The Influence of Coherent and Semi-Coherent TiCu Precipitates on the Martensitic Transformation of Melt-Spun Ti₅₀Ni₂₅Cu₂₅ Shape Memory Ribbons

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Thin coherent as well as thicker semi-coherent plate-like precipitates of the same type, *i.e.* TiCu, were generated by different heat treatments of melt-spun Ti₅₀Ni₂₅Cu₂₅ ribbons. Their influence on the martensitic transformation behavior was investigated by means of differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). It was found that thin coherent plate-like precipitates lower the temperatures of both martensitic and its reverse transformation and broaden the peak form of the DSC signal. On the other hand, thicker semi-coherent plates act to raise both transformation temperatures. The role of coherency stresses, arrangements of misfit dislocations, and compositional aspects are discussed.

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1. Introduction

Ni-rich TiNi shape memory alloys (SMAs) are known to be very sensitive to compositional changes regarding the martensitic transformation temperatures.¹⁾ Alloying additives as for instance Cu for Ni reduces the composition sensitivity of the martensite start temperature M_s and leads to a smaller transformation hysteresis.^{1,2)} The necessary phase transformation in TiNi SMAs which enables the shape memory effect as well as pseudoelasticity takes place between a high-temperature phase, the cubic B2 structure called austenite, and a low-temperature phase, the monoclinic B19' structure called martensite. Substituting Cu contents of more than 20 at% for Ni leads to orthorhombic martensite having the B19 structure.^{3,4)}

Precipitation phenomena in binary TiNi alloys, *e.g.* the all-round effect created by Ti₃Ni₄ precipitates,⁵⁾ are affecting the martensitic transformation and therefore the shape memory behavior. In principle, two aspects are essential for these changes, that is, coherency stresses owing to the lattice mismatch between the precipitates and their surrounding matrix and/or compositional changes as a result of the precipitation process.^{5,6)} In the case of Ti₃Ni₄ precipitates, it was reported that the martensitic transformation temperature, M_s , was raised in the stressed regions around the precipitates.^{6,7)} However, owing to the composition sensitivity of binary TiNi, it has always been a question which of these contributions, internal stresses and/or compositional changes, are dominant.

Among the variety of precipitates in TiNi-based SMAs, the formation of plate-like TiCu precipitates with the tetragonal B11 structure was observed for Ti₅₀Ni₂₅Cu₂₅ alloys.^{8,9)} The corresponding lattice parameters of the relevant phases ap-

pearing in Ti₅₀Ni₂₅Cu₂₅ alloys are listed in Table 1.

These alloys offer the opportunity that the high content of Cu makes M_s less sensitive to variations in the Ti/Ni ratio compared with binary TiNi.^{1,3,4)} Therefore, chemical changes as a result of TiCu precipitates can be neglected since the Ti/(Ni + Cu) ratio remains constant and thus, non-chemical contributions like internal stresses can be observed separately. In the present study, the influence of coherency of TiCu precipitates on the martensitic transformation behavior was investigated by means of DSC and TEM observations.

2. Experimental

Amorphous Ti₅₀Ni₂₅Cu₂₅ ribbons with cross-sectional dimensions of 7 mm × 0.05 mm were produced by melt-spinning. A detailed description of the single-roller melt-spinning technique is given elsewhere.^{11,12)} Three heat treatments were chosen in order to achieve a different morphology of precipitates. First of all, the amorphous ribbon material was homogenized at 800°C for 168 h in encapsulated

Table 1 Crystal structures and lattice constants of the different phases appearing in Ti₅₀Ni₂₅Cu₂₅ alloys.

Phase	Austenite	Martensite	Plate-like precipitates
Crystal structure	Cubic B2	Orthorhombic B19	Tetragonal B11
Lattice constants	$a = 0.305 \text{ nm}$	$a = 0.2918 \text{ nm}$ $b = 0.4290 \text{ nm}$ $c = 0.4504 \text{ nm}$ after Potapov <i>et al.</i> ¹⁰⁾	$a = 0.311 \text{ nm}$ $c = 0.591 \text{ nm}$ $c/a = 1.9$

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quartz ampoules filled with pure argon followed by water quenching. This led to fully crystallization without any TiCu precipitates. This material was taken as reference. Secondly, a part of the homogenized material was further annealed at 600°C for 48 h following the same procedure as described above in order to create semi-coherent plate-like TiCu precipitates. Thirdly, thin coherent TiCu plate-like precipitates were generated by annealing the initial amorphous material at 460°C for 2 h which was close to the crystallization temperature, T_c , of 455°C.^{13–15} For that purpose, the specimens were put into a container made of Ti-foil. The subsequent heat treatment was performed in a vacuum furnace. It is emphasized here that only a heat treatment below or even near T_c starting from the amorphous state could guarantee the formation of densely precipitated thin coherent plates. This behavior is supposed to be related to an enhanced amount of point defects quenched in by the rapid cooling during the melt-spinning process.¹⁶ These vacancies disappear after a homogenization heat treatment.

The DSC experiments were carried out by a Netzsch DSC 204. For each specimen, two heating and cooling cycles were performed in the temperature range from –100 to 130°C using a scanning rate of 10°C/60 s. A Philips CM 30 ST TEM equipped with a NORAN high-purity germanium detector was employed to analyze the microstructures. Use of a Gatan double tilt holder was made. TEM specimens, 3 mm in diameter and $\sim 30\mu\text{m}$ in thickness, were prepared by twin-jet electropolishing in a solution of 1/3 nitric acid and 2/3 methanol at –25°C and –V.

3. Results

3.1 DSC measurements

Figure 1 summarizes the results of the DSC measurements. Firstly, the martensitic transformation behavior of homogenized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons without precipitates is displayed in Fig. 1(a). A reversible martensitic single step transformation is visible. Here, influences on the transformation behavior owing to the presence of precipitates can be definitely excluded since ascertained by TEM observations this material did not contain any.

Secondly, the heating and cooling curves of homogenized $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons additionally annealed for 48 h at 600°C containing semi-coherent plate-like TiCu precipitates are shown in Fig. 1(b). As well a reversible martensitic single step transformation was found, but the transformation temperatures are about 5°C raised.

Thirdly, in contrast to the two preceding DSC plots, the DSC runs of Fig. 1(c) for the material aged at 460°C for 2 h show the opposite effect, that is, the transformation temperatures are lowered. Furthermore, the peak form became broad.

3.2 TEM observations

TEM investigations carried out on homogenized ribbons revealed no plate-like pre-cipitates of the TiCu type. Only a small amount of spherical $\text{Ti}_2(\text{Ni}, \text{Cu})$ precipitates was found. The composition was checked several times by EDX analysis and found to be homogeneous and very close to the nominal composition of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$.

According to the transformation behavior of Fig. 1(b), a

Fig. 1 DSC curves of melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons after different heat treatments. (a) After homogenization for 168 h at 800°C without precipitates. (b) Cooling and heating transformation curves of a homogenized melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon additionally annealed at 600°C for 48 h. This state contains thicker semi-coherent plate-like TiCu precipitates. (c) DSC curves of an amorphous melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 460°C for 2 h. This state contains thin coherent plate-like TiCu precipitates.

heat treatment of 48 h at 600°C after homogenization led two well defined two-phase microstructure as shown in Figs. 2(a), (b).

The plate-like precipitates are formed homogeneously within the grains. Two variants, arranged nearly horizontally and vertically to each other, appeared in Figs. 2(a), (b). The average width of the precipitates is around 80 nm. The habit planes of the precipitates are {011}-planes of the martensite B19 phase. It is noted that the different {011} habit planes are not exactly perpendicular to each other since the b- and c-axes of the orthorhombic elementary cell have different lengths. As previously mentioned, the precipitates were identified as

Fig. 2 TEM bright field micrographs of a homogenized melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon heat-treated at 600°C for 48 h. Beam direction $\parallel \langle 100 \rangle$ direction of the martensitic B19-phase. (a), (b) Overview of the well defined two-phase structure. Plate-like precipitates are marked by arrow heads. Note that twins appeared frequently. Furthermore, spherical $\text{Ti}_2(\text{Ni}, \text{Cu})$ precipitates are marked by crosses. (c) Enlarged micrograph of a plate-like precipitate from part (a) demonstrating details at the interfaces of matrix/precipitates. Dislocations are marked by arrow heads indicating the loss of coherency.

binary TiCu (tetragonal B11) with its c -axis normal to the $\{011\}$ habit planes.⁹ Twins were often seen illustrating the martensitic structure of the matrix. Their growth is stopped at the precipitates as shown in Fig. 2(b). A closer view on the interface precipitate/matrix is shown in Fig. 2(c). Several misfit dislocations, marked by arrow heads, appeared around the precipitates indicating their semi-coherent character. The corresponding selected area electron diffraction (SAED) patterns of Fig. 2(b) are displayed in Fig. 3.

Figure 3(a) shows the $[100]$ zone axis of the martensitic matrix in Fig. 2(b). Figure 3(b) stems from another area of Fig. 2(b) exhibiting both, precipitates and matrix. The difference compared to Fig. 3(a) is that we find here the overlapping diffraction patterns of two phases, that is, reflections from the martensitic B19 phase as shown in Fig. 3(a) and from the $[100]$ zone axis of the tetragonal TiCu precipitates. Figure 3(c) shows a schematic illustration indicating the composition of the diffraction pattern observed in Fig. 3(b). Furthermore, the splitting of some reflections in Fig. 3(b) is due to twinning in the B19 phase. EDX spot analyses of the matrix near the TiCu precipitates showed a composition of 50 ± 1 at%Ti, 22 ± 1 at%Ni and 28 ± 1 at%Cu. Moreover, the matrix was found to be homogeneous. The precipitates were composed of 51 ± 1 at%Ti, 42 ± 1 at%Cu, and 7 ± 1 at%Ni.⁹

The microstructure corresponding to the transformation behavior observed in Fig. 1(c) after annealing 2 h at 460°C is manifested in Fig. 4.

Thin coherent plate-like TiCu precipitates are formed homogeneously within the grains as shown in Fig. 4. Because of the chosen imaging conditions, only one of the two variants of plate-like precipitates is visible here. Their habit planes are determined to be $\{011\}$ of the surrounding martensitic B19 phase, too. Moreover, coherency stresses become visible since a strong strain contrast appeared around plate-like precipitates owing to the existing lattice mismatch between the surrounding martensitic matrix (orthorhombic B19) and the TiCu precipitates (tetragonal B11). This indicates the existence of a kind of elastic accommodation. Values of the calculated mismatch between the TiCu precipitates along and normal to the $\{011\}$ habit planes of the B19 matrix are summarized in Table 2.

No misfit dislocations have been found. The absence of dislocations at the interface was already demonstrated by high-resolution TEM in a similar morphology of thin coherent TiCu precipitates.¹⁷⁾

The formation of new platelets seems to proceed easier than their widening after aging for 2 h at 460°C . Consequently, a much higher density of plates can be observed compared to Figs. 2(a), (b). EDX analyses revealed a composition of

Table 2 Calculated mismatch between the tetragonal TiCu precipitates along and normal to the $\{011\}$ habit planes of the orthorhombic B19-matrix. The corresponding lattice parameters are taken from Table 1.

Orientation relation	Calculated mismatch
$[100]_{\text{TiCu}} \parallel [100]_{\text{B19}}$	+6.6% (tensile stresses)
$[010]_{\text{TiCu}} \parallel [022]_{\text{B19}}$	0%
$[001]_{\text{TiCu}} \parallel [011]_{\text{B19}}$	-5.0% (compressive stresses)

Fig. 3 Corresponding diffraction patterns of Fig. 2(b). (a) [100] zone axis pattern of the martensitic matrix. (b) Overlapping diffraction patterns of both, matrix and precipitates. The splitting of some reflections is due to twinning. (c) Schematic illustration indicating the composition of the diffraction pattern observed in (b) by two variants of plate-like precipitates arranged nearly horizontally and vertically to each other as well as their surrounding martensitic matrix, respectively.

50 ± 1 at%Ti, 26 ± 1 at%Ni, and 24 ± 1 at%Cu which is close to the nominal one.

4. Discussion

Based on the results of the preceding section, we found that thin coherent TiCu precipitates shifted the transformation temperatures downwards whereas thicker semi-coherent precipitates of the same type raised them compared with homogenized material containing no TiCu precipitates. Compositional changes owing to the precipitation process as potential contribution elucidating the above mentioned transformation behavior can be ruled out for the present case since the martensitic transformation start temperature, M_s , and its reverse transformation was found to be insensitive concerning variations in the Ni/Cu ratio in ternary $\text{Ti}_{50}\text{Ni}_x\text{Cu}_{50-x}$ SMAs containing 20–30 at%Cu.^{1,3,4)} Moreover, ordering/disordering processes as a result of Cu depletion in the matrix can be considered in the same manner.

Effects owing to different grain sizes can also be neglected since the grain size ranged between 1–5 μm for all the heat-treated melt-spun ribbons used in the present work.

The basic idea explaining the present observations is that two independent mechanism are operating which cause a different martensitic transformation behavior displayed in Figs. 1(b), (c). That are in detail: firstly, coherency stresses owing to thin coherent plate-like precipitates form obstacles hindering the martensitic transformation; secondly, an arrangement of misfit dislocations at the semi-coherent interfaces of the thicker TiCu precipitates acts as preferential nucleation sites favoring the formation of martensite. Several authors^{17–20)} observed that densely precipitated thin plates stabilize the parent phase hindering the nucleation and propagation of the martensite. Our interpretation is that coherency stresses are representing obstacles counteracting to the driving shear stress re-

quired to initiate and/or propagate the martensitic interfaces with the consequence that further undercooling is necessary to start the martensitic transformation. A more detailed description is presented elsewhere.¹⁷⁾ Applied to the observation shown in Fig. 4, this interpretation is as follows: because of the two different variants of TiCu precipitates lying on $[0\bar{1}1]_{\text{B19}}$ and $[011]_{\text{B19}}$ habit planes respectively, only compressive stress fields exist along each direction in the plane of the TEM foil. Thus, coherency stresses are not favoring any specific martensite variant with the consequence that the martensitic transformation is hindered. Further undercooling is required to initiate the martensitic transformation leading to lower transformation temperatures as depicted in Fig. 1(c).

The broad peak form is related to an inhomogeneous stress distribution as a result of the densely precipitated thin plates considering different local equilibrium conditions at the individual interfaces for the transformation behavior in Fig. 1(c).¹⁷⁾ Finally, the formation of densely precipitated thin plates is supposed to be related to an enhanced amount of point defects quenched in by the rapid cooling during the melt-spinning process.¹⁶⁾

The remaining question is to explain the raised transformation temperatures for the semi-coherent fitting TiCu precipitates in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloys shown in Fig. 1(b). First of all, the loss of coherency stresses associated with the appearance of misfit dislocations at the interfaces would only return the transformation temperatures to the initial values of the homogenized material shown in Fig. 1(a). It is once more emphasized here that Cu depletion in the matrix owing to the precipitation process is negligible. Further, a depletion zone of Cu in the matrix would only explain decreasing transformation temperatures but not raising ones since the Ti content remains constant.

Thus, another mechanism certainly becomes operative. It is well known that the martensitic transformation is nucleated

Fig. 4 TEM bright field micrograph showing the microstructure of a melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbon annealed at 460°C for 2 h. Thin plate-like TiCu precipitates marked by arrow heads are observed. Note the strain contrast around the precipitates owing to coherency stresses. Beam direction $\approx [100]_{\text{B19}}$ direction of the martensitic B19-matrix using a g -vector $\parallel [011]$.

heterogeneously at lattice defects especially at arrangements of dislocations.^{21,22} The semi-coherent interfaces between the TiCu precipitates and the matrix as shown in Fig. 2(c) provide an arrangement of misfit dislocations. The strain fields around these dislocations being largest directly at the interfaces lead to displacements of matrix atoms favoring the first transformation shear. Consequently, the semi-coherent interfaces act as preferential nucleation sites and cause an increase of both, martensitic and its reverse transformation temperatures, compared to the homogenized material.

Finally, the observation of sharp transformation peaks compared to the broad ones in Fig. 1(c) can be related to a homogeneous distribution of the TiCu precipitates including the formation of martensite at all interfaces simultaneously.

5. Conclusions

(1) It was found that thin coherent plate-like TiCu precipitates in melt-spun $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons act to lower the transformation temperatures and broaden the DSC peak form. The explanation is that the coherency stresses at the interfaces of the densely precipitated thin plates act to stabilize the parent phase and thus hindering the martensitic transformation. Therefore, further undercooling is required to start the martensitic transformation.

(2) Thicker semi-coherent TiCu precipitates produce the opposite effect; that is, martensitic and reverse transformation temperatures were raised. It is believed that arrangements of misfit dislocations at the TiCu/matrix interfaces act as preferential nucleation sites for the formation of martensite governing this transformation behavior.

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