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

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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$_2$Cu 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 Ti$_{53.7}$Ni$_{24.7}$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$_2$Cu precipitates ($\sim$ 60 nm). Films annealed at 700 °C result in the growth of Ti$_2$Cu precipitates ($\sim$ 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$_2$Cu 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 $\sim$ 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
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 films, fine precipitates which are not observed in bulk 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 Ti2Ni, Ti2Cu, 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]$_{B2}$ planes along the [001] and [010] directions. The orientation relationships at low annealing temperatures (500 °C) are [100]$_{GP}$ zone/∥100]$_{B2}$ and (001)$_{GP}$ zone/∥(001)$_{B2}$, 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 Ti2Cu precipitates with the matrix similar to the GP zones, which evolves at higher temperatures. Incoherent or semi-coherent precipitates like Ti2Ni obstruct the growth of martensite twins, whereas coherent GP zones and intergranular Ti2Cu only slightly suppress the lateral growth resulting in zigzag-shaped twin boundaries or in a change of direction of the twins in case of Ti2Cu [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 Ti54.7Ni30.7Cu12.3Co2.3 stoichiometry annealed at 700 °C solely exhibiting Ti2Ni precipitates, but none of Ti2Cu, also withstanded $10^7$ cycles perhaps related to outstanding crystalllographic compatibility, as well as small grain sizes in the sub μm range [15, 21].

To minimize the effect of Ti2Ni precipitates in this study, a composition for which mostly Ti2Cu precipitates are expected for sputtered TiNiCu films [23] is chosen. Preliminary studies on the Ti53.7Ni24.7Cu21.6 composition have been reviewed by Gu et al. [15] indicating that an increased size and irregular distribution of Ti2Cu precipitates reduces the cyclic stability. The addition of cobalt benefits a high efficient elastocaloric material, enabling the material to withstand $2 \times 10^7$ cycles [24]. In this study we give a detailed discussion of different factors influencing the cyclic stability, enabling Ti53.7Ni24.7Cu21.6 annealed at 550 °C to show near perfect reversibility of superelasticity after $1 \times 10^7$ cycles, whereas annealing at higher temperatures (700 °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 $\times 10^{-3}$ 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 °C and 700 °C for 15 min. The composition of the amorphous film was determined to be Ti53.7Ni24.7Cu21.6, 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-Kα radiation source (λ = 1.5406 Å), a Kβ filter and 2-D Hypix3000 detector operated in 1D-mode up to 2θ = 100°. 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 LaB6 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-3m, austenite), TiNiCu-B19 (SG51, Pnmb, martensite), Ti2Cu (SG139, I4/mmm), and Ti2Ni (SG227, Fd-3m). 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 °C min⁻¹ for cycle 1, 10, 20, 30 and 40 °C min⁻¹ in between. Latent heat as well as transformation temperatures were determined using the tangent method. Thermal hysteresis was calculated according to ΔT = 1/2(Aₐ + Aᵢ - Mᵢ - Mᵢ), where Aₐ and Aᵢ correspond to the austenite start and finish temperatures and Mᵢ and Mᵢ 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 ± 1 °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 × 10⁷ 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 μm 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 Ti2Cu precipitates at the grain boundaries (Fig. 1 and Appendix Figs. 6, 7). The Ti2Cu precipitates in the LT sample have an average size of 60 nm and are regularly dispersed at the grain boundaries. In comparison the Ti2Cu precipitates in the HT sample exhibit averaged dimensions of approximately 280 nm and scatter irregularly between the TiNiCu grains. Further, distinct intragranular 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
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$_2$Ni-type and that the precipitates at the TiNiCu grain boundaries are mainly Ti$_2$Cu-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$_2$Ni and plate precipitates within the grains and spherical Ti$_2$Ni 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$_2$Ni 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$_2$Ni or Ti-rich precipitates exist 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 Ti$_{54}$Ni$_{34}$Cu$_{12}$ and pointed out that grain boundary Ti$_2$Cu 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$_2$Ni precipitates. Therefore this study focusses on the orientation relation of Ti$_2$Cu 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$_2$Cu precipitates in the HT sample exhibit no coherency relation. In this study, a deepened evaluation of the Ti$_2$Cu/TiNiCu orientation relationship for the LT and HT samples could identify the coherency relation (001)$_{Ti2Cu}$(001)$_{B2}$ for the LT sample as presented in Fig. 2. For the HT sample an orientation relation between larger precipitates (280 nm) of Ti$_2$Cu and the B2/B19 phase was not observed on a reasonable number of about 10 adjacent Ti$_2$Cu and TiNiCu grains (Fig. 2b). However, the identical (001)$_{Ti2Cu}$(001)$_{B2}$ relation could be observed on occasion between a small Ti$_2$Cu 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$_2$Cu 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$_2$Cu precipitates located at the grain boundaries in the LT sample, areas with patchy contrast of orthogonal stripes exhibiting dimensions of ~ 20 nm × 1–2 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$_2$Cu precipitates with C11b 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 <100> directions originating at B2 reflections which is in close resemblance to the diffuse intensities observed in electron diffraction patterns recorded on SMA films.
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 \<100\> 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 TiNi/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 Ti2Cu like structure (SG 139, I4/mmm or C11b) and smaller tetragonality leaving only grain boundary Ti2Cu precipitates at higher temperatures. In this study Ti2Cu precipitates are present at the grain boundaries and Ti2Cu plate-like precipitates have not been observed at 550 °C within the grains, which would typically show additional diffraction spots of Ti2Cu along the \[010\]* and \[001\]* directions in the SAED pattern [28]. Therefore grain boundary Ti2Cu precipitates and GP zones may co-exist. Considering the results from Cheng et al. [33] who propose a superposition of Ti2Ni and Ti3Ni5 structures and the Ni-rich nature of the Ti2Cu 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 Ti2Ni (Ti-rich, Cu-poor

**Fig. 2** Bright field images of the LT (a) and HT (b) samples display Ti2Cu precipitates and TiNiCu grains. The area of interests are marked with white circles. (a) The orientation relationship \(\langle001\rangle_{Ti2Cu}||\langle001\rangle_{B2}\) 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 Ti2Cu 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 \<100\> 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].

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precipitates) like cubic structure with a potential coherency relation to the matrix suggested by their orthogonal arrangement (see Appendix Fig. 8) and spherical Ti$_2$Ni precipitates which are semi-coherent and incoherent Ti$_2$Ni 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$_2$Cu and Ti$_2$Ni precipitates. The Ti$_2$Ni reflections for the HT sample exhibit a distinct reflection splitting, which could be interpreted assuming two types of Ti$_2$Ni 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$_2$Ni cells. This is in line with the TEM observation, which indicated two types of Cu-poor (Ti$_2$Ni) precipitates. The lattice mismatch of the assumed Ti$_2$Ni precipitate with the austenite matrix can be defined for

$$\frac{(100)_{B2}}{(100)_{Ti2Ni}} = \frac{4c(B2)}{c(Ti2Ni)} - 1$$

[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$_2$Ni phase with the smaller unit cell and therefore larger misfit, which indicates that only incoherent spherical Ti$_2$Ni precipitates are stabilized. The presence TiCu [23] as previously reported in a similar compositional range (for TiNiCu) or Ti$_2$Ni$_3$ [34] phases can be excluded due to missing reflections. The LT sample contains the TiNiCu phase and Ti$_2$Cu precipitates with reduced intensity in diffraction patterns compared to the HT sample.

Reflections related probably to Ti$_2$Ni precipitates can be merely identified at around 38° and 45° 20. 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° 20 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 C11b-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.

| Sample | B2-α0 [Å] | B19-a [Å] | B19-b [Å] | B19-c [Å] | λ₂ | CC1(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    |
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 $k_2 = b/(H^2 * a_0)$).

The epitaxial strain $\varepsilon$ of the Ti$_2$Cu and B2 phase parallel ($\varepsilon_||$) and perpendicular ($\varepsilon_\perp$) to the viewing direction for the epitaxial relation observed in Fig. 2 can be calculated with $\varepsilon_|| = \frac{a(B2)}{a(TiCu)} - 1$ and $\varepsilon_\perp = \frac{b(B2)}{b(TiCu)} - 1$ (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 Ti$_2$Cu and the B2 phase presented by Chluba et al. [21] for “Cu lean” Ti–rich.

Table 2 Lattice parameters of the precipitate phases Ti$_2$Cu and Ti$_2$Ni at $\sim 60$ °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.
Ti$_{54}$Ni$_{34}$Cu$_{12}$ composition, which might explain that in their case Ti$_2$Cu precipitates with a size of 300 nm show an epitaxial relation, whereas in this case Ti$_2$Cu precipitates with a similar size do not show a coherency relation, but only smaller Ti$_2$Cu 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).
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$_2$Cu, 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$_2$Cu precipitates around the grains might facilitate the formation and growth of martensite phase due to the dual epitaxy [22].

With increasing annealing temperatures the Ti$_2$Cu 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$_2$Ni precipitates with different lattice parameters. Further annealing to ~ 800 °C leads to extinction of coherent/semicoherent Ti$_2$Ni precipitates. Both samples show a good crystallographic compatibility $\lambda_2$ ~ 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$_2$Cu precipitates for the LT sample. Apparently, a sub µm grain size of the TiNiCu phase with infrequently observed coherency to small precipitates of Ti$_2$Cu 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$_2$Cu 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.

### Summary and Conclusion

We have demonstrated, that Cu-rich Ti$_{53.7}$Ni$_{24.7}$Cu$_{21.6}$ SMAs are able to withstand $1 \times 10^7$ 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$_2$Cu 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.

### Appendix

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

| Sample | $M_s$ (°C) | $M_f$ (°C) | $A_s$ (°C) | $A_f$ (°C) | $\Delta T$ (°C) | $\Delta H_{A,M}$ (J g$^{-1}$) | $\Delta H_{M-A}$ (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                        |
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$_2$Cu 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$_2$Cu phase. In addition Ti-rich and Cu-poor precipitates (Ti$_2$Ni) 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$_2$Ni 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 Ti₂Ni 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 Ti₂Ni phase is clearly visible and is contributed to the continuous growth and discontinuous growth the Ti₂Ni 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 Ti₂Ni 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 $-11^\circ$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.

References

1. Hornbogen E (2004) Review Thermo-mechanical fatigue of shape memory alloys. J Mater Sci 39(2):385–399. https://doi.org/10.1023/B:JMSc.0000014922.88523.d3

2. Fähler S, Rößler UK, Kastner O et al (2012) Caloric effects in ferroic materials: new concepts for cooling. Adv Eng Mater 14(1–2):10–19. https://doi.org/10.1002/adem.201100178

3. Miyazaki S, Nomura K, Ishida A et al (1997) Recent developments in sputter-deposited Ti-Ni-base shape memory alloy thin films. J Phys IV France. https://doi.org/10.1051/jp4:1997543

4. Lasalmonie A, Strudel JL (1986) Influence of grain size on the mechanical behaviour of some high strength materials. J Mater Sci 21(6):1837–1852. https://doi.org/10.1007/BF00547918

5. Sertseueva AV, Song C, Valiev RZ et al (2003) Structure and properties of amorphous and nanocrystalline NiTi prepared by severe plastic deformation and annealing. Mater Sci Eng. A 339(1–2):159–165. https://doi.org/10.1016/S0921-5093(02)00122-3

6. Allafi JK, Dluhy A, Neuking K et al (2001) Influence of precipitation and dislocation substructure on phase transformation temperatures in a Ni-rich NiTi-shape memory alloy. J Phys IV France. https://doi.org/10.1051/jp4:2001888

7. Ishida A, Sato M, Gao Z (2014) Effects of Ti content on microstructure and shape memory behavior of Ti_xNi_{53.5-S_x}Cu_{15.5} (x = 44.6–55.4) thin films. Acta Mater 69:292–300. https://doi.org/10.1016/j.actamat.2014.02.006

8. Gall K, Sehitoglu H, Chuimlyakov YI et al (1999) the influence of aging on critical transformation stress levels and martensite start temperatures in NiTi: Part II—discussion of experimental results. J Eng Mater Technol 121(1):28. https://doi.org/10.1115/1.2815995

9. Gall K, Maier HJ (2002) Cyclic deformation mechanisms in precipitated NiTi shape memory alloys. Acta Mater 50(18):4643–4657. https://doi.org/10.1016/S1359-6454(02)00315-4

10. Song Y, Chen X, Dabade V et al (2013) Enhanced reversibility and unusual microstructure of a phase-transforming material. Nature 502(7469):85–88. https://doi.org/10.1038/nature12532

11. Zarnetta R, Tahakashi R, Young ML et al (2010) Identification of quaternary shape memory alloys with near-zero thermal hysteresis and unprecedented functional stability. Adv Funct Mater 20(12):1917–1923. https://doi.org/10.1002/adfm.200902336

12. Zhang Z, James RD, Müller S (2009) Energy barriers and hysteresis in martensitic phase transformations. Acta Mater 57(15):4332–4352. https://doi.org/10.1016/j.actamat.2009.05.034

13. Chen X, Srivastava V, Dabade V et al (2013) Study of the cofactor conditions: conditions of supercompatibility between phases. J Mech Phys Solids 61(12):2566–2587. https://doi.org/10.1016/j.jmps.2013.08.004

14. James RD, Zhang Z (2005) A Way to Search for Multiferroic Materials with “Unlikely” Combinations of Physical Properties. In: Hull R, Parisi J, Osgood RM et al (eds) Magnetism and Structure in Functional Materials, vol 79. Springer. Berlin Heidelberg, pp 159–175

15. Gu H, Bumke L, Chluba C, Quandt E, James RD (2018) Phase engineering and supercompatibility of shape memory alloys. Mater Today 21(3):265–277. https://doi.org/10.1016/j.mattod.2017.10.002

16. Ishida A (2015) Application of the sputtering method in the study of shape memory alloys. Materials Today: Proceedings 2:S529–S534. https://doi.org/10.1016/j.mattod.2015.07.340

17. Nakata Y, Tadaki T, Tanaka A et al (1995) Effect of heat treatments on morphology and transformation temperatures of sputtered Ti-Ni thin films. J Phys IV France. https://doi.org/10.1051/jp4:199558671

18. Ishida A, Sato M, Ogawa K (2006) Microstructure and shape-memory behavior of annealed Ti_xNi_{53.5-Cu}_{15.5} thin films. Philos Mag Lett. 86(1):13–20. https://doi.org/10.1080/09500630500482308

19. Meng XL, Sato M, Ishida A (2008) Structure of martensite in Ti-rich Ti-Ni-Cu thin films annealed at different temperatures. Acta Mater 56(14):3394–3402. https://doi.org/10.1016/j.actamat.2008.03.015

20. Meng XL, Sato M, Ishida A (2008) Influence of Ti_xCu precipitates on B19 martensite structure in a Ti-rich Ti-Ni-Cu thin film.
Chluba C, Ge W, Lima de Miranda R et al (2015) Ultralow-fatigue shape memory alloy films. Science 348(6238):1004–1007. https://doi.org/10.1126/science.1261164

Dankwort T, Strobel J, Chluba C et al (2016) Martensite adaption through epitaxial nano transition layers in TiNiCu shape memory alloys. J Appl Crystallogr 49(3):1009–1015. https://doi.org/10.1107/S160057671600710X

Ishida A, Sato M, Gao ZY (2015) Microstructure and shape memory behavior of $\text{Ti}_{51.5}\text{Ni}_{48.5-x}\text{Cu}_x$ ($x = 11.8–23.5$) thin films. Intermetallics 58:103–108. https://doi.org/10.1016/j.intermet.2014.11.011

Bumke L, Zamponi C, Jetter J et al (2020) Cu-rich Ti$_{52.8}$Ni$_{22.2}$Cu$_{22.5}$Co$_{2.5}$ shape memory alloy films with ultra-low fatigue for elastocaloric applications. J Appl Phys 127(22):225105. https://doi.org/10.1063/5.0006301

Lima de Miranda R, Zamponi C, Quandt E (2013) Micropatterned freestanding superelastic TiNi Films. Adv Eng Mater 15(1–2):66–69. https://doi.org/10.1002/adem.201200197

Pawley GS (1981) Unit-cell refinement from powder diffraction scans. J Appl Crystallogr 14(6):357–361. https://doi.org/10.1107/S0021889881009618

Chen X, Song Y, Tamura N et al (2016) Determination of the stretch tensor for structural transformations. J Mech Phys Solids 93:34–43. https://doi.org/10.1016/j.jmps.2016.02.009

Ishida A, Sato M (2007) Microstructure and shape memory behaviour of annealed $\text{Ti}_{51.5}\text{Ni}_{48.5-x}\text{Cu}_x$ ($x = 6.5–20.9$) thin films. Phil Mag 87(35):5523–5538. https://doi.org/10.1080/14786430701654394

Ishida A, Sato M, Takei A et al (1995) Effect of Heat Treatment on Shape Memory Behavior of Ti-rich Ti-Ni Thin Films. Mater Trans, JIM 36(11):1349–1355. https://doi.org/10.2320/matertrans1989.36.1349

Ishida A, Ogawa K, Sato M et al (1997) Microstructure of Ti-48.2 at Pct Ni shape memory thin films. MMTA 28(10):1985–1991. https://doi.org/10.1007/s11661-997-0155-x

Hou X, Li J, Liu F et al (2019) Coherent strain of Guinier-Preston II zone in an Al-Zn-Mg-Cu alloy. Micron 124:102711. https://doi.org/10.1016/j.micron.2019.102711

Konno TJ, Kawasaki M, Hiraga K (2001) Direct imaging of Guinier-Preston zones by high-angle annular detector dark-field scanning transmission electron microscopy. J Electron Microsc (Tokyo) 50(2):105–111. https://doi.org/10.1093/micro/50.2.105

Cheng S-Y, Chen C-H, Wu S-K (2013) A study of the structure of G-P zones in Ti-rich TiNi shape memory melt-spun ribbons. Phil Mag 93(23):3167–3176. https://doi.org/10.1080/14786435.2013.805273

Chang L, Grummon DS (1997) Structure evolution in sputtered thin films of Ti$_x$ (Ni, Cu)$_{1-x}$ I: Distortive transformations. Philos Mag A 76(1):163–189. https://doi.org/10.1080/01418619708209968

Zhang JX, Sato M, Ishida A (2003) On the Ti$_2$Ni precipitates and Guinier-Preston zones in Ti-rich Ti–Ni thin films. Acta Mater 51(11):3121–3130. https://doi.org/10.1016/S1359-6454(03)00012-4

Fukuda T, Saburi T, Kakeshita T et al (1997) Shape Memory Behavior of Ti–40.5Ni–10Cu Alloy Affected by C11b-Type Precipitates. Mater Trans JIM 38(2):107–111. https://doi.org/10.2320/matertrans1989.38.107

Rösnner H, Schloßmacher P, Shelyakov AV et al (2001) The influence of coherent ticu plate-like precipitates on the thermoelectric martensitic transformation in melt-spun Ti$_{50}$Ni$_{25}$Cu$_{25}$ shape memory alloys. Acta Mater 49(9):1541–1548. https://doi.org/10.1016/S1359-6454(01)00055-6

Stebner AP, Bigelow GS, Yang J et al (2014) Transformation strains and temperatures of a nickel–titanium–hafnium high temperature shape memory alloy. Acta Mater 76:40–53. https://doi.org/10.1016/j.actamat.2014.04.071

Kajiwara S (2010) Strengthening of Ti-Ni shape-memory films by coherent subnanometric plate precipitates. Philos Mag Lett 74(3):137–144. https://doi.org/10.1080/09500830802322152

Sawaguchi T, Sato M, Ishida A (2002) Microstructure and shape memory behavior of Ti (Pd Ni ) and Ti (Pd Ni ) thin films. Mater Sci. Eng.: A 332(1-2):47–55. https://doi.org/10.1016/S0921-5093(01)01714-2

Zarnetta R, Zelaya E, Eggeler G et al (2009) Influence of precipitates on the thermal hysteresis of Ti Ni-Pd shape memory thin films. Scr. Mater. 60(5):352–355. https://doi.org/10.1016/j.scriptamat.2008.11.001