

Structural transformations in Ti-Ni-Cu shape memory ribbons

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Ti-Ni-Cu shape memory alloy ribbons produced by melt-spinning were investigated in order to assess the crystallinity and the influence of further crystallization on the martensitic transformation. The as-quenched ribbons are partially crystalline, with grains in the range of microns and typical martensitic structure. As result of heating the ribbons, a peak develops around 460°C and, on further cooling, the physical evidence of the martensitic transformation reflected in the DSc peak is increased several times. Both the crystallization and the martensitic transformation have been investigated as a function of the heating and cooling rates. It is concluded that a significant part of the Ti-Ni-Cu shape memory alloy ribbons produced by melt-spinning fully crystallizes only after a heat treatment that leads to a full martensitic transformation and the shape memory effect.

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1. Introduction

Shape memory alloys undergo a thermoelastic reversible phase transformation as a base for the shape memory effect and associated properties. In addition, some alloys are also known to exhibit shape control using the magnetic field.

The thermally controlled martensitic phase transition occurs between crystalline states of the high temperature phase and the low temperature phase. However, recent approaches intend to further expand the limits of the investigation to alloys that are manufactured via amorphous materials technological paths [e.g. 1-3]. While an amorphous state is often achieved by depositing films on unheated substrates [4-6], it can also be obtained by melt-spinning or suction techniques. The melt spinning technique has the advantage that that it can lead to higher productivity compared to thin films, but on the other hand, the parameters are more difficult to control in order to obtain homogenous structures.

NiTi are among the most used shape memory alloys and their properties have been extensively investigated using various techniques, like electric resistivity (ΔR), differential scanning calorimetry (DSC), internal friction and resonance methods [7-10]. Additional alloying elements are often used to further improve the shape memory behavior. Thus, the addition of Pd increases the transformation temperatures [11-13] and Nb is effective for increasing the thermal hysteresis of the transformation [14,15]. The Ni-Ti -Cu system is interesting due to the fact that it allows control of various properties (e.g. a high actuation or a low hysteresis) by changing the Cu content [16]. Since amorphous-crystalline melt-spun Ti-Ni-Cu systems, having interesting mechanical properties [17-19], can be obtained, the crystallization process has also attracted attention.

Melt-spun NiTiCu ribbons were investigated in the present work. The aim of the research was to study the crystallization process of the as-solidified ribbons, to analyse the changes in the martensitic transformation as a result of the crystallization process and to determine the activation energy of the crystallization process.

2. Experimental details

Ti-Ni-Cu shape memory ribbons of 30 μm thickness and 2 mm width were produced by melt-spinning. A master alloy with nominal composition $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ was prepared by arc melting in high vacuum. The as-manufactured alloy was then melted in an induction furnace and melt-spun on the outer surface of a copper drum. The cooling rate was in the range of 10^{-6} K/s.

The structure of the ribbons was examined using optical microscopy (OM), high resolution electron microscopy (HRTEM) and X-ray diffraction (XRD); the phase transformation was studied using DSC and ΔR measurements.

3. Results and discussion

$\text{Ti}_{50}\text{Ni}_{50-x}\text{Cu}_x$ shape memory alloys can be manufactured by melt-spinning, and their properties are influenced by the Ni/Cu ratio. For Cu contents higher than 20at % it has been shown that a B2-orthorhombic single transition occurs, in contrast with lower Cu contents where B2-orthorhombic-monoclinic (higher than 8.5 at % Cu) or B2-monoclinic transition (less than 7.5 at % Cu) [20]. The martensitic transformation hysteresis is much lower during the B2-orthorhombic transition, compared to other types of transformation [16]. Therefore the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ is considered a convenient composition for manufacturing micro-actuators based on shape memory properties and

ribbons produced by melt-spinning could further enlarge the limits of application.

According to the X-ray diffraction data in Fig. 1.a, the structure is only partially crystalline and not amorphous in the as-quenched state, due to the high cooling rate of the melt during the spinning process. The optical microstructure of the ribbons, as shown in Fig. 1.b in cross-section, reveals a fine double columnar structure, also as a result of the rapid solidification.

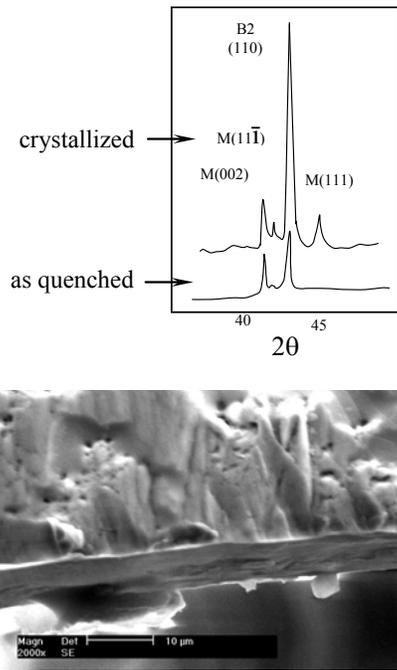


Fig. 1. a) XRD data and b) SEM picture of the as-solidified $Ti_{50}Ni_{25}Cu_{25}$ ribbons.

Shape memory effect can be observed in materials that are not fully crystallized. For example, it has been found that the shape memory effect can be detected only in later stages of crystallization of Ni-Mn-Ga films, while ferromagnetic behavior occurs in earlier stages of the process [21]. During crystallization, the fraction of material undergoing martensitic transformation and shape memory effect gradually increases.

Partial crystallization in the ribbon can result in a two way shape memory effect due to the bimetal effect, this time in a natural composite. The crystalline part of the alloy undergoes a phase transition and causes the shape recovery on heating, while the other part does not and leads to a shape memory effect on cooling. Such a behavior has been observed in the as-quenched ribbons.

Even in the as-quenched state, the evidence of the martensitic structure can be observed, as shown in the X-ray data. Figure. 2 a,b, is strengthening the observation that the samples are not amorphous in this state. Parallel twins of about 40 nm width have been observed and are detailed in Fig 2b.

Low peaks are observed on the DSC scans of the as quenched ribbons, however during heating, a peak develops around 460 °C, as shown in fig. 3. The position of the peak is influenced by the heating rate and is consistent with a crystallization process that occurs in the ribbons

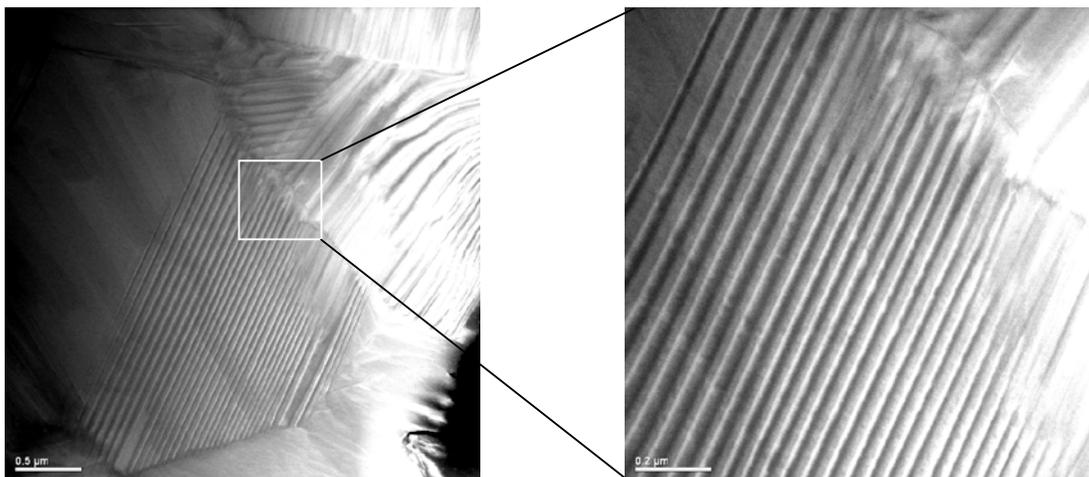


Fig. 2. Transmission electron microscopy of the $Ti_{50}Ni_{25}Cu_{25}$ shape memory ribbons.

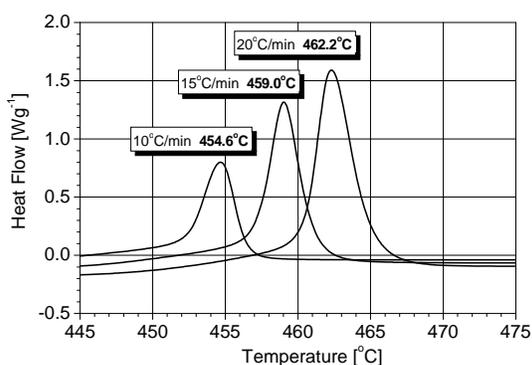


Fig. 3 Crystallization thermal scans of $Ti_{50}Ni_{25}Cu_{25}$ at different heating rates ($^{\circ}C/min$). The position of the peak shifts toward higher temperatures as the heating rate is increased.

A study of the martensitic transformation before and after the full crystallization reveals an increase in the temperature of the peak (T_p) in the crystalline samples, as well as a significant increase in the features of the peak area, as shown in table 1. The results observed so far, corroborated with DSC analysis strengthen the opinion that the ribbons are only partially crystalline in the as-quenched state and the fact that they become fully crystalline only as result of annealing. This observation is further strengthened by the fact that a more than six times increase in the DSC area, observed as result of crystallization (fig. 5 for $20^{\circ}C/min$ before and after crystallization).

Table 1. Characteristics of $Ti_{50}Ni_{25}Cu_{25}$ alloy (at $20^{\circ}C/min$ heating rate).

Sample state	Peak temperature T_p [$^{\circ}C$]	DSC area [J/g]	Crystallization peak T_x [$^{\circ}C$]
Partially crystalline	57.3	1.731	462.2
Fully crystalline	74.6	11.85	-

The electric resistivity vs temperature dependence in the specimens, both as-quenched and fully crystallized, as plotted in Fig. 4 shows a martensitic transition, with a hysteresis of approx. $10^{\circ}C$ and $15^{\circ}C$, respectively. As stated before, a low hysteresis is characteristic for Ti-Ni-Cu shape memory alloys with high copper content and the results obtained in the crystallized ribbons is in the similar temperature range.

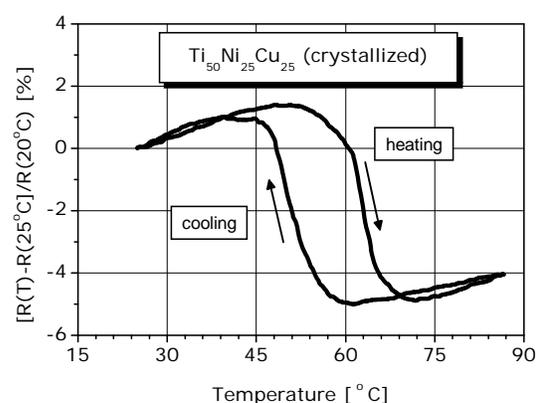
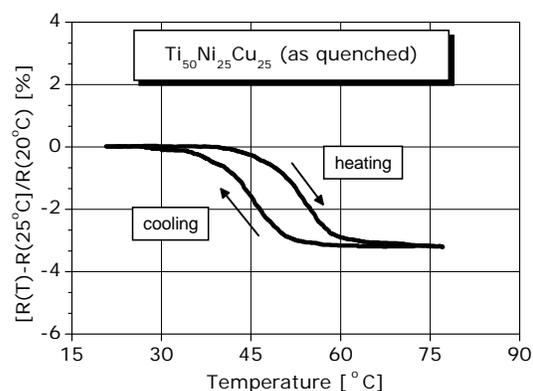


Fig. 4. Resistivity change during martensitic transformation in $Ti_{50}Ni_{25}Cu_{25}$ ribbons.

Further experiments allowed us to evaluate the activation energy for the processes governing the crystallization and the phase transition in the ribbons. For example, fig. 5 shows the results obtained for the as-quenched ribbons tested at rates from 10 to $20^{\circ}C/min$ and the results are compared with the fully crystallized sample.

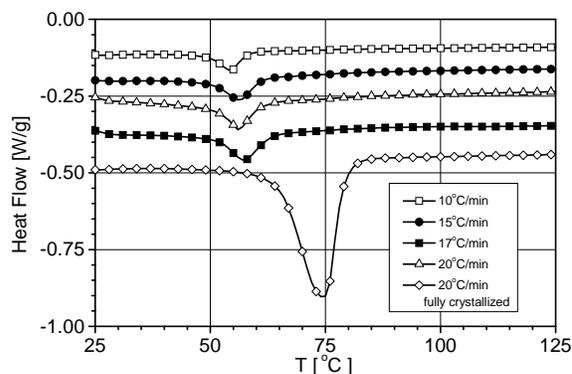


Fig. 5. Martensitic transformation in $Ti_{50}Ni_{25}Cu_{25}$ at different heating rates ($^{\circ}C/min$).

The Kissinger equation

$$\frac{\alpha}{T_p^2} = C \exp\left(\frac{E_x}{kT_p}\right)$$

was used for determination (Fig. 6) of the effective activation energy E_x . According to our data, the crystallization process requires an activation energy of 4.19 eV (fig. 6 a), while the activation energy for the martensitic transformation in the partially crystalline ribbons is 2.16 eV and 2.29 eV in the crystallized ribbons respectively (fig. 6 b).

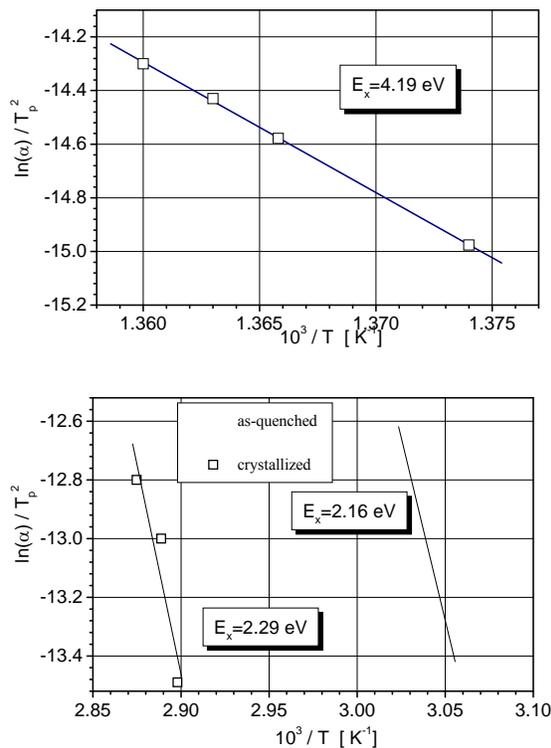


Fig. 6. Kissinger plot of the $Ti_{50}Ni_{25}Cu_{25}$ alloy. a) crystallization peak b) martensitic transformation peak

The results for the continuous heating activation energy for crystallization are close to the ones determined by Liu and Duh [22] for continuous heating of thin NiTi films and slightly higher than the one determined by Schlossmacher et al. [23] for Ti-Ni-Cu ribbons crystallized under non-isothermal conditions. Chang et al. [24] showed that compared to NiTi, the addition of Cu lowers the crystallization activation energy, but suggested that long annealing times may lead to an increase of Cu content in the crystallized grains resulting in an increased fragility.

Our study shows that a crystallization process occurs in the temperature range of 450–470 °C, depending on the heating rate. The martensitic transformation developed in the ribbon proves that the shape change observed optically

is associated with the memory effect in both the as-quenched and crystallized state.

4. Conclusions

Rapidly solidified ribbons made out of $Ti_{50}Ni_{25}Cu_{25}$ shape memory alloys are only partially crystalline in the as solidified state. They become fully crystalline during the crystallization process that takes place around 460 °C and leads to a well developed phase transition, compared to the phase transition observed in the as-quenched state. Further studies have shown that the crystallization process needs an activation energy of about 4.19 eV, while for the martensitic phase transition and energy of about 2.16 to 2.29 eV are needed, depending on the degree of crystallinity.

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