Coherent Precipitates as a Condition for Ultra-Low Fatigue in Cu-Rich $\text{Ti}_{53.7}\text{Ni}_{24.7}\text{Cu}_{21.6}$ Shape Memory Alloys

L. Bumke¹ · N. Wolff² · C. Chluba^{1,3} · T. Dankwort² · L. Kienle² · E. Quandt¹

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Abstract Sputtered Ti-rich TiNiCu alloys are known to show excellent cyclic stability. Reversibility is mostly influenced by grain size, crystallographic compatibility and precipitates. Isolating their impact on cyclic stability is difficult. Ti_2Cu precipitates for instance are believed to enhance reversibility by showing a dual epitaxy with the B2 and B19 lattice. Their influence on the functional fatigue, if they partly lose the coherency is still unknown. In this study, sputtered $\text{Ti}_{53.7}\text{Ni}_{24.7}\text{Cu}_{21.6}$ films have been annealed at different temperatures leading to a similar compatibility ($\lambda_2 \sim 0.99$), grain size and thermal cyclic stability. Films annealed at 550 °C exhibit a superior superelastic fatigue resistance but with reduced transformation temperatures and enthalpies. TEM investigations suggest the formation of Guinier–Preston (GP) zone-like plate precipitates and point towards a coherency relation of the B2 phase and finely distributed Ti_2Cu precipitates (~ 60 nm). Films annealed at 700 °C result in the growth of Ti_2Cu precipitates (~ 280 nm) with an irregular distribution and a partial loss of their coherency. Thus, GP zones are assumed to cause the reduction of transformation temperatures and enthalpies due to increased internal stresses, whereas the coherency relation of both, Ti_2Cu and GP zones, help to increase the superelastic stability, well beyond 10^7 cycles.

Keywords Fatigue · Shape memory films · Superelasticity · Hysteresis · Coherent precipitates · X-ray diffraction

Introduction

Tailoring and understanding the fatigue mechanism in shape memory alloys (SMAs) is crucial for biomedical implants, actuation applications or possible future applications like elastocaloric cooling. These devices demand for a high cyclic stability exceeding millions of cycles [1, 2]. Despite the large progress in SMAs in recent years, a deeper understanding, how certain factors can influence the cyclic stability is necessary to define boundary conditions for a directed search of SMAs with high cyclic reversibility of the martensitic phase transformation, which is the base for SMAs. In case of TiNiCu shape memory alloys with a Cu content larger than approximately ~ 9.5 at% the structural transformation is following the B2 (cubic) to B19 (orthorhombic) path [3]. Typically, the transformation is altered with increasing cycle number by the generation and movement of dislocations leading to a stabilization of martensite and ultimately to a breakdown of the materials itself, which is especially true for the effect of superelasticity. It is nowadays well-accepted that grain size [4, 5], coherent precipitates [6, 7], crystal orientation [8, 9] and a good crystallographic compatibility [10, 11] can improve the functional stability by increasing the resistance to dislocation formation and movement. Crystallographic compatibility describes the fitting of the austenite and martensite phase at the interface and can be defined by a set of three equations, also called cofactor conditions. If fulfilled, also called supercompatibility, an infinite number of possibilities exists to form an interface without elastic

✉ L. Bumke
labu@tf.uni-kiel.de

¹ Inorganic Functional Materials, Institute for Materials Science, Faculty of Engineering, Kiel University, Kiel, Germany

² Synthesis and Real Structure, Institute for Materials Science, Faculty of Engineering, Kiel University, Kiel, Germany

³ Acquandas GmbH, Kaiserstrasse 2, 24143 Kiel, Germany

energy (the case with the ordered middle eigenvalue $\lambda_2 = 1$ of the transformation stretch matrix U) between the austenite and twinned martensite lattice [12–14]. Materials satisfying $\lambda_2 = 1$ show the smallest thermal hysteresis and best functional stability, when other microstructural features among a set of different samples are similar [10, 11]. Recent findings and developments using the cofactor conditions based on the geometrically non-linear theory of martensite lead to the discovery of SMAs showing ultra-low fatigue properties and vanishing thermal hysteresis [10, 15]. Being a rather strict condition in terms of alloy development, a diversification of the boundary conditions is desirable by taking other microstructural features into account. SMAs fabricated by the sputter deposition technique allow for the fabrication of materials with low inclusion content and high purity making them the ideal candidate for high fatigue applications. Since these films are amorphous in the as-deposited state, a particular fine microstructure is formed upon crystallization. In sputtered films, fine precipitates which are not observed in bulk materials e.g. for Ti-rich NiTi can evolve. Extensive research by Ishida et al. [16] on magnetron sputtered Ti-rich TiNiCu SMA films revealed grain sizes below 1 μm and identified Ti_2Ni , Ti_2Cu , TiCu precipitates as well as Guinier–Preston zone-like precipitates (GP zones) influencing the shape memory response significantly. The studies point out that coherent GP zones are intragranular precipitates with disk shape and dimensions of a few atomic layers forming on $\{100\}_{\text{B}_2}$ planes along the $[001]$ and $[010]$ directions. The orientation relationships at low annealing temperatures (500 $^{\circ}\text{C}$) are $[100]_{\text{GP zone}} // \langle 100 \rangle_{\text{B}_2}$ and $(001)_{\text{GP zone}} // \{001\}_{\text{B}_2}$, which is known to increase the slip resistance significantly (e.g. [7, 17, 18]) due to coherency of the strain fields. The studies also notice an orientation relationship of intergranular Ti_2Cu precipitates with the matrix similar to the GP zones, which evolves at higher temperatures. Incoherent or semi-coherent precipitates like Ti_2Ni obstruct the growth of martensite twins, whereas coherent GP zones and intergranular Ti_2Cu only slightly suppress the lateral growth resulting in zigzag-shaped twin boundaries or in a change of direction of the twins in case of Ti_2Cu [19, 20]. However, a cyclic dependency of the shape memory characteristics were not reported. Chluba et al. reported that GP zones are not necessary to create materials with ultra-low fatigue properties exceeding 10^7 cycles in a $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ alloy. Small grain sizes < 500 nm and Ti_2Cu precipitates present at the grain boundaries with a dual epitaxy to austenite and martensite with retained austenite, which is likely to guide the phase transformation [21, 22], are responsible for the outstanding fatigue resistance. Though, the influence of Ti_2Ni precipitates present in large amounts in their films could not be ruled out completely. SMA films with

$\text{Ti}_{54.7}\text{Ni}_{30.7}\text{Cu}_{12.3}\text{Co}_{2.3}$ stoichiometry annealed at 700 $^{\circ}\text{C}$ solely exhibiting Ti_2Ni precipitates, but none of Ti_2Cu , also withstood 10^7 cycles perhaps related to outstanding crystallographic compatibility, as well as small grain sizes in the sub μm range [15, 21].

To minimize the effect of Ti_2Ni precipitates in this study, a composition for which mostly Ti_2Cu precipitates are expected for sputtered TiNiCu films [23] is chosen. Preliminary studies on the $\text{Ti}_{53.7}\text{Ni}_{24.7}\text{Cu}_{21.6}$ composition have been reviewed by Gu et al. [15] indicating that an increased size and irregular distribution of Ti_2Cu precipitates reduces the cyclic stability. The addition of cobalt benefits a high efficient elastocaloric material, enabling the material to withstand 2×10^7 cycles [24]. In this study we give a detailed discussion of different factors influencing the cyclic stability, enabling $\text{Ti}_{53.7}\text{Ni}_{24.7}\text{Cu}_{21.6}$ annealed at 550 $^{\circ}\text{C}$ to show near perfect reversibility of superelasticity after 1×10^7 cycles, whereas annealing at higher temperatures (700 $^{\circ}\text{C}$) lead to a strong degradation within 200 superelastic cycles.

Experimental

Materials and Processing

Amorphous TiNiCu films with a thickness of around 20 μm were deposited on a structured 4 inch silicon wafer by using a Von Ardenne CS730S (Von Ardenne, Germany, base pressure $< 3 \times 10^{-7}$ mbar) cluster magnetron sputtering device with a 4 inch TiNiCu target (300 W, 2.3×10^{-3} mbar, 20 sccm Ar). The films were released from the Si-substrates by wet etching of a Cu sacrificial layer. The basic structuring process is described in detail by Lima de Miranda et al. [25]. Films were crystallized by using rapid thermal annealing (RTA) (Createc Fischer RTA-6 SY09, Germany, base pressure $< 1 \times 10^{-7}$ mbar) at 550 $^{\circ}\text{C}$ and 700 $^{\circ}\text{C}$ for 15 min. The composition of the amorphous film was determined to be $\text{Ti}_{53.7}\text{Ni}_{24.7}\text{Cu}_{21.6}$, averaged over an 4 inch wafer, using a Helios NanoLab 600 scanning electron microscopy (SEM) (FEI, Germany) equipped with an energy-dispersive X-ray spectroscopy (EDS) silicon drift detector (Oxford Instruments, UK). To increase the precision of the quantitative analysis, a binary TiNi standard was used.

Microstructural Analysis

To investigate the microstructure of each sample by transmission electron microscopy (TEM), film cross-section samples were prepared by the focused ion beam (FIB) method, attached to a Cu grid and milled to electron transparency using standard procedures on the Helios

NanoLab 600 SEM. Scanning (S)TEM and EDS measurements were conducted using a Tecnai F30 G2 STwin microscope operated at 300 kV (TFS, USA) and a JEM2100 instrument operated at 200 kV (JEOL, Japan). Lattice parameters and microstructural characteristics were analysed by X-ray diffraction (XRD) using a SmartLab 9 kW diffractometer (Rigaku, Japan) equipped with a Cu- K_α radiation source ($\lambda = 1.5406 \text{ \AA}$), a K_β filter and 2-D Hypix3000 detector operated in 1D-mode up to $2\theta = 100^\circ$. The temperature variation between -40°C and 90°C was realized using a DCS350 cooling stage (AntonPaar, Germany). Lattice parameters were determined by using a Pawley [26] refinement with the software TOPAS-Academic V6 (Coelho Software, Australia). The instrumental profile was obtained by measuring a LaB_6 powder (NIST660C) and incorporated into the fitting procedure. Reflection shapes were described by using a size and strain contribution from Lorentzian and Gaussian functions as implemented in the TOPAS software. The following crystal structures were used for the determination of the lattice parameters: TiNiCu-B2 (SG221, $Pm\bar{3}m$, austenite), TiNiCu-B19 (SG51, $Pmmb$, martensite), Ti_2Cu (SG139, $I4/mmm$), and Ti_2Ni (SG227, $Fd\bar{3}m$). First, the background was manually fitted, then reflection positions and the strain and crystallite size parameter were adjusted. The cofactor conditions were calculated based on the determined lattice parameters using a Matlab script, which is based on the theoretical calculations presented by Chen et al. [13, 27].

Shape Memory Properties

The thermal analysis as well as thermal cycling were conducted with a differential scanning calorimeter (DSC) Perkin Elmer DSC 1 (Perkin Elmer, USA) with a heating and cooling rate of $10^\circ\text{C min}^{-1}$ for cycle 1, 10, 20, 30 and $40^\circ\text{C min}^{-1}$ in between. Latent heat as well as transformation temperatures were determined using the tangent method. Thermal hysteresis was calculated according to $\Delta T = 1/2(A_s + A_f - M_s - M_f)$, where A_s and A_f correspond to the austenite start and finish temperatures and M_s/M_f correspond to the martensite start and finish temperatures. The mechanical properties were evaluated using stripes with a width of 1.5 mm utilizing a universal tensile testing device Z.05 (Zwick Roell, Germany) under controlled ambient temperatures. The transformation plateau was similar for both samples. The strain was corrected by the stiffness of the traverse. High fatigue cycling was conducted with a self-built tensile tester using a P-601.4SL piezoactuator (Physik Instrumente, Germany) and a load-cell ALF318 (Althen, Germany) with a DMS amplifier. Stable ambient temperatures were reached by a PID controlled chamber surrounding the setup ($40 \pm 1^\circ\text{C}$ close to sample). Dogbone-shaped samples with a parallel length of

4 mm and a width of 0.5 mm were used. To minimize the effect of edge defects, the samples were electrochemically polished. Slow cycles at a strain rate of 0.01 Hz were conducted at the beginning, in between and at 1×10^7 cycles. Fast cycling was realized with a frequency of 20 Hz.

Results and Discussion

Microstructure Overview

The microstructures of the samples annealed at 550°C (referred to as LT) and 700°C (referred to as HT) exhibit strong differences with respect to the sizes of the precipitates. The high-angle annular dark field (HAADF) STEM micrographs (Fig. 1) allow to differentiate between precipitates and grains of TiNiCu due to a specific Z-contrast. Ti-rich precipitates are displayed with less intensity compared to the brighter grains of the TiNiCu-B2/B19 phase.

Electron diffraction experiments reveal an overall austenite state for the LT sample and a coexistence of austenite and martensite for the HT sample at room temperature, which is for the B19 phase further evidenced by the appearance of characteristic twinned structures. The TiNiCu maximum grain size is below $1 \mu\text{m}$ for both heat treatments but is slightly larger for the HT sample. Such invariance of the grain size of the TiNiCu phase is in line with other investigations from Ishida et al. for Ti-rich TiNiCu shape memory alloys [7, 28] and can be explained by the complex crystallization process in sputtered SMAs from the amorphous phase. Typically, first nucleation and crystallization processes of the precipitates followed by the formation of the TiNiCu phase [22], for which large grain growth is constrained by the presence of precipitates. Both samples show Ti_2Cu precipitates at the grain boundaries (Fig. 1 and Appendix Figs. 6, 7). The Ti_2Cu precipitates in the LT sample have an average size of $\sim 60 \text{ nm}$ and are regularly dispersed at the grain boundaries. In comparison the Ti_2Cu precipitates in the HT sample exhibit averaged dimensions of approximately 280 nm and scatter irregularly between the TiNiCu grains. Further, distinct intra-granular precipitation is observed in the HT sample, which differentiate in shape and size: Larger roundish (Appendix Figs. 7 and 8) and rectangularly shaped precipitates which seem to exhibit an incoherent or semicoherent connection to the matrix and very small rectangularly shaped precipitates (Appendix Fig. 8), which potentially exhibit a coherent or semicoherent relationship to the matrix according to their orthogonal arrangement. However, experimental evidence for any orientation relationship or their crystal structure could not be determined by selected area electron diffraction (SAED) due to their small

Fig. 1 STEM-HAADF images of the LT (a) and the HT sample (b) at room temperature reveal a similar grain size of TiNiCu for both samples, but a large difference in the sizes and arrangement of Ti_2Cu precipitates (dark contrast). The sizes of the precipitates is approx. 60 nm for the LT sample and 280 nm for the HT sample, respectively.

dimensions, nor by high-resolution imaging which was severely limited by the sample thickness. Chemical analysis by EDS measurements, as well as structure determination by X-ray diffraction (Appendix Fig. 9), suggest that the larger intragranular precipitates could be mainly Ti_2Ni -type and that the precipitates at the TiNiCu grain boundaries are mainly Ti_2Cu -type (Appendix Fig. 7). Though, a small amount of Ti- and Ni-rich precipitates can be found at the grain boundaries as well for 700 °C annealed TiNiCu. In contrast, for binary Ti-Ni alloys Ishida et al. observed only metastable spherical precipitates of Ti_2Ni and plate precipitates within the grains and spherical Ti_2Ni precipitates at the grain boundaries after long annealing times (10–100 h) and/or high temperatures [29, 30]. Additional X-ray diffraction measurements of TiNiCu films annealed at higher temperatures (800 °C) suggest that only incoherent Ti_2Ni precipitates remain at higher temperatures (see Appendix Fig. 9) and are regarded as the stable phase in the investigated composition. At lower annealing temperatures (700 °C) two types of cubic Ti_2Ni or Ti-rich precipitates exists with different lattice parameter, but with the same cubic crystal structure as will be discussed below.

Orientation Relationship Precipitate-Matrix

Previous results from Chluba et al. [21] investigating the high cyclic stability in $\text{Ti}_{54}\text{Ni}_{34}\text{Cu}_{12}$ and pointed out that grain boundary Ti_2Cu precipitates are coherently coupled to both the austenite and martensite. Those could act as sentinels for the phase transformation and are believed to be the reason for the high cyclic stability compared to samples which contain only Ti_2Ni precipitates. Therefore this study focusses on the orientation relation of Ti_2Cu precipitates with the TiNiCu matrix. In a previous review by Gu et al. [15], first results and measurements of the presented material suggested that Ti_2Cu precipitates in the HT sample exhibit no coherency relation. In this study, a

deepened evaluation of the Ti_2Cu /TiNiCu orientation relationship for the LT and HT samples could identify the coherency relation $(001)_{\text{Ti}_2\text{Cu}}// (001)_{\text{B2}}$ for the LT sample as presented in Fig. 2. For the HT sample an orientation relation between larger precipitates (280 nm) of Ti_2Cu and the B2/B19 phase was not observed on a reasonable number of about 10 adjacent Ti_2Cu and TiNiCu grains (Fig. 2b). However, the identical $(001)_{\text{Ti}_2\text{Cu}}// (001)_{\text{B2}}$ relation could be observed on occasion between a small Ti_2Cu precipitate (ca. 150 nm) and remaining austenite. The following scenario for the development of the orientation relationship as a function of the heat treatment is possible: With increasing annealing temperature from 550 °C to 700 °C the grain boundary Ti_2Cu precipitates grow in size and scatter along the grain boundaries. At a critical size ($>$ ca. 150 nm) they likely do not establish coherency to the matrix and act as a passive phase. Besides the description of Ti_2Cu precipitates located at the grain boundaries in the LT sample, areas with patchy contrast of orthogonal stripes exhibiting dimensions of $\sim 20 \text{ nm} \times 1\text{--}2 \text{ nm}$ have been observed within some of the TiNiCu grains (Fig. 3). In literature, the appearance of such HRTEM phase contrast patterns in SMA alloys is related to local strain fields surrounding small intragranular plate-like precipitates, which are fully coherent with the matrix [18, 31, 32]. For Ti-rich TiNiCu alloys, the formation of intragranular plate-like precipitates is described occurring between 500 °C and 600 °C and have been typically indexed as GP zones (500 °C) or Ti_2Cu precipitates with C11_b structure (600 °C) [18]. A HRTEM investigation on the cause of the strain fields, was however precluded by the sample quality. Therefore, an electron diffraction experiment (Fig. 3b) was performed to obtain structural information to be compared with literature. The presented SAED pattern features cross-like diffuse streaks along the $\langle 100 \rangle$ directions originating at B2 reflections which is in close resemblance to the diffuse intensities observed in electron diffraction patterns recorded on SMA films

Fig. 2 Bright field images of the LT (a) and HT (b) samples display Ti_2Cu precipitates and TiNiCu grains. The area of interests are marked with white circles. (a) The orientation relationship $(001)_{\text{Ti}_2\text{Cu}}// (001)_{\text{B2}}$ for the precipitate with the B2 matrix of the LT sample is extracted from the experimental electron diffraction patterns and the corresponding superposition simulation. The

precipitate size was determined to be around 60 nm. (b) For the HT sample, no systematic orientation relation was observed between larger precipitates and the B2/B19 matrix. The presented micrograph displays a grain of remaining austenite (B2) and larger Ti_2Cu precipitates which exhibit no structural orientation relationship with the matrix as concluded from SAED experiments.

Fig. 3 Plate-like precipitates in the LT sample with a width of app. 1–2 nm and length of 20 nm (a), which could be identified as GP zones running along $\langle 100 \rangle$ directions visible by the low intensity streaks around the reflections in the SAED pattern of the phase (b), in resemblance to [18]. Zone axis is $[001]$.

exhibiting plate-like precipitates referenced as GP zones [18]. Their coherency with the matrix is related to the orientation coupled appearance of the diffuse intensities along the $\langle 100 \rangle$ directions, which are subject of lattice parameter variation in the strain field regions surrounding the precipitates. Hence, we conclude that the observed strain fields could originate from plate-like precipitates as well and potentially indicate the presence of GP zones formed on the $\{100\}$ planes in the direction of $[010]$ and $[100]$ as previously reported for Ti-rich binary and ternary $\text{TiNi}/\text{TiNiCu}$ SMAs fabricated by sputtering, (i.e. [7, 17, 18]). The GP zones form due to excess of Ti in the amorphous matrix composition and are known to be unstable at temperatures above 600 °C. The crystal structure of these precipitates could not be determined due to the limited resolution caused by the thickness of the FIB cut. It is likely that they have the same body centered tetragonal structure as reported for sputtered Ti-rich binary and ternary TiNiCu alloys. Ishida et al. discussed the

crystal structure evolution of the GP zones in dependence of heat treatment temperature with annealing times of 1 h in detail. GP zones with a body centered tetragonal structure form at 500 °C grow and evolve at 600 °C into Ni-rich plate precipitates with Ti_2Cu like structure (SG 139, $I4/mmm$ or $C11_b$) and smaller tetragonality leaving only grain boundary Ti_2Cu precipitates at higher temperatures. In this study Ti_2Cu precipitates are present at the grain boundaries and Ti_2Cu plate-like precipitates have not been observed at 550 °C within the grains, which would typically show additional diffraction spots of Ti_2Cu along the $[010]^*$ and $[001]^*$ directions in the SAED pattern [28]. Therefore grain boundary Ti_2Cu precipitates and GP zones may co-exist. Considering the results from Cheng et al. [33] who propose a superposition of Ti_2Ni and Ti_3Ni_5 structures and the Ni-rich nature of the Ti_2Cu type plate precipitates, we assume that in this composition range first GP zones (plate precipitates) form and with higher annealing temperatures start to grow and evolve into a Ti_2Ni (Ti-rich, Cu-poor

precipitates) like cubic structure with a potential coherency relation to the matrix suggested by their orthogonal arrangement (see Appendix Fig. 8) and spherical Ti_2Ni precipitates which are semi-coherent and incoherent Ti_2Ni at even higher temperatures, which is also supported by EDS measurements and X-ray diffraction experiments (see Appendix Fig. 9). However, further in situ studies are needed with small increment of annealing temperatures coupled with TEM on very thin samples and high-resolution X-ray diffraction to eventually exactly determine the evolution of the crystal structure of the plate precipitates with increasing annealing temperatures.

Temperature-Dependent X-ray Diffraction

The influence of the described precipitation process on the microstructure and lattice parameters of the LT and HT in the austenite and martensite (Table 1) are revealed by temperature-dependent X-ray diffraction experiments (Fig. 4). In close agreement with the TEM study, the HT sample contains the TiNiCu phase, Ti_2Cu and Ti_2Ni precipitates. The Ti_2Ni reflections for the HT sample exhibit a distinct reflection splitting, which could be interpreted assuming two types of Ti_2Ni precipitates with slightly different lattice parameter. Annealing the film at 800 °C (Appendix Fig. 9) results in the extinction of the reflections for the larger Ti_2Ni cells. This is in line with the TEM observation, which indicated two types of Cu-poor (Ti_2Ni) precipitates. The lattice mismatch of the assumed Ti_2Ni precipitate with the austenite matrix can be defined for

$$(100)_{\text{B2}} \parallel (100)_{\text{Ti}_2\text{Ni}} = \frac{4c(\text{B2})}{c(\text{Ti}_2\text{Ni})} - 1$$

[21], resulting in a mismatch of 6.44% and 5.56% for $a = 11.39(8)$ Å and $a = 11.50(5)$ Å (Table 2). Annealing at higher temperatures (Appendix Fig. 9) only leaves the Ti_2Ni phase with the smaller unit cell and therefore larger misfit, which indicates that only incoherent spherical Ti_2Ni precipitates are stabilized. The presence TiCu [23] as previously reported in a similar compositional range (for TiNiCu) or Ti_2Ni_3 [34] phases can be excluded due to missing reflections. The LT sample contains the TiNiCu phase and Ti_2Cu precipitates with reduced intensity in diffraction patterns compared to the HT sample.

Reflections related probably to Ti_2Ni precipitates can be merely identified at around 38° and 45° 2 θ . The most prominent change with reduced annealing temperatures is the significant reflection broadening of the LT sample with diffuse scattering and can be explained by the intergranular growth of GP zones on the {100} planes with coherency strain fields around them. The GP zones thereby do not show any distinct sharp reflections, due to their small size, their high disorder and their coherent nature with the matrix. However, they likely contribute to the increased background between 38° and 44° 2 θ for the austenite state and increased background at the position where typically the B2 phase is present for the martensite phase. It was pointed out by several authors that the tetragonality of the GP zones can vary strongly and thereby also their lattice parameter, which contributes to this diffuse scattering [33].

Crystallographic Compatibility of the Corresponding Phases

The lattice parameters of the TiNiCu phases at 60 °C and – 11 °C are listed in Table 1 and are calculated from a Pawley [26] refinement (Appendix Figs. 10, 11, 12, 13 for details). The lattice parameter of the B2 phase at ~ 60 °C are similar for both heat treatments. However, the lattice parameter of the B19 phase differ for the LT and HT sample and shows an overall elongation along the a -direction and a contraction in c -direction, whereas the changes in b -direction are small. The exact reason for this is unclear, but might be related to the growth of the GP zones originating from the cubic lattice [35]. Similar lattice parameter changes were found for Ti-poor TiNiCu SMAs with C11 $_b$ -type plate precipitates similar as in our studies by Fukuda et al. [36]. As reported by Meng et al. [19] the GP zones have an influence on the martensitic twin structure. It is known that the GP zones do not stop the growth of martensite variants, but they are elastically distorted and can change the growth, width and type of the martensite twins into i.e. a zigzag like motion, depending on their size. Another reason could be the change in film composition due to precipitation growth with increasing annealing time. Thereby the description of the martensite structure and determination of lattice parameter is difficult to be compared to the austenite lattice and hence the error is larger.

Table 1 Lattice Parameters of the B2 and B19 phases for the LT and HT sample measured at ~ 60 °C for the austenite lattice parameter and – 11 °C for the martensite lattice parameter and the corresponding Cofactor conditions for type I and type II twins.

Sample	B2- a_0 [Å]	B19-a [Å]	B19-b [Å]	B19-c [Å]	λ_2	CCI(10^{-4})	CCII (10^{-4})
550 °C	3.045 (2)	2.92 (6)	4.27 (1)	4.50 (1)	0.9917	– 1.515	– 1.279
700 °C	3.0457 (2)	2.905 (7)	4.274 (9)	4.522 (4)	0.9924	– 1.555	– 1.187

Fig. 4 X-ray diffraction in the austenite state (a) and the martensite state (b) at similar ambient temperatures. For the LT sample a prominent reflection broadening of the B2/B19 phase is visible. The HT sample shows in addition to Ti₂Cu precipitates, Ti₂Ni precipitates with slightly different lattice parameters, probably attributed to

continuous and discontinuous growth of those related to the matrix. The martensite phase in the LT sample exhibits a similar diffraction pattern as in the LT austenite but features a reflection shift of the B19 020 reflection to a larger lattice parameter compared to the HT sample. The insets display the 2-θ range from 35°–50°, respectively.

Table 2 Lattice parameters of the precipitate phases Ti₂Cu and Ti₂Ni at ~ 60 °C for the HT and LT sample and the corresponding epitaxial misfits to the B2 phase.

Sample	a-TiNiCu [Å]	a-Ti ₂ Cu [Å]	c-Ti ₂ Cu [Å]	a-Ti ₂ Ni-1 [Å]	a-Ti ₂ Ni-2 [Å]	Misfit Ti ₂ Cu (%)	Misfit Ti ₂ Ni-1 (%)	Misfit Ti ₂ Ni-2 (%)
550 °C	3.045(2)	2.94(5)	10.63(5)	–	–	3.40	–	–
700 °C	3.0457(2)	2.946(1)	10.62(3)	11.39(8)	11.50(5)	3.38	6.44	5.56

See [21, 22] for the calculation of the epitaxials misfits

From the determined lattice parameters the compatibility of both phases expressed by the cofactor condition can be calculated and is similar, since the lattice parameter *b* of the B19 phase is nearly unaffected (note $\lambda_2 = b/(\sqrt{2} \cdot a_0)$). The epitaxial strain ε of the Ti₂Cu and B2 phase parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) to the viewing direction for the

epitaxial relation observed in Fig. 2 can be calculated with $\varepsilon_{\parallel} = \frac{a(B2)}{a(Ti_2Cu)} - 1$ and $\varepsilon_{\perp} = \frac{b(B2)}{b(Ti_2Cu)} - 1$ (compare to Dankwort et al. [22]) and are determined to be 3.40% and 3.38% for the LT and HT sample (Table 2) and are slightly larger compared to the misfits (2.8%) of the Ti₂Cu and the B2 phase presented by Chluba et al. [21] for “Cu lean” Ti-rich

Ti₅₄Ni₃₄Cu₁₂ composition, which might explain that in their case Ti₂Cu precipitates with a size of 300 nm show an epitaxial relation, whereas in this case Ti₂Cu precipitates with a similar size do not show a coherency relation, but only smaller Ti₂Cu precipitates with sizes $\sim < 150$ nm.

Functional Fatigue – Thermal and Stress-Induced Transformation

The differences in the described microstructure result not in a different cyclic stability of the thermal-induced transformation, but in a difference of the cyclic stability of the stress-induced transformation (Fig. 5). The cyclic stability of the thermally induced transformation is for both heat treatments within the experimental error, which can be attributed besides the fine microstructure to the good crystallographic compatibility of both samples. Noteworthy, the transformation temperatures are reduced by more than 30 °C and the latent heat is reduced by a factor of 2 for the LT sample. The thermal hysteresis is lowered for the LT sample (Table 3). The forward transformation

shows a distinct shoulder, which is not present for the reverse transformation (see Appendix Fig. 14). These results are in accordance with other investigation for Ti-rich TiNiCu-based SMA alloys. It was found that mainly GP zones or TiCu plate precipitates formed at low annealing temperatures, reduce the transformation temperatures and stabilize the austenite since additional energy is needed for the elastic deformation of the fine plate precipitates [35, 37]. The HT sample still shows somewhat lower transformation temperatures as typical for TiNiCu alloys, indicating that internal stresses still have a slight, but compared to the LT sample a reduced effect, as visible from small Ti-rich plate precipitates as already discussed above. The reduced thermal hysteresis of the LT sample can be understood with elastic backstress originating from the elastically deformed GP zones [35]. A similar effect was also reported for H-phase precipitates in TiNiHf shape memory alloys [38]. The broadened DSC-peak stems from a heterogeneous stress distribution, similar as observed for TiCu plate precipitates [37], within the material by the GP zones. Under an uniaxial stress the cyclic stability behavior

Fig. 5 The cyclic stability within 30 consecutive thermally induced transformation cycles during the forward transformation shows no deviation for both LT (a) and HT (b) sample. The cyclic stability for the stress-induced transformation reveals no degradation for the LT sample (c) and a strong degradation for the HT sample (d) within 200

cycles at 45 °C and 64 °C ambient temperatures. The data for (c) and (d) are taken from [15] and the original figure for (c) and (d) was first published in materials today, Vol 21, H. Gu, L. Bumke, C. Chluba, E. Quandt, R. D. James, Phase engineering and supercompatibility of shape memory alloys, 265–277, Elsevier (2018).

Table 3 Transformation temperatures, thermal hysteresis and the corresponding transformation enthalpies of the forward and reverse transformation.

Sample	M_s (°C)	M_f (°C)	A_s (°C)	A_f (°C)	ΔT (°C)	ΔH_{A-M} (J g ⁻¹)	ΔH_{M-A} (J g ⁻¹)
550 °C	9.1	− 1	7.6	18.4	9	− 4.9	4.8
700 °C	37	29.8	42.4	50.3	12.7	− 10.7	10.3

changes drastically. The LT sample shows excellent cyclic stability, whereas the HT sample shows a strong degradation within 200 cycles up to a stress of 400 MPa. In fact the LT sample is able to show the same behavior after 10^7 cycles (see Appendix Fig. 15). In addition the LT sample exhibits reduced critical transformation stress in dependence of the austenite finish temperature (LT sample 25 °C above A_f and HT ~ 15 °C above A_f) which might be explained by additional nucleation centers for the martensite from GP zones, but also from finely distributed grain boundary precipitates like Ti_2Cu , ease nucleation. The similar grain size, as well the similar good crystallographic compatibility are not responsible for the difference in cyclic stability of stress-induced transformation, but the formation of GP zones, which can ultimately increase the strength of the matrix and thus increase the resistance against plastic deformation, since dislocation movements are suppressed by the GP zones due to elastic strain fields and cannot cut through the GP zones [35, 39]. In addition the regularly distributed Ti_2Cu precipitates around the grains might facilitate the formation and growth of martensite phase due to the dual epitaxy [22].

Summary and Conclusion

We have demonstrated, that Cu-rich $Ti_{53.7}Ni_{24.7}Cu_{21.6}$ SMAs are able to withstand 1×10^7 superelastic cycles with neglectable fatigue when annealed at temperatures of 550 °C for 15 min. Annealing at 700 °C leads to a fast degradation of the superelastic stability. TEM analysis suggested the probable existence of GP zones, which would cause an increased resistance to dislocation movement, reduced transformation temperatures, enthalpies and transformation hysteresis due to elastic strain fields and the ability of GP zones to be elastically deformable by martensitic twins. The sample annealed at 700 °C only showed minor effects of elastic internal stresses. In addition both samples showed Ti_2Cu precipitation, whereas the TiNiCu film annealed at 550 °C shows a fine dispersion of precipitates at grain boundaries exhibiting a coherency relation, which is believed to improve the reversibility.

With increasing annealing temperatures the Ti_2Cu precipitates grow from ~ 60 nm to ~ 280 nm resulting in a random distribution around the grain boundaries. For these large precipitates, no coherency relation with the matrix could be observed, reducing the stability even further. For the HT sample many types of precipitates are found, small rectangular precipitates which show certain coherency with the matrix and larger Ti-rich ones which seem to be already incoherent. X-ray diffraction analysis suggest that these are Ti_2Ni precipitates with different lattice parameters. Further annealing to ~ 800 °C leads to extinction of coherent/semicoherent Ti_2Ni precipitates. Both samples show a good crystallographic compatibility $\lambda_2 \sim 0.99$ which in turn results in the observed small thermal and stress hysteresis. However, since the deviation is small the main reason for the high cyclic stability of the stress-induced transformation is assigned to the formation of GP zones and finely distributed Ti_2Cu precipitates for the LT sample. Apparently, a sub μm grain size of the TiNiCu phase with infrequently observed coherency to small precipitates of Ti_2Cu and a more random distribution is not sufficient. It has to be pointed out that such a high cyclic stability is not observed for binary NiTi containing GP zones and we propose that the combination of a good crystallographic compatibility with the presence of GP zones and/or finely distributed coherent Ti_2Cu precipitates enables the high cyclic stability. In accordance with other investigation one can assume that a high superelastic cyclic stability can be obtained in a large compositional range in the Ti-rich TiNiCu system as extensive research by our group and Ishida et al. suggest. Though future analysis should focus on an exact determination and the evolution of the crystal structure of the observed GP zones. Other material systems like TiNiPd where a good crystallographic compatibility and a similar precipitation landscape as in TiNiCu [11, 12, 40, 41] is given could show outstanding cyclic stability as well.

Appendix

Figures 6, 7, 8, 9, 10, 11, 12, 13, 14 and 15.

Fig. 6 STEM-HAADF image of the LT sample (a) and the EDS elemental maps (at%) (b) of the framed region for Cu, Ti and Ni showing a regular dispersion Ti-rich and Ni-poor precipitates at the grain boundaries corresponding to Ti_2Cu precipitates.

Fig. 7 STEM-HAADF image of the HT sample (a) and the EDS elemental maps (at%) (b) of the framed region for Cu, Ti and Ni showing Ti-rich and Ni-poor precipitates. Precipitates at the grain boundaries of the SMA phase corresponding to the Ti_2Cu phase. In addition Ti-rich and Cu-poor precipitates (Ti_2Ni) are present within the TiNiCu grains and at the grain boundaries.

Fig. 8 STEM-HAADF image of the HT sample (a) and the EDS elemental maps (at%) of the enlarged region (b) for Cu, Ti and Ni showing Ti-rich and Cu-poor precipitates with a spherical and rectangular shape. In (a) different morphologies are highlighted, where spherical precipitates are marked with a star, rectangular

precipitates with a triangle and small rectangular precipitates with a presumed orientation relationship with each other and to the matrix are marked with a circle. For better clarity the inset in (a) shows the small rectangular precipitates.

Fig. 9 Pawley refinement of TiNiCu annealed at 700 °C (a) and 800 °C (c) displaying the observed, calculated and the difference between calculated and observed diffractogram. (b) shows the enlarged regions of different areas of the diffractogram of the

recorded data with the different phases marked with ticks. The reflection (see red ticks) corresponding to the assumed coherent Ti_2Ni precipitates are not observed at 800 °C.

Fig. 10 Pawley refinement of the LT sample in the austenite state at 60 °C displaying the observed, calculated and the difference between calculated and observed pattern (a). In (b) an enlarged region of the fit

with corresponding phases is displayed. The Ti_2Ni phase is merely detected and is used for the diffuse scattering.

Fig. 11 Pawley refinement of the HT sample in the austenite state at 60 °C displaying the observed, calculated and the difference between calculated and observed pattern (a). In (b) an enlarged region of the fit

with corresponding phases is displayed. The splitting of the Ti_2Ni phase is clearly visible and is contributed to the continuous growth and discontinuous growth the Ti_2Ni phase.

Fig. 12 Pawley refinement of the LT sample in the martensite state at ~ -11 °C displaying the observed, calculated and the difference between calculated and observed pattern (a). In (b) the details about the fit with the contributions of the different phases are visible. Note

that Ti_2Ni with varying intensities compared to the austenite is mostly used for diffuse scattering simulation of the B19 phase, formed due to the complex interaction of GP zones and the martensite phase.

Fig. 13 Pawley refinement of the HT sample in the martensite state at $\sim -11^\circ\text{C}$ displaying the observed, calculated and the difference between calculated and observed pattern (a). In (b) details about the fit with the contributions of the different phases are visible.

Fig. 14 The forward and reverse martensitic transformation for the LT (a, c) and HT (b, d) sample for 30 thermal cycles do not show signs of degradation. The latent heat, as well as the transformation

temperatures of the LT sample is reduced and the transformation temperature window is broadened.

Fig. 15 The sample annealed at 550 °C displays after 10^7 uniaxial tensile test nearly the same superelasticity behaviour as in the first cycle. The slight increased slope in the transformation plateau can be attributed due to slight uneven electropolishing of the small sample.

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Data Availability The data that support the findings of this study are available from the corresponding author upon request.

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