was solution treatment followed by quenching into water in order not to permit phase separation and diffusion of atoms during cooling. Such a typical method was first applied for steels and also necessary for shape memory alloys which reveal the martensitic transformation, because the single phase region of the parent phase for steels and shape memory alloys existed only at a high-temperature region in their equilibrium phase diagrams.

There had been many difficult phenomena to be understood for the Ti–Ni, such as the control and roles of microstructures, involvement of unstable phase transformation which appears sometimes but not always and was known later as the R-phase (Rhombohedral-phase), etc. The author could not obtain any acceptable established experimental methods for studying Ti–Ni alloys from published information. The present author started investigating the effect of heat treatment on the properties of Ti– Ni alloys, considering that even the equilibrium phase

Table 2 Findings in Ti-basedalloys

Category	Finding	Year	Reference		
A	(Alloy development)				
	Ti–Nb	2004-	[61–65]		
	Ti–Nb–Al	2004-	[66–70]		
	Ti–Mo–Ga	2004-	[71, 72]		
	Ti–Nb–Ga	2004	[73]		
	Ti–Nb–O	2005	[74]		
	Ti–Nb–Zr	2005-	[75, 76]		
	Ti–Nb–Mo	2010-	[77, 78]		
	Ti–Nb–Ta	2006	[79, 80]		
В	(Crystallography and microstructure)				
	Martensitic transformation	2006-	[62, 65, 69, 80, 81]		
	Texture	2006	[68, 80]		
	Microstructure	2008-	[63, 65, 81, 82]		
	ω phase	2006-	[62, 63]		
С	(Interstitial element addition)				
	0	2011-	[83–88]		
	Ν	2008-	[89, 90]		
	В	2015	[91]		
D	(Unique properties)				
	Non-linear elastic deformation	2011-	[83, 92]		
	Invar effect	2013-	[84, 86, 88]		
	Large shape recovery	2015	[93–95]		
	Cyclic deformation	2009-	[64, 94]		
	Twinning deformation	2014	[96]		
	Heating-induced martensitic transformation	2014	[85]		
Е	(High-temperature SMA)				
	Ti–Ta	2009	[97, 98]		
	Ti–Ta–Al	2011	[99]		
	Ti–Ta–Sn	2011	[100]		
F	(Reviews)				
	TiNb-based	2006-	[92, 101]		
	Ti–Nb–Zr, Ti–Nb–Ta	2015-	[95, 102]		

diagram was not perfect and Ti is easily contaminated by oxygen.

The author applied solution treatment followed by cooling in a furnace for a Ni-rich Ti–50.6 at.%Ni [3]. (This heat treatment condition was misdescribed as rapidly quenched into iced water in Ref. [3] due to some confusion at that time.) The specimen was tensile tested at various temperatures, revealing quite stable shape memory effect and superelasticity, the latter of which had never been observed in Ti–Ni alloys. It was lucky for the author to use a Ni-rich Ti–50.6 at.%Ni instead of an equiatomic Ti–Ni, because the latter would not reveal superelasticity after solution treatment. The author wanted to know what happened in the specimen. Then, a variety of heat treatment conditions were applied to both alloys of near-equiatomic Ti-49.8 at.%Ni and Ni-rich Ti–50.6 at.%Ni [4]. The Ti-

49.8 at.%Ni revealed stable shape memory effect and superelasticity only when annealed at intermediate temperatures such as 673 K after cold drawing. However, it revealed neither perfect shape memory effect nor superelasticity if solution treated at 1273 K. Ti–50.6 at.%Ni revealed both stable shape memory effect and superelasticity when annealed at 673 K after cold drawing or solution treated at 1273 K followed by aging treatment at 673 K.

Typical microstructures of such specimens prepared by cold-rolling are shown in Figs. 1 and 2. Figure 1a shows that the as-rolled Ti-49.8 at.%Ni reveals rolling-induced many dislocations in severely strained martensite and parent phases. By annealing the specimen at 673 K, a high density of dislocations still existed but the strained condition was removed as shown in Fig. 1b. Annealing at 773

and 873 K revealed recrystallization and grain growth as shown in Figs. 1c, d, respectively. The Ti-49.8 at.%Ni annealed at 673 K revealed superelasticity as well as stable shape memory effect. The Ti–50.6 at.%Ni revealed Ti₃Ni₄ precipitates when aging treated at 673 and 773 K after solution treatment at 1273 K as shown in Fig. 2a, b, respectively. The alloy composition of the precipitates was not known at that time and later determined by other researches, but it was clear even at that time that the precipitates were Ni-rich because such precipitates appeared only in Ni-rich Ti–Ni but not in an equiatomic Ti–Ni. When the annealing temperature was 873 K, there was no precipitate any more as shown in Fig. 2c.

The Ti–50.6 at.%Ni aging treated at 673 K revealed stable shape memory effect and superelasticity due to the formation of the fine Ti_3Ni_4 precipitates. Then, the mechanism of achieving stable shape memory effect and superelasticity was clarified such that fine microstructures consisting of dislocations or fine Ti_3Ni_4 precipitates play a role of increasing the critical stress for plastic deformation. This finding was followed by further improvement of shape memory effect and superelasticity in Ti–50.6 at.%Ni which was annealed at 673 K without preceding solution treatment, because the specimen included both a high density of dislocations and fine Ti_3Ni_4 precipitates. Such properties

revealed in the specimen are shown in Fig. 3, where almost perfect superelasticity was observed even after subjected to 800 MPa. After the findings of the above phenomena, it was natural to reconsider the existing equilibrium phase diagram of Ti–Ni in such a way that there must be a single phase region of the B2 parent phase until down to near room temperature and a metastable phase of Ni-rich Ti–Ni phase at an intermediate temperature region, which is shown in Fig. 4.

Another basic property of Lüders-like deformation was observed in a Ti–Ni alloy [5], and texture dependence of deformation behavior was investigated in Ti–Ni rolled plates [6]. Detailed investigation of Ti_3Ni_4 precipitates was conducted in Ni-rich Ti–Ni alloys by changing aging and annealing conditions [4, 7–11].

Development of Application Market of Ti-Ni

The above thermomechanical treatment method to achieve superelasticity as well as quite stable shape memory effect in Ti–Ni was filed for a patent in Japan in 1982 and patented in 1990 [103]. After this invention, the history of Ti–Ni moved quickly as shown in Fig. 5. The shape memory effect of Ti–Ni was found in USA in 1961 [1, 2], while the superelasticity of Ti–Ni was achieved in Japan in



Fig. 1 Transmission electron micrographs of Ti-49.8 at.%Ni annealed at various temperatures. a as-rolled, b 673 K, c 773 K, and d 873 K





1981 [3, 4]. After understanding the relationship between microstructures versus functions and phenomena in Ti–Ni, the basic characteristics including many other unknown features of Ti–Ni had been clarified during the following 20 years. By the control of microstructures and compositions, the monoclinic martensitic transformation and the R-phase transformation could be separated to be investigated independently, and fatigue properties could be systematically understood as a function of transformation temperature, test temperature, and alloy composition.

Meantime, many useful applications using superelasticity in addition to shape memory effect appeared on the market. Materials manufacturing companies started producing and selling Ti–Ni devices using the above-mentioned thermomechanical treatment as shown in Figs. 6 and 7, and many users could obtain such devices for their own applications. In Japan, many people became to know shape memory alloys through mass-communications such as newspapers, television, magazines, and books since 1981, then a variety of application ideas valid or invalid when considering the properties of Ti–Ni appeared as shown in Fig. 8, which shows the number of patents filed for applications and materials in Japan since 1978. The number increased drastically from 1981. These numbers are probably 70% of those of the world; thus, it is equivalent to the world tendency of filing patents relating shape memory alloys. The number of patents filed every year in Japan seems keeping 200–300 even at present.

Figure 9 shows some examples of applications appeared on the market as a function of year. The patents of new



Fig. 3 Stress-strain curves measured at various temperatures in Ti-50.6 at.%Ni annealed at 673 K for 3.6 ks, revealing stable shape memory effect and superelasticity



Fig. 4 An equilibrium phase diagram of Ti-Ni



Fig. 5 A brief history of the development and applications of Ti-Ni



Furukawa Techno Material Co., Ltd.

Fig. 6 Ti-Ni shape memory devices



Fig. 7 Shape memory alloy actuators



Fig. 8 Number of application patents filed in Japan

materials filed by the present author are also shown. A very famous application of pipe coupling can be seen in an early stage of 1970s. The application demanded only one time shape recovery and required neither perfect shape recovery nor many times cycling use; thus, the application was successful even though the application could not use the perfect shape recovery. However, many other successful



Revised version of Furukawa Techno Material's Data

Fig. 9 History showing materials development and applications using shape memory effect and superelasticity

applications utilizing shape memory effect required perfect shape recovery for many times. These applications appeared from 1981 when the thermomechanical treatment method was invented. Many applications also appeared utilizing superelasticity since 1981. Without the invention of the thermomechanical treatment achieving the superelasticity, all these applications could not be possible to appear. The ratio between the number of applications using superelasticity and that of applications using shape memory effect will be 80-20. Since eighty percent of the applications utilizing superelasticity belong to medical fields, it seems that much material is used for medical applications. Figure 10 shows a photograph of a conference circular of SMST in 2005, revealing many medical stents using superelasticity and each stent being supplied by each corresponding company, indicating the great advantage of superelasticity for medical applications. By the present more than 10 years later since then, the stent market has grown intensively. A book on biomedical shape memory alloys was published due to the demand of information of medical applications of shape memory alloys [104]. Another book on technologies and applications of shape memory alloys was also published due to requests from many people in engineering and medical fields [105].

Martensitic Transformation

There are two types of martensites depending on alloy composition. One type is the monoclinic structure B19' which appears in Ti–Ni [12], while another type of orthorhombic structure B19 appears in Ti–Ni–Cu [31]. Depending on the type of crystal structures, there are 12 lattice correspondences between B2 and monoclinic martensite [13, 14], while 6 lattice correspondences between B2 and orthorhombic martensite. Accordingly,



Fig. 10 Various stents made of Ti-Ni superelastic alloys

there are 24 habit plane variants for the monoclinic martensite, while 12 for the orthorhombic martensite. By tensile testing single crystals of Ti–Ni with various crystal directions for tensile axes, the orientation dependence of recoverable strain could be measured as shown in Fig. 11 [15]. Habit planes were also measured in the tensile-tested single crystals [13, 14]. The stress–strain curves at various temperatures were also investigated to show shape memory and superelastic behavior in single crystals [16].

Using a single crystal of aging treated Ti–Ni, the specimen was tensile loaded to reveal stress-induced martensite variants which could be indexed correctly because the orientation of the single crystal was determined by X-ray diffraction as shown in Fig. 12a [17]. Following cooling induced the self-accommodation morphologies of triangles as shown by a circle in Fig. 12b. The triangle morphology consists of three habit plane variants on the photograph as shown in Fig. 13, but probably of four habit plane variants in three dimensionally [17]. After cooling the specimen down to below M_f temperature, it was tensile loaded to observe martensite variants reorientation to reach the maximum recoverable strain. Then, it was heated to



Fig. 11 Orientation dependence of the transformation strain calculated and experimentally measured in Ti–Ni single crystals



Fig. 12 Optical micrograph showing **a** stress-induced martensite variants and **b** the formation of the self-accommodation morphology of martensite variants

observe the reverse martensitic transformation from the martensite to the parent B2 through the R-phase [18]. The shape memory mechanism was clarified by the observation.

R-phase Transformation

The R-phase was curious and difficult to understand since the finding of Ti–Ni until 1981, i.e., appearing at room temperature but disappearing by the transmission electron microscope observation due to heating by electron beams. Such curious phenomena appeared due to the narrow transformation temperature hysteresis of only several K. However, the R-phase transformation could be clearly separated from the martensitic transformation by controlling microstructures consisting of dislocations and precipitates since 1981.

Figure 14 shows the B2 parent phase in a solutiontreated Ti-50.6 at.%Ni. A near-equiatomic Ti-49.8 at.%Ni shows the R-phase in a microstructure consisting of a high density of dislocations as shown in Fig. 15. The Ti-50.6 at.%Ni reveals the R-phase in a microstructure consisting of fine Ti₃Ni₄ precipitates after solution treatment followed by aging treatment at 673 K as shown in Fig. 16. Figure 17 also shows the R-phase in a microstructure consisting of dislocations and fine precipitates in an annealed Ti-50.6 at.%Ni. From these observations [11] and further investigation on Ti-Ni-X ternary alloys [34], it was concluded that the R-phase does not appear when the R-phase transformation start temperature $T_{\rm R}$ is lower than the martensitic transformation start temperature M_s (M_s (a)) as shown in Fig. 18. However, when $T_{\rm R}$ is higher than $M_{\rm s}$ such as $M_s(b)$ and $M_s(c)$, the R-phase transformation appears prior to the martensitic transformation upon cooling. This can be achieved by using some of the following factors which decrease $M_{\rm s}$ effectively more than $T_{\rm R}$.

- 1) Ni-content (solid solution)
- 2) Aging (Ti₃Ni₄ precipitates)
- 3) Cold working + annealing (dislocations)
- 4) Third element addition (Fe, Al etc.) (solid solution)
- 5) Thermal cycling (dislocations)

Among these factors, the first one of increasing Nicontent cannot reveal the R-phase transformation, because increasing Ni-content also decreases $T_{\rm R}$ effectively as $M_{\rm s}$ in a solid-solution condition; thus, $T_{\rm R}$ cannot be higher than $M_{\rm s}$. The fourth factor of adding the third element decreases $M_{\rm s}$ more effectively than $T_{\rm R}$, thus revealing the R-phase transformation upon cooling in a solid-solution condition. Other factors (2), (3), and (5) form microstructures consisting of dislocations and/or Ti₃Ni₄ precipitates which suppress the martensitic transformation more effectively than the R-phase transformation, thus revealing the R-phase transformation. Using the above factors (2)–(5), it became easy to investigate the R-phase transformation by separating from the martensitic transformation. Such investigations clarified the basic characteristics of the Fig. 13 Schematic figures showing **a** a triangular morphology and **b** corresponding to twinned microstructures of three variants

Fig. 14 A transmission electron micrograph showing B2 in a solution-treated Ti– 50.6 at.%Ni



R-phase transformation and related deformation behavior as follows.

Since the R-phase transformation is essentially same as the martensitic transformation which is the crystal structure change without being accompanied by diffusion, it causes the shape memory effect and superelastic deformation to occur. The two-stage deformation behavior occurs when both the two phase transformations are involved in a specimen [4, 20]. Such deformation behavior as a function of test temperature is schematically shown in Fig. 19 [4]. The lattice correspondence between the B2 parent phase and the R-phase is shown in Fig. 20 [20]. The length of the three axes of the R-phase are same as that of the B2, while the rhombohedral angle α decreases with decreasing temperature from T_R . The angle α versus temperature relationship measured by X-ray diffraction is shown in Fig. 21 [20]. The recoverable strain due to the R-phase transformation can be calculated using the data of Fig. 21, resulting in the contour lines revealing the orientation dependence of the recoverable strain as shown in Fig. 22. The corresponding experimental data were obtained by tensile testing Ti–Ni single crystals with various tensile orientations, and the results are also shown by closed circles in Fig. 22. Both the experimental data and the calculated data are very much consistent.

The self-accommodation morphology appeared in an aging treated Ni-rich Ti–Ni single crystal as shown in Fig. 23a [19]. Four types of traces can be seen, representing four twinning planes of the R-phase. The self-accommodation morphology was analyzed carefully, resulting in the morphology consisting of four R-phase variants which make the net strain zero as shown in Fig. 24. This somehow complex morphology of self-accommodation is formed by the effect of stress distribution around Ti₃Ni₄

Fig. 15 A transmission electron micrograph showing the R-phase and a high density of dislocations in Ti– 49.8 at.%Ni annealed at 673 K

Fig. 16 A transmission electron micrograph showing the R-phase and fine precipitates in Ti–50.6 at.%Ni aging treated after solution treatment



precipitates. By applying a small force, the self-accommodation morphology easily changes to another morphology clearly revealing two twinning planes of (011) and (100) as shown in Fig. 23b, where four R-phase variants coexist. By further tensile loading, twinning planes move and disappear resulting in the most favorable R-phase variant formed, corresponding to the maximum recoverable strain condition. After unloading followed by heating, the specimen revealed shape memory effect by the reverse R-phase transformation [19, 20]. It was reported later by other researchers that a simpler morphology of self-accommodation consisting of four R-phase variants appeared in a solution-treated Ti–Ni–Fe, since fine precipitates were not included.

Fatigue Properties

Fatigue properties of shape memory alloys include functional degradation and fatigue behavior. The functional degradation appears as the changes in the transformation temperatures and deformation behavior. Thermal cycling changes M_s in the solution-treated Ti–49.8 at.%Ni as shown in Fig. 25a [21], the M_s being measured by the electrical resistance versus temperature curves. However, when the same alloy is annealed at 673 K without solution treatment after cold-rolling, the M_s does not change even after 100 thermal cycling as shown in Fig. 25b. The former specimen induced dislocations during the forward martensitic transformation and its reverse transformation upon cooling and heating, resulting in the formation of







Fig. 18 A schematic figure explaining the appearance of the R-phase transformation by depressing the martensitic transformation



Fig. 19 Schematic stress-strain curves at various temperatures showing the two-stage transformation

dislocation barriers against the martensitic transformation to decrease M_s . In the latter case of the annealed specimens, a stable microstructure consisting of a high density of dislocations exists. Such a dislocation microstructure is so stable that introduction of further dislocations is suppressed during the forward and reverse transformations, resulting in less change in M_s as shown in Fig. 25b. Similar functional stability was achieved both in Ti–50.6 at.%Ni and Ti–51.6 at.%Ni which were aging treated at 673 K after solid solution treatment at 1273 K as shown in Fig. 26. Both the specimens included fine Ti₃Ni₄ precipitates, which suppressed introduction of dislocations during thermal cycling due to the precipitation hardening mechanism.

Stable superelastic deformation behavior appeared in Ti–Ni alloys which include a high density of dislocations and/or fine Ti₃Ni₄ precipitates as shown in Fig. 27 [22]. Stress cycling exerts severe effects on the microstructure, hence the critical stress for inducing the martensitic transformation decreases with increasing the number of stress cycling as shown in Fig. 27a–d. This indicates that the effect of stress cycling is more severe than that of thermal cycling. However, such stress cycling effect was suppressed by the training effect as shown in Fig. 27e, where stable superelastic deformation behavior appeared in the specimen which was 100 times stress cycled prior to the experiments in Fig. 27e.

Figure 28 shows the strain amplitude ($\Delta \varepsilon$) versus fatigue life (N_f) curves measured by a rotary bending machine at various temperatures [25]. Each $\Delta \varepsilon - N_f$ curve is divided into three lines which correspond to cyclic deformation below the proportional limit strain, between the proportional limit and elastic limit strains and above the elastic limit strain, where the specimens were rotary bending **Fig. 20** Crystal structures of **a** B2 phase and **b** R-phase

89.2

T_R - 60

C [001]B2

a [100]_{B2}

a' [110]₈₂ [100]_R

b [010]_{B2}

(b) R-phase



TR

T_R + 20

Fig. 21 Temperature dependence of the rhombohedral angle of the R-phase, $T_{\rm R}$ being the R-phase transformation start temperature

T_B - 40

T_R-20

Temperature(K)



Fig. 22 Orientation dependence of the R-phase transformation strain calculated and experimentally measured in Ti–Ni single crystals, the strains being the values at $(T_R - 35)$ K

cycled by pure elastic deformation, macroscopically elastic but locally martensitic transformation and macroscopically martensitic transformation, respectively. The overall fatigue life at each temperature increases with decreasing test temperature.

Figure 29 shows the stress versus fatigue life curves measured by tensile loading and unloading fatigue tests at



Fig. 23 a A self-accommodation morphology of the R-phase and b twinned morphology after applying a small force to (a)

three test temperatures during controlling the applied maximum stress. The fatigue life was also measured during controlling the applied maximum strain, and the corresponding stress versus fatigue life curve is also shown in Fig. 29. Each of the stress versus fatigue life curve is divided into two regions at around the critical stress (σ_M) for inducing the martensitic transformation. The deformation mode above σ_M is the stress-induced martensitic transformation. The fatigue life below σ_M is the elastic deformation. The fatigue life below σ_M is the prevent temperature; however, the fatigue life above σ_M is almost similar irrespective of test temperature.



Fig. 24 a A self-accommodation morphology of the R-phase and b the corresponding morphology consisting of four R-phase variants

Figure 30 shows the fracture surface of the annealed Ti– 50.8 at.%Ni which was prepared by a high-frequency vacuum induction melting method using a carbon crucible, where a TiC inclusion was found at the crack nucleation site as shown in Fig. 30a and the magnification is shown in Fig. 30b. This suggests that pure Ti–Ni alloys are necessary for not supplying crack nucleation sites like TiC inclusions. Then, pure Ti–Ni specimens with similar Nicontents were prepared by the electron beam melting method. However, the stress versus fatigue life curves of the specimens prepared by both the melting methods were similar; thus, the fatigue life was not improved by purification. The reason of this is explained as follows.

Figure 31 shows that a fatigue crack nucleation site was a grain boundary where stress concentration occurred due to the strain misfit along the grain boundary after forming different martensite variants in each of the grains connected at the grain boundary. After the crack nucleation along the grain boundary, the crack propagates transgranularly into neighboring grains as shown in Fig. 31. This result indicates that a fatigue crack nucleates at a TiC inclusion for a specimen prepared by the high-frequency vacuum induction melting method using a carbon crucible or at a grain boundary for a specimen without TiC inclusions. Both crack nucleation sites provide similar stress concentration so that the fatigue life seems not to be improved by purification.



Fig. 25 Effect of thermal cycling on $M_{\rm s}$ measured by the electrical resistance versus temperature curve of a Ti–49.8 at.%Ni aging treated following solution treatment and b Ti–49.8 at.%Ni annealed without solution treatment

The fatigue crack propagation is also an important phenomenon. Figure 32 shows the fatigue crack propagation rate $(\Delta a / \Delta N)$ as a function of stress intensity factor (ΔK) measured at various test temperatures [27]. The crack propagation rate is lowest when tested at 253 K which is below $M_{\rm s}$, while it increases with increasing test temperature above M_s up to 333 K, because the critical stress for inducing the martensitic transformation increases with increasing test temperature. It becomes constant irrespective of test temperature when the test temperature is higher than 333 K, where the critical stress for inducing the martensitic transformation is so high that the martensitic transformation is not effective to suppress the crack propagation by decreasing the stress concentration at the crack tip or conventional plastic deformation occurs. The crack propagation rates measured at above 333 K are similar to that predicted by the empirical equation for conventional



Fig. 26 Effect of thermal cycling on M_s measured by the electrical resistance versus temperature curve of a Ti–50.6 at.%Ni and b Ti–51.6 at.%Ni aging treated following solution treatment

metals and alloys, which do not reveal the martensitic transformation $(\Delta a/\Delta N = 5.1 \times 10^6 (\Delta K/E)^{3.5})$, using ΔK and Young's modulus *E* of Ti–Ni as shown by the dashed line in Fig. 32.

Ti-Ni-X Alloys

The Ti–Ni–Cu alloys showed interesting transformation and deformation behavior. It was found that the stress hysteresis was affected by alloy composition [28]. The Ti– 40Ni–10Cu (at.%) revealed superelastic deformation with low stress hysteresis of 100 MPa which was less than a half of that of the binary Ti–50.6 at.%Ni as shown in Fig. 33 [28]. The superelastic deformation was stable against cyclic deformation due to the small stress hysteresis.

The transformation temperatures and crystal structures of Ti–(50 - X)Ni–XCu (at.%) were investigated within a range of X = 0–13 at.% as shown in Fig. 34 [29, 30]. The martensitic transformation start temperature M_s decreases with increasing Cu content until 7.5 at.%, then decreases rapidly with further increasing Cu content. The martensite



Fig. 27 Cyclic superelastic deformation in Ti–Ni with different alloy compositions and different heat treatment conditions



Fig. 28 Strain amplitude ($\Delta \varepsilon$)-fatigue life (N_f) curves of Ti–Ni wires measured at various temperatures by a rotary bending fatigue tester



Fig. 29 Effect of test temperature on fatigue life of Ti–50.8 at.%Ni which was annealed at 673 K $\,$

appeared at the M_s is the monoclinic B19' martensite. Another martensitic transformation, orthorhombic B19 martensite, appears prior to the B19' martensitic transformation when Cu content is higher than 7.5 at.%. This means that two-stage martensitic transformation appears when Cu content is higher than 7.5 at.%. The B19 martensitic transformation is characterized by a small temperature hysteresis, causing the small stress hysteresis of the superelastic deformation as shown in Fig. 33. The effect of Ti content on the transformation and deformation behavior was also systematically investigated in XTi– (92 - X)Ni-8Cu (at.%) alloys [31].

Ti–Ni–Nb alloys reveal a wide temperature hysteresis which is useful in applying for pipe coupling applications for jet airplanes [32, 33], because they are used at temperature of 223 K during flight, while the temperature is around 293 K during staying at the ground. The M_s must be

lower than 223 K, and the reverse martensitic transformation finish temperature $A_{\rm f}$ must be higher than around 293 K for safe usage and easy setting.

The mechanical behavior associated with the R-phase transformation was first clarified in a Ti-47Ni-3Fe (at.%) alloy [34]. It was found that the superelasticity appeared associated with the R-phase transformation. Two-stage deformation behavior was clarified depending on test temperature. In case of a binary Ti-Ni alloy, two-stage superelastic behavior was also observed as shown in Fig. 19 [11].

High-Temperature SMAs

High-temperature shape memory alloys have been extensively investigated because of keen demands for applications used at temperatures above 373 K (100 °C). Figure 35 shows some examples of applications utilizing shape memory effect appeared on the market. All these applications have been only used at temperatures between room temperature and 80 °C, because the Ti-Ni alloys supplied by material manufacturers do not show the reverse transformation above 80 °C. There have been developed many high-temperature shape memory alloys such as Ti-Ni-Hf, Ti-Ni-Zr, and Ti-Ni-Pd. However, these alloys are not ductile enough, so that the development of deformable high-temperature shape memory alloys has been demanded. One of such deformable hightemperature shape memory alloys which were developed by the present author's group is $(Ti-49.5Ni-15Hf)_{100-X}$ XNb (X = 0-20 at.%) alloy. The ternary Ti–Ni–Hf alloy is not ductile as shown in Fig. 36, where the Ti-Ni-Hf

Fig. 30 Scanning electron micrographs of a fatiguefractured-surface of Ti– 50.8 at.%Ni which was solution treated at 1273 K





Fig. 31 A scanning electron micrograph showing a fatigue crack nucleation along a grain boundary



Fig. 32 Effect of test temperature on the fatigue crack propagation rate $(\Delta a/\Delta N)$ versus stress intensity factor (ΔK)

reveals only 20% cold workability. However, the cold workability of Ti–Ni–Hf–Nb quaternary alloys increases with increasing Nb content, revealing more than 60% when Nb content exceeds 10%. The reason why the quaternary alloys become ductile is shown in Fig. 37 which is a scanning electron images observed in back-scattered electron mode. With increasing Nb content, a lamellar microstructure consisting of B2 and Nb phases appears and increases its volume fraction. This microstructure is formed by a eutectic solidification. The Ti–Ni–Hf–15 at.%Nb reveals a full eutectic phase



Fig. 33 Comparison between the cyclic superelastic deformation behaviors in Ti–50.6 at.%Ni and Ti–40Ni–10Cu (at.%) which were annealed at 673 K



Fig. 34 A phase diagram of Ti-(50 - X)Ni-XCu (X = 0-13) (at.%) showing the effect of Cu content on transformation temperatures



Fig. 35 Temperature range covering application examples on the market



Fig. 36 Effect of Nb content on the cold workability of Ti-49.5Ni-15Hf–Nb alloys. Images of cold-rolled specimens are included in the lower side (Ti-49.5Ni-15Hf) and at the center [(Ti-49.5Ni-15Hf)– 15Nb]

microstructure. The B2 phase causes the shape memory effect to occur, while the Nb phase deforms plastically during cold working. Similar results were obtained in the Ti–Ni–Zr–Nb alloys.

The Ti–Ni–Pd–Cu alloy was also developed as to reveal stable shape memory effect at temperatures above 100 °C [36, 37]. The stability at high temperatures was achieved by precipitation hardening. Two types of precipitates, TiPdCu and Ti2Pd types, were formed in Ti–50Ni–15Pd–10Cu [36]. These precipitates are stable even at 873 K, where dislocations disappear due to recrystallization. A review paper on the Ti–Ni–Pd–Cu is available [38].

Beta Ti-based high-temperature shape memory alloys such as Ti–Ta, Ti–Ta–Al, and Ti–Ta–Sn were also developed [97–100], and they will be described later in one section of the next chapter for Ni-free Ti-based alloys.

Sputter-Deposited SMA Thin Films

Micro-electro-mechanical systems (MEMS) such as microvalves, micropumps, and micromachines require microactuators with high power and high frequency. Shape memory alloys were considered to be useful for such purposes. Thus, the sputter-deposition technique could be the first candidate for fabricating thin film shape memory alloys. However, it was not easy to make perfect shape memory effect in sputter-deposited thin films, because the



Fig. 37 Back-scattered scanning electron images of (Ti-49.5Ni-15Hf)-(0-20)Nb alloys. **a** Ti-49.5Ni-15Hf, **b** (Ti-49.5Ni-15Hf)-1Nb, **c** (Ti-49.5Ni-15Hf)-5Nb, **d** (Ti-49.5Ni-15Hf)-10Nb, **e** (Ti-49.5Ni-15Hf)-15Nb, and **f** (Ti-49.5Ni-15Hf)-20Nb sputter-deposition technique had not been used for making thin film shape memory alloys successfully. The present author's group started to develop sputter-deposited thin film shape memory alloys since 1990, and succeeded in achieving perfect shape memory effect and superelasticity [39–41, 60].

The sputter-deposited thin films revealed unique precipitates which are formed in Ti-rich Ti–Ni thin films. After sputter-deposition at room temperature, the films are always amorphous. Heat treatment for crystallization is needed to make thin film shape memory alloys. Figure 38 shows such precipitates formed in a Ti–48.2 at.%Ni thin film. Plate-shaped precipitates are observed aligning on {100} planes of B2 phase [42, 43]. These precipitates are useful for increasing strength so as to increase the stability of shape recovery. Grain size refining is also useful in obtaining stable shape recovery [44].

In order to achieve actuation of high frequency, it is necessary to increase the transformation temperatures or decrease the transformation temperature hysteresis when the actuator is operated by joule heating method without any cooling devices: the former method is effective for increasing cooling rate by operating it at high temperatures, while the latter is effective to narrowing the temperature variation range for actuation so as to increase the frequency. Ti–Ni–Pd [50] and Ti–Ni–Zr [51] thin films were developed to increase the transformation temperatures, while Ti–Ni–Cu [48, 49] thin films were fabricated for narrowing the temperature variation necessary for actuation.

Fabrication of Microactuators

Prototypes of microactuators were fabricated utilizing Ti-Ni, Ti-Ni-Pd, and Ti-Ni-Cu thin films [48, 49, 53]. An example of such microactuators is shown schematically in Fig. 39, where a thin film (Ti-Ni, Ti-Ni-Pd, or Ti-Ni-Cu) of 2 μ m thickness is sputter-deposited on a SiO₂ layer of 1 µm thickness. During heating and cooling, the diaphragm-type microactuator changed the shape to flat and convex, respectively. An example of the movement of such microactuator is shown in Fig. 40 [53]. The duty ratio of heating and cooling (switching on and off electrical current) is 3:97, because longer cooling time is necessary to wait the temperature decreasing down without any specific cooling device and shorter heating time is enough for increasing temperature because of high heating rate. Figure 41 shows that the maximum height of the diaphragm of the microactuator as a function of frequency. The Ti-Ni binary alloy thin film actuator shows that the maximum height suddenly decreases with increasing frequency. However, the Ti-Ni-Pd ternary alloy thin film actuator reveals efficient movement because 80% of the maximum height at frequency of 1 Hz is maintained at frequency of 100 Hz. This is the proof that higher transformation temperature thin films are effective for high speed actuation. Such high speed actuation was also observed in Ti-Ni-Cu with narrow transformation temperature hysteresis [48]. Microactuators utilizing the R-phase transformation in Ti-Ni binary alloy also revealed similar high speed actuation [52].

Another unique characteristic of such sputter-deposited thin films is shown in Fig. 42, where textures of sputterdeposited thin films are compared [53]. When a thin film is sputter-deposited at room temperature, the film is amorphous. Following heat treatment induces crystallization from amorphous phase to B2 phase. In such a case, the thin film shows a texture shown in Fig. 42a: this texture is not so strong. However, when sputter-deposition is conducted on a heated substrate with a temperature higher than crystallization temperature, the texture is strong as shown



Fig. 38 A high-resolution electron micrograph showing plate precipitates in a sputter-deposited Ti-48.2 at.%Ni thin film



Fig. 39 A schematic figure showing a diaphragm-type microactuator consisting of a Ti–Ni thin film deposited on a SiO_2 layer of Si substrate



Fig. 40 Dynamic characteristics showing the height of a diaphragmtype microactuator versus time relationship



Fig. 41 The maximum height of microactuators with Ti–Ni and Ti– Ni–Pd thin films as a function of cyclic frequency

in Fig. 42b, which reveals a typical fiber texture with the maximum intensity of 100. Because of the attractive function of such microactuators, a book on thin film shape memory alloys was published [106].

Further Investigation on Thin Film Shape Memory Alloys

Superelastic microtubes are attractive for medical applications such as stents. If thinner tubes are required, the sputter-deposition method is available. Such superelastic tubes were successfully fabricated by applying sputter-deposition during rotating a Cu wire substrate [54]. Sputterdeposition technique was also applied to make Ti–Ni multilayer thin films consisting of Ti and Ni films layered alternately [55, 56]. After sputter-deposition of the multilayer thin films, the films were heat treated for alloying to make Ti–Ni thin film shape memory alloys. Unique alloying process was observed. Another method, meltspinning, is applicable for making thin plate shape memory alloys with thickness of 10–30 μ m. It was also shown that the melt-spun ribbons reveal perfect shape memory effect and specific microstructures [57, 58].

Ni-Free Ti-Based Alloys

The motivation of developing β Ti-based shape memory alloys is to develop materials which are more biocompatible and possess better properties than Ti–Ni alloys by the replacement of Ni with other elements which are safe for human bodies. Such safe elements are Nb, Mo, Zr, Ta, Sn, Au, Ge, Ga, O, N, etc. The author's group has developed β Ti-based alloys which reveal shape memory effect and superelasticity as shown in Fig. 43. The detailed basic properties of some of these alloys can be seen in [61–65] for Ti–Nb, [66–70] for Ti–Nb–Al, [71, 72] for Ti–Mo–Ga, [73] for Ti–Nb–Ga, [74] for Ti–Nb–O, [75, 76] for Ti–Nb– Zr, [77, 78] for Ti–Nb–Mo, and [79, 80] for Ti–Nb–Ta.

The comparison between the basic characteristics of Ti– Ni-based and Ti-based alloys is shown in Table 3. The parent phases of Ti–Ni-based alloy and Ti-based alloy are B2 ordered structure and BCC disordered structure, respectively. The martensite phases for these two alloys are monoclinic, orthorhombic, and rhombohedral phases for the former alloy and orthorhombic phase for the Ti-based alloy. The precipitates available for modification of properties are Ti₃Ni₄ for the former alloy and ω and α phases for the latter alloy. Major application fields are both engineering and medical fields for the former alloy and mainly medical fields for the latter alloy.

Another comparison between the basic characteristics between these two alloys is shown in Fig. 44. The critical stress is plotted as a function of test temperature for Ti– 50 at.%Ni and Ti–26 at.%Nb alloys in the left figure included in Fig. 44. From these data and their stress–strain curves, the basic characteristics of these two alloys can be obtained as shown in the table included in Fig. 44. The





- (1) Ti-Nb
- (2) Ti-Nb-X(X=Zr, Ta, Mo, Au, Pd, Pt, Al, Ga, Ge, Si, O, N, B, C)
- (3) Ti-Mo-X(X=Ta, Nb, Zr, Au, Pd, Pt, Al, Ga, Ge)
- (4) Ti-Ta-X(X=Si, Al)
- (5) Ti-Nb-Ta-Zr
- (6) Ti-Nb-Ta-Zr-Mo
- (7) Ti-Nb-Ta-Zr-Mo-(Au, Pt, Al, Sn, Si, O, N)

Fig. 43 Ni-free Ti-based alloys which show the shape memory effect and superelasticity found by the present author's group

slope of the Ti-50 at.%Ni is steeper than that of Ti-26 at.%Nb by more than two times, so that the figure below the table in Fig. 44 can be drawn schematically. From this figure, the stress hysteresis of the Ti-Nb alloy becomes smaller than that of the Ti-Ni even if the temperature hysteresis is larger for the former than the latter. Some examples of the superelastic deformation behavior are shown in Fig. 45, where the stress-strain curves revealing the superelastic deformation of the Ti-22Nb-6Zr with three different heat treatment conditions are compared. The first cycle stress-strain curves of these specimens show that the stress hysteresis is smaller than 100 MPa, which is smaller than that of the Ti-Ni which reveals stress hysteresis larger than 200 MPa. The stability of the superelastic deformation behavior is attractive, but the superelastic strain is only about 2%. It is possible to obtain

Ti-50Ni Ti-26Nb 800 Ti-50at%Ni(673K/3 6ks) $d\sigma/dT$ o Ti-26at%Nb(1173K/1.8ks) 6 2.5 (MPa/K) 600 ε_M (%) 6 3 Stress (MPa) $T_0(K)$ 280 260 400 ∆H(J/mol) -1000 -200 200 σ Ti-Ni Ti-Nb 0 0 100 200 300 400 500 Temperature (K) Ť ΔT Δ

Fig. 44 Comparison of the basic characteristics of Ti-Ni and Tibased alloys

superelastic strain of 6% by alloy design and microstructure control, this is explained in a later section.

Alloy Development

In order to design new shape memory alloys, one of the important topics is to investigate the effect of element addition on M_s . Figure 46 shows the critical stress for inducing the martensitic transformation or the twinning deformation in martensite for four alloys of Ti–22Nb–XZr (X = 2, 4, 6 and 8). The minimum point represents the temperature of M_s . By plotting these M_s temperatures as a function of Zr content, Fig. 47 is obtained, revealing that one percent Zr addition is effective to decrease M_s by 37 K.

Table 3 Basic characteristics of Ti-Ni-based and Ti-based alloys

	Parent	Martensite	Precipitates	Applications
Ti–Ni-based Ti-based	B2 (ordered) BCC (disordered)	Monoclinic orthorhombic R-phase Orthorhombic	Ti ₃ Ni ₄ (Ti ₂ Ni, TiNi ₃) ω phase α phase	Engineering & Medical Medical



Fig. 45 Effect of annealing temperature on the superelastic deformation behavior of Ti-22Nb-6Zr

The effects of other elements addition were also investigated resulting in Fig. 48. For example, oxygen is effective to decrease M_s by 160 K per one % addition.

Orthorhombic Martensitic Transformation

Martensitic transformation can be easily observed on the specimen surface by the optical microscopy as shown in Fig. 49. The Ti–20 at.%Nb and Ti–22 at.%Nb alloys reveal surface relief due to the orthorhombic α'' martensitic transformation, because the M_s temperatures of these specimens are higher than the room temperature. With increasing Nb content, M_s decreases. The Ti–24 at.%Nb shows the combination of martensite and parent phases, because the M_s is around the room temperature revealing no martensite, suggesting that this specimen reveals superelastic behavior.

More precisely, the transmission electron microscopy is applicable to observe the microstructures as shown in



Fig. 46 Effect of test temperature on the critical stress of yielding in Ti-22Nb-XZr alloys



Fig. 47 Effect of Zr content on M_s in Ti-22Nb-XZr alloys



Fig. 48 Effect of the third element on M_s in solution-treated Ti–Nb alloys

Fig. 50, where α " martensite variants can be observed in the three specimens with less Nb contents, but the Ti-26 at.%Nb reveals the parent β phase with fine ω phase particles. The ω phase plays important roles in the Ti-based shape memory alloys, and the effect of ω phase will be explained in a later section on ω phase. Figure 51 shows three phases of the β parent phase, α " martensite phase, and ω phase [63]. The ω phase seems suppressing the growth of the martensite variant.

The transmission electron microscopy also revealed a typical self-accommodation morphology consisting of three martensite variants in two-dimensional morphology or four variants in three-dimensional morphology [65, 69, 81].

Texture

The maximum recoverable strain is estimated by calculating the lattice distortion due to the martensitic transformation utilizing lattice constants of parent β phase and α'' martensite. Figure 52 shows the crystal structures and the lattice constants (a_0 and a', b', c') of the β phase and α'' martensite, respectively, and their lattice correspondence [62]. By using these data, the distortions can be estimated



Fig. 49 Effect of Nb content on the microstructure observed by the optical microscopy on the specimen surface in solution-treated Ti–Nb alloys



Fig. 50 Effect of Nb content on the microstructure observed by the transmission electron microscopy in solution-treated Ti–Nb alloys



Fig. 51 Microstructure consisting of β , α'' , and ω phases in a solution-treated Ti–26 at.%Nb after tensile straining up to a strain of 2.5%



Fig. 52 Nb content dependence of the lattice distortion due to the martensitic transformation in Ti–Nb alloys



Fig. 53 Nb content dependence of transformation strain along [011] in Ti–Nb alloys



Fig. 54 Orientation dependence of the calculated transformation strain in Ti–26 at.%Nb $\,$



Fig. 55 Inverse pole figures corresponding to RD, 45° from the tensile axis and TD

for the three principal axes: η_1 , η_2 , and η_3 . The first distortion η_1 contracts, the second one η_2 expands and the third one η_3 shows few change. The absolute values of η_1 and η_2 decrease with increasing Nb content, indicating that the lattice distortion or shape change due to the martensitic transformation decreases with increasing Nb content. The shape change along [011] direction (ε_{M} [011]) calculated by the above lattice distortions is potted as a function of Nb content in Fig. 53, where $\varepsilon_{M}[011]$ decreases with increasing Nb content. The strain is more than 5% when the Nb content is 18 at.%; however, the M_s is about 500 K which is too high for applications. The M_s is around room temperature for 26 at.%Nb specimen, which is good for applications. But, in this case, the transformation strain is only 2.5%, which is not attractive enough for applications. The orientation dependence of transformation strain is shown in Fig. 54, where the maximum strain is along the [011] direction, while the minimum strain is along [001] direction. There are two problems to be solved: one is increasing the transformation strain by alloy design, while another is controlling the texture in order to have a strong [011] texture along the rolling direction in order to maximize the available strain. The alloy design for achieving large strain is explained in a later section. Here, the texture topic is described in some detail as follows.



Fig. 56 Inverse pole figures corresponding to the rolling direction for Ti-18Zr-XNb-YSn (at.%) alloys

The Ti-22Nb-6Ta (at.%) alloy which was solution treated at 1173 K for 1.8 ks was investigated to know the texture. Figure 55 shows that the inverse pole figures corresponding to three directions on the rolling plane, i.e., the rolling direction (RD), 45° from RD and the transverse direction (TD) show high axis densities at [011], [012], and

303

[111], respectively [80, 95]. When the same alloy was heat treated at 873 K, a different texture was observed, indicating that heat treatment condition affects the texture.

Alloy composition also affects the texture. Figure 56 shows the inverse pole figure for RD of Ti-18Zr-(9-16)Nb-(0-4)Sn (at.%) alloys, revealing that the texture changes by modifying the alloy composition [94]. The distribution of crystal directions is rather random and the intensity is weak in the 0 at.%Sn alloy. On the other hand, the Sn-added alloys show a strong axis density distribution, indicating that the $\langle 011 \rangle_{\beta}$ direction aligns parallel to RD preferentially. Large transformation strain can be expected in such Sn-added specimens. Figure 57 shows the stress–strain curves obtained by cyclic deformation until 500 times [94]. These curves show the superelastic deformation with recoverable strain of about 5% and very stable properties until 500 cycling.

Omega Phase

There are two types of ω phases, athermal and thermal types. The athermal ω phase appears always even in solution-treated specimens. The thermal ω phase is formed by aging treatment at intermediate temperatures. Both of them affect the properties of Ti-based alloys. The crystal structure of ω phase can be constructed by collapsing two adjacent $\{111\}_{\beta}$ planes toward each other, leaving the third plane intact. When the collapse is perfect, the ideal ω phase is formed having the hexagonal structure. When the collapse is not perfect, the diffused ω phase is formed having the trigonal structure. Because of this ω phase formation process, there are four ω phase variants which have the orientation relationship with the parent β phase as shown in Fig. 58: $\{0001\}_{\omega}//\{111\}_{\beta}$, $[11-20]_{\omega}//[110]_{\beta}$ [62].



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 $[0001]_{\omega} //[1\overline{1}1]_{\beta}, \ [10\overline{1}1]_{\omega} //[1\overline{1}0]_{\beta}$



Fig. 58 A high-resolution electron micrograph showing the lattice correspondence between the β parent phase and ω phase

Figure 59 shows the effect of aging time on the ω phase formation in solution-treated and aged Ti–26 at.%Nb samples. The solution-treated sample reveals very fine small athermal ω phase particles, while the thermal ω phase particle formed by aging increases the size and density with increasing the aging temperature until 573 K, then decreases with further increasing temperature until 873 K [62]. This indicates that 573 K is most effective aging temperature for the formation of thermal ω phase.

Aging time is also one of the important factors affecting the ω phase formation. Figure 60 shows the effect of aging time at 573 K on the formation of ω phase. The size and density of ω phase continuously increase with increasing time until 36 ks.

Effects of Adding Elements and Large Shape Recovery

Sn reveals another interesting effect on deformation behavior other than increasing transformation strain as shown in the above section. Figure 61 shows the effect of adding Sn on the deformation behavior in Ti-15Nb-3Mo (at.%) [78]. Sn addition is also effective to decrease the size and density of ω phase by comparing the photographs of Ti-15Nb-3Mo and Ti-15Nb-3Mo-1Sn in the figure. This indicates that Sn addition is effective to increase M_s and decrease friction force against the movement of the habit planes of martensites, because Sn suppresses the formation of ω phase. Therefore, the critical stress for inducing the martensitic transformation (σ_M) decreases with increasing Sn content until 1.0Sn addition, suggesting that $M_{\rm s}$ increases. This is an opposite sense if considering the intrinsic effect of Sn addition: M_s decreases with increasing Sn content if not considering the ω phase. This can be understood when considering that the effect of ω phase is more effective on M_s than the intrinsic effect of adding Sn. Therefore, the σ_M starts to increase with further increasing Sn from 1.0 at.% although the corresponding stress-strain curves are omitted, because the density of ω phase has become already low enough at 1.0 at.%Sn, so that further decrease in ω phase will not affect effectively, then the intrinsic effect of adding Sn becomes prominent in decreasing $M_{\rm s}$. On the other hand, the critical stress for the reverse martensitic transformation ($\sigma_{\rm R}$) monotonically increases with increasing Sn content. This can be



Fig. 59 Effect of aging temperature on the formation of ω phase in Ti–26 at.%Nb aging treated for 3.6 ks





Fig. 61 Effect of Sn addition on microstructure and superelastic properties of Ti– 15Nb–3Mo



understood by considering that the ω phase disappears after the martensitic transformation, hence the ω phase does not affect σ_R or the reverse martensitic transformation temperature. The O addition also affects the properties of Ti-based alloys. It is clearly shown that O addition increases $\sigma_{\rm M}$ and the strength by comparing the stress–strain curves of Ti–22Nb–XO (at.%) alloys in Fig. 62 [74].



Fig. 62 Effect of oxygen addition on stress-strain curve in Ti-22Nb-XO alloys



Fig. 63 Alloy composition dependence of the transformation strain and deformation behavior in Ti–Nb–Zr alloys

The effect of Zr addition on the transformation strain is shown in Fig. 63, where contour bands with darker color show the higher transformation strain region, and alloy composition regions revealing shape memory effect and superelasticity are also shown by open circles and closed circles, respectively [95, 102]. From these data, it is possible to pick up the alloy composition which shows the superelasticity with a large recovery strain. In these ternary alloys, Zr is substituted for Nb in order to increase the transformation strain with keeping the transformation temperature unchanged so as to reveal the superelasticity at room temperature. The reason why this is possible is explained below. In the Ti-Nb binary alloys, Nb addition is effective to decrease M_s by about 43 K/ at.% and to decrease the transformation strain by 0.34%/ at.%. Zr addition to Ti-Nb alloys is also effective to decrease M_s

- + **Zr:** increases transformation strain but accelerate the formation of ω phase.
- + Sn(Al) : suppresses formation of ω phase and increases transformation strain.
- + O, N: create nano-domains and increase critical stress for slip deformation.
- Further improvement by thermomechanical treatment and texture control.
- More than 6% of superelastic recovery.



Fig. 64 Effects of each element (Zr, Sn, Al, O, or N) on transformation strain, formation of ω phase, strength, and superelastic properties



Fig. $65\,$ Comparison of the stress–strain curves of steel, Gum metal, and Ti–Ni

and the transformation strain by 36 K/ at.% and 0.13%/ at.%, respectively. It is clear that Zr addition has a weaker effect on the transformation strain, while it decreases M_s similarly to the Nb addition. As a result of this consideration, the increase in Zr content as a substitute for Nb while maintaining the same transformation temperature to keep the superelasticity increases the transformation strain [95, 102].

Figure 64 summarizes the effects of adding elements on the deformation behavior of Ti–Nb alloys as follows: Zr increases the transformation strain but accelerates the formation of ω phase. Sn or Al suppresses the formation of ω phase and increases the transformation strain. O or N creates nano-domains and increases the critical stress for slip deformation. Regarding the nano-domains, detailed description is found in the next section. By considering the above effects, Ti–Nb–Zr(Sn, Al)–(O, N) alloys have been found to possess the superelasticity with a large recovery strain of 6% [93, 94].



Fig. 66 Effect of O addition on the stress–strain curve of Ti–26Nb– (0–1.0)O and X-ray diffraction peak position variation upon loading



Fig. 67 A Nano-domain formed around an oxygen atom

Nano-domain Transformation

Non-linear Elastic Deformation

Addition of interstitial elements such as O and N reveal unique effects on the deformation behavior in Ti-based alloys. Figure 65 shows the stress–strain curves of steel, Gum metal (Ti-based alloy), and Ti–Ni. The Young's modulus of Gum metal is lower than that of steel which has a similar strength as Gum metal. The Gum metal including 1.2%O is characterized by the low Young's modulus and



Fig. 68 Micrographs showing dark field images of **a**, **b** annealed and **c**, **d** as-rolled specimens, revealing two types of nano-domain variants V5 and V6 among six nano-domain variants

non-linear large elasticity. If compared with the superelasticity of Ti–Ni alloy which shows the apparent Young's modulus of only 10 GPa, which is much smaller than that of the Gum metal 50 GPa. But, people feel the Young's modulus of the Gum metal is small if compared with conventional metals and alloys. This unique non-linear elasticity and the low Young's modulus of the Gum metal can be understood as follows.

Figure 66 shows the result of simple Ti-Nb-O alloys [83]. Even in this simple alloy system, the non-linear elasticity and the low Young's modulus can be achieved by adding 1%O. Without adding oxygen, this alloy shows typical superelasticity induced by the martensitic transformation upon loading and its reverse transformation upon unloading as shown by the stress-strain curve of Ti-26Nb. The Ti-26Nb binary alloy reveals typical first-order martensitic transformation, because a X-ray diffraction peak of the α'' martensite appears at a different position apart from the parent β phase position once the transformation occurs upon loading, representing the characteristics of the first-order transformation. However, in case of 1% oxygen added specimen, such a first-order martensitic transformation does not occur. The β phase peak shifts continuously to the higher angle position during the nonlinear elastic deformation upon loading. This suggests that the non-linear elastic deformation appears due to the second-order phase transformation.



Fig. 69 Invar effect of Gum metal

Figure 67 shows the lattice distortion elements for the α " martensitic transformation [83]. From the β phase structure to the α " martensite, shuffling along $\pm [011]_{\beta}(0-11)_{\beta}$ is necessary in addition to lattice contraction along

Fig. 70 Diffraction pattern and nano-domains V5 and V6 at room temperature in Gum metal

[100] and expansion along [011], which correspond to a shear mode of $(-211)_{\beta}[111]_{\beta}$. The O locates at the center of the octahedron, and hence the lattice of the parent β phase is distorted to generate strain energy. In order to reduce the strain energy around the oxygen atom, the shuffling is effective. This indicates that oxygen assists the martensitic transformation, because the shuffling is necessary to form the martensite structure. However, the perfect lattice distortion to form the martensite is suppressed by the surrounding oxygen-induced strain fields. This local lattice distortion around O is named nano-domain which is an intermediate phase between the β phase and the α'' martensite [83]. Thus, there are six nano-domain variants similarly to the martensite variants [83].

Nano-domains can be observed by the transmission electron microscopy as shown in Fig. 68. These micrographs show dark field images of (a), (b) annealed and (c), (d) as-rolled specimens, revealing two types of nano-domain variants V5 and V6 among six nano-domain variants. The two nano-domains equally exist in the annealed specimen as shown in Fig. 68a, b, while favorable nano-



Ti-23Nb-2Zr-0.7Ta-1.2O Gum metal

As-rolled specimen observed at RT.

Fig. 71 Diffraction pattern and nano-domains V5 and V6 at 90 K in Gum metal





As-rolled specimen observed at 90K.



Fig. 72 The mechanism of Invar effect of Gum metal

domain V6 is grown due to the internal stress induced by the cold-rolling as shown in Fig. 68d but the volume fraction of nano-domain V5 is similar to that of the annealed specimen as shown in Fig. 68c. This indicates that the applied stress or internal stress grows the favorable nano-domain variant V6 inducing specimen distortion, causing for the non-linear elastic deformation or Invar effect. It was also observed by the in situ transmission electron microscopy that the intensity of the diffraction spot of the most favorable nano-domain V6 increased by applying stress to the specimen, indicating that the applied stress grows the V6 nano-domain variant [83].

Invar Effect

Another unique property of Gum metal is Invar effect as shown in Fig. 69 [84], where the thermal expansion of Cu is shown as an example of normal metals. An annealed plate specimen of Gum metal also reveals similar thermal expansion along both rolling direction (RD) and transverse direction (TD). However, an as-rolled specimen reveals Invar effect along the RD, but normal thermal expansion behavior appears along the TD even for the as-rolled specimen.

In the annealed specimen, all nano-domain variants exist equally and uniformly indicating no favorable variant,



Fig. 73 Heating-induced forward martensitic transformation in Ti-23Nb-1.00

because there is no stress field in the annealed specimen. However, in the as-rolled specimen, the growth of V6 nano-domain can be observed due to the internal stress field as shown in Fig. 68d for oxygen-added Ti–Nb or Fig. 70c for the Gum metal, suggesting that the specimen expanded along the rolling direction due to the growth of V6 nano-domain. The nano-domain can also further grow by cooling under stress as shown in Fig. 71c [84]. Heating up to room temperature shrinks the nano-domain V6 as shown in Fig. 70c.

Now, the mechanism of Invar effect of Gum metals can be understood as shown in Fig. 72 [84]. The as-rolled plate has a strong texture of $\{001\}_{\beta}$ $\langle 110 \rangle_{\beta}$, thus the plate is similar to a single crystal with this crystal orientation. In such an as-rolled specimen, the possible nano-domains are V5 and V6 considering the contraction along the normal direction (ND), because the two nano-domain variants have a' axis of the nano-domain (or the α'' martensite) along the



Fig. 74 Variation of strain and X-ray diffraction peak positions during the heating-induced martensitic transformation upon heating in Ti-23Nb-1.0O





Fig. 75 A schematic phase diagram showing α , β , and ω phases for Ti–Mo, Ti–Nb, and Ti–Ta systems

normal direction. However, if the elongation along the rolling direction is considered, only V6 nano-domain is the favorable variant, because V6 nano-domain has the extended b' axis along the rolling direction. If the specimen is cooled, V6 nano-domain grows resulting in further elongation along the rolling direction. However, by cooling the specimen shrinks by the normal thermal expansion effect. Both the effects are cancelled by each other,



Fig. 76 Ms temperatures of Ti-Ta-1X solution-treated specimens and specimens aged at 573 K for 3.6 ks

resulting in no shape change during cooling and heating only along the RD. This is the Invar effect of Gum metals.

Heating-Induced Martensitic Transformation

Now, another unique property was observed in oxygen added Ti alloys. This is heating-induced forward martensitic transformation. Usually, the martensitic transformation occurs during cooling. Thus, the heating-induced martensitic transformation is unique behavior. Figure 73 shows the heating-induced martensitic transformation observed in Ti-23Nb-10 [85]. Cooling down to 173 K, then heating, cooling and heating were conducted as shown in Fig. 73a. During this temperature variation, the specimen revealed shape change under load as shown in Fig. 73b. During the first heating, the specimen shows elongation after reaching temperature T_1 . This elongation occurs due to the forward martensitic transformation. By further heating, the reverse transformation occurs showing shape recovery finishing at temperature T_2 . However, during the following cooling, normal martensitic transformation takes place at M_s followed by elongation. This is the intrinsic M_s of this specimen without the effect of O. Next heating induces the normal reverse transformation followed by shape recovery finishing at $A_{\rm f}$. This unique behavior can be understood as follows: Nano-domains suppress the growth of other nano-domains. So the martensitic transformation does not occur even if the temperature is below the intrinsic M_s of this specimen. After reaching T_1 temperature upon heating, oxygen atoms become easy to move by enhanced diffusion condition at high temperatures. Then, the martensitic transformation starts at T_1 , because it is lower than M_s and the martensite is stable at T_1 , and by further heating the martensite phase becomes unstable so that the reverse transformation takes place to induce shape recovery. After reaching at high temperatures, oxygen atoms move easily, so that oxygens do not suppress the lattice distortion for the martensitic transformation and the reverse transformation anymore above T_1 . The conventional martensitic transformation occurs at M_s inducing normal elongation upon cooling as shown by the dashed line. After cooling down to 173 K, the specimen was again heated. The reverse martensitic transformation occurs followed by shape recovery, showing the normal shape memory effect.

Figure 74a shows the shape change A–J due to the heating-induced martensitic transformation. Figure 74b shows the corresponding X-ray diffraction peaks, revealing the formation of martensite peak at 393 K, followed by the growth of the peak until 433 K and the following shrinkage of the peak until 493 K. This in situ observation clearly reveals the heating-induced martensitic transformation. More details about this transformation are explained in Ref. [85].

High-Temperature SMAs

Ti-based high temperature shape memory alloys, Ti-Tabased alloys, were also developed by the present author's group. The Ti–Ta is a β Ti-based alloy, so that cold workability exceeds 90%. There is no problem of cold workability for these alloys, but functional stability is a problem to be solved for practical applications. The shape memory effect is generally deteriorated by the formation of ω phase at an intermediate temperature region. Figure 75 shows a schematic phase diagram of Ti-X systems, where three types of alloys are compared, i.e., Ti-Mo, Ti-Nb, and Ti-Ta. Each element of Mo, Nb, and Ta has a specific effect on M_s, i.e., -80 K/at.%Mo, -40 K/at.%Nb, and -30 K/at.%Ta, respectively. In order to have the same M_s to reveal the superelasticity at room temperature, the necessary elements are Ta, Nb, Mo in order of amount. This means that Ta is most effective to reduce the amount of ω phase, while Mo is least effective among the three elements. Therefore, Ta was considered as the most promising element for developing the high-temperature shape memory alloy among Ti-based alloys [97].

In order to further reduce the formation of ω phase to increase functional stability, the candidates for the effective third elements were selected by conducting the investigation as shown in Fig. 76 [98, 99], where the M_s temperatures of a solution-treated specimen and a following aging-treated specimen are compared for each third element. Two elements, Sn and Al, were found to be effective to minimize the decrease of M_s by aging treatment. Thus, Ti–Ta–Sn and Ti–Ta–Al alloys had been found as deformable high-temperature shape memory alloys [98, 99].

Concluding Remarks

The present author's research results on shape memory alloys are compactly summarized including Ti–Ni-based alloys and Ni-free Ti-based alloys. If the readers need to know more in detail about each topic on these alloys, reference papers are available for this purpose. Review papers on some of the above-mentioned topics on Ti–Ni-based alloys are available for bulk Ti–Ni alloys [59], sputter-deposited thin films [60], and high-temperature shape memory alloys [38]. Review papers on some of the above-mentioned topics are available for Ti-based alloys are available for Ti-based alloys are available for Ti-based alloys [92, 102], and Ti–Nb–(Zr, Ta) alloys [95].

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