Role of Austenite Microstructure on Martensitic Transformation in Fe–Ni–Co–Ti–Shape Memory Alloys

N. Jost, Institut für Werkstoffe, Ruhr–Universität Bochum, D–4630 Bochum

Introduction

The most important prerequisite for the occurrence of shape memory is the thermoelasticity of the martensite. A definition of thermoelasticity can be given by the following conditions:

1. Reversibility of the transformation
2. A small temperature hysteresis between the forward and the reverse transformation
3. A mobile phase boundary γ/α, which should not be blocked by dislocations due to plastic deformation during the growth of the martensite

For iron–based alloys these points seems very difficult to fulfill. One possible way is the hardening of the parent phase (i.e. the austenite γ) by lattice defects, which can be systematically described with the four principle hardening–mechanisms derived from zero– to three–dimensional obstacles (1):

0 → point defects	(solid solution–, radiation–hardening)
1 → dislocations	(work–hardening)
2 → grain boundaries	(fine grain hardening)
3 → precipitates	(precipitation–, dispersion–hardening)

The zero– to two–dimensional defects interact with the transformation interface and influence the additional undercooling $\Delta T_{\gamma \to \alpha}$ below, or the overheating $\Delta T_{\alpha \to \gamma}$ above the thermodynamical equilibrium temperature T_0. Precipitation also changes the chemical composition of the matrix and thus T_0. The martensite–start–temperature M_s as well as the austenite–start–temperature A_s may be raised or lowered (2):

$$M_s = T_0 - \Delta T_{\gamma \to \alpha} \tag{1a}$$

$$A_s = T_0 + \Delta T_{\alpha \to \gamma} \tag{1b}$$

Work– and precipitation hardening are of special interest because the yield–stress of the austenite can be influenced in a wide range. If the austenite hardness reaches a very high value, a subsequent martensitic transformation may lead only to elastic deformation of the matrix, which is favourable for a small temperature hysteresis of a transforming cycle, a lathlike martensite morphology and, thereby, for thermoelastic martensite. In this condition the alloy should show a shape memory effect (3).

A combined thermomechanical treatment (for example hot rolling with subsequent aging) causes quite a complex microstructure consisting of austenite, shear bands and homogeneously and inhomogeneously distributed precipitates. The martensitic transformation should be influenced in a wide range.

The purpose of this work is to investigate the influence of all described microstructures on the course and temperatures of the martensitic transformation and to define an optimal treatment for introducing a shape–memory–effect in Fe–Ni–Co–Ti–alloys. Additional, some results of thermal fatigue experiments shall give first criterions for the application of these new shape memory alloys.

Experimental procedure

Two Fe–Ni–Co–Ti alloys were prepared by arc–melting in an Ar–atmosphere. The chemical composition of both alloys is given in table 1.

Alloy	Ni	Co	Ti	C	O	N	Fe
I	29.1	15,1	3.9	<0.005	<0.004	<0.005	bal.
II	32.0	12.0	3.8	<0.005	<0.004	<0.005	bal.

Table 1: Composition of the alloys investigated (wt.%)

After 60% hot–rolling at 1150 °C the material was solution treated in evacuated quartz—capsules (20h/1250 °C) and water quenched. After solution treatment both alloys were austenitic even at room–temperature (RT).

The alloys were deformed by hot–rolling between $\epsilon = 0$ % and $\epsilon = 70$ % reduction in thickness in steps of $\epsilon = 10$ % at a temperature of $T_\epsilon = 1250$ °C and subsequent water quenching. After this they were aged at $T_a = 600$ °C for various times t_a and water quenched.

In order to investigate the transformation behavior after thermal fatigue, undeformed but aged specimens of alloy II were thermally cycled up to 2.500 times.

The transformation temperatures were determined by dilatometric measurements in a temperature range between 400 °C and liquid nitrogen temperature (– 196 °C). They are defined by the first detectable deviation from linearity of the dilatation vs. temperature curve on cooling and heating. The thermal hysteresis is characterized as the temperature difference between 50 % forward transformation ($\gamma \rightarrow \alpha$) and 50 % reverse transformation ($\alpha \rightarrow \gamma$).

$$\Delta T_h = A_{50} - M_{50} \tag{2}$$

Dilatation is defined by the maximum linear expansion induced by complete $\gamma \rightarrow \alpha$ transformation down to – 196 °C.

The microstructure before and after deformation, ausaging and the subsequent martensitic transformation were analyzed by light– (LM) and scanning electron microscopy (SEM).

Results and Discussion

a) Thermomechanical treatment

Fig. 1 shows the change in M_s–temperature, thermal–hysteresis and dilatation with ausaging time at $T_a = 600$ °C after different amounts of prior plastic deformation. In the unaged conditions, martensite start temperatures of $M_s = -90$ °C for the undeformed and 30 % deformed state and $M_s = -140$ °C for the 70% deformed state respectively can be observed. The hysteresis amounts about $\Delta T_h = 500$ °C. As the aging time is increased, the M_s–temperature first decreases and then gradually increases. Aging for 10 minutes leads to a very strong decrease of the thermal hysteresis to about 100 °C. Thereby the deformed specimens show a lower hysteresis as the undeformed. M_s and ΔT_h becomes a minimum at an aging time of $t_a = 30$ min. The dilatation is at first in good aggreement with M_s: the higher M_s, the higher is the possible dilatation. But the dilatation strongly decreases after 20 h aging for the undeformed and 5 h for the 70% deformed state.

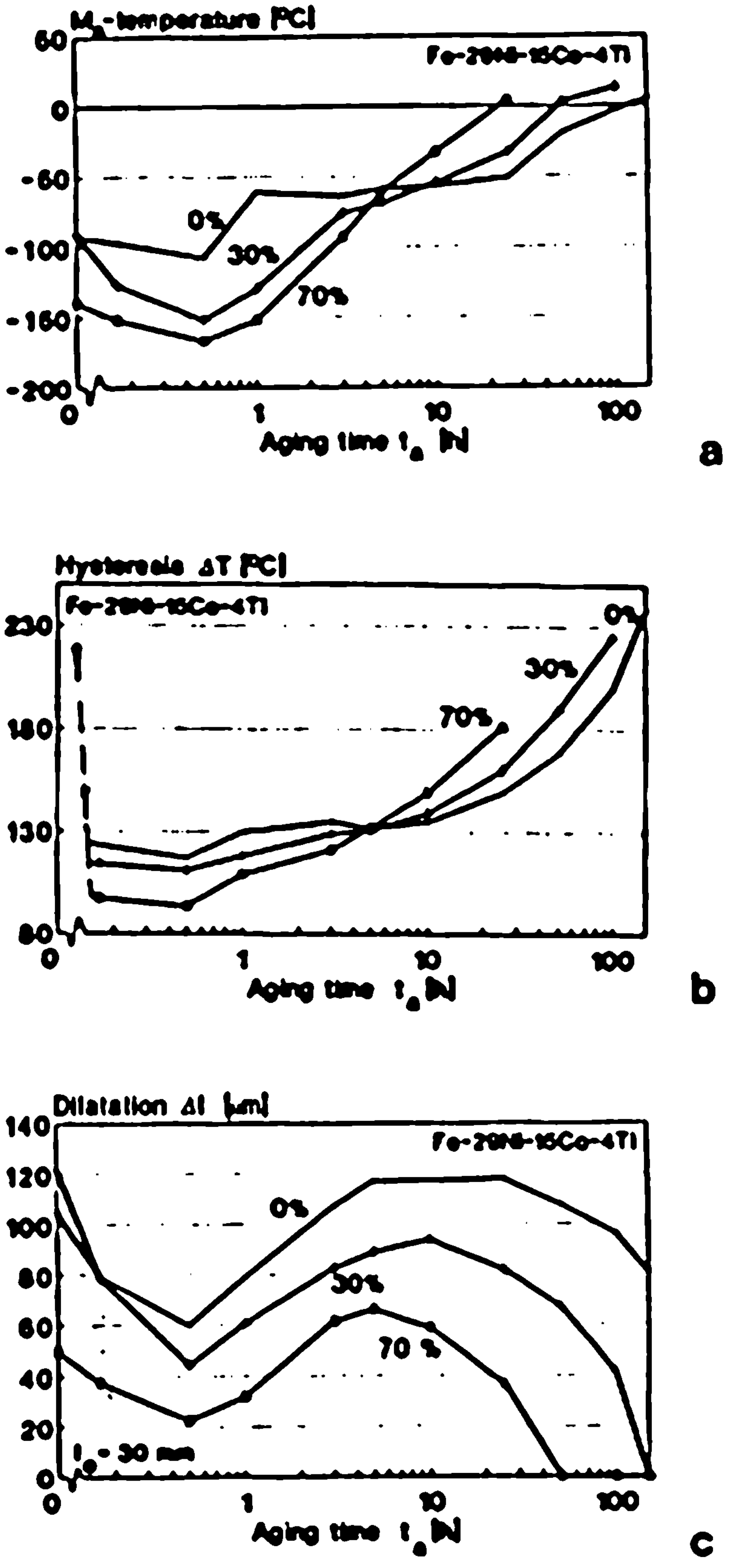

Fig. 1a–c: Measurements of M_s–temperatures (a), hysteresis (b) and dilatation (c) after different amounts of prior deformation and aging times

Fig. 2a: Microstructure of alloy I without prior deformation, (1h/600 °C → −196 °C → RT), typical thin plate martensite (LM)

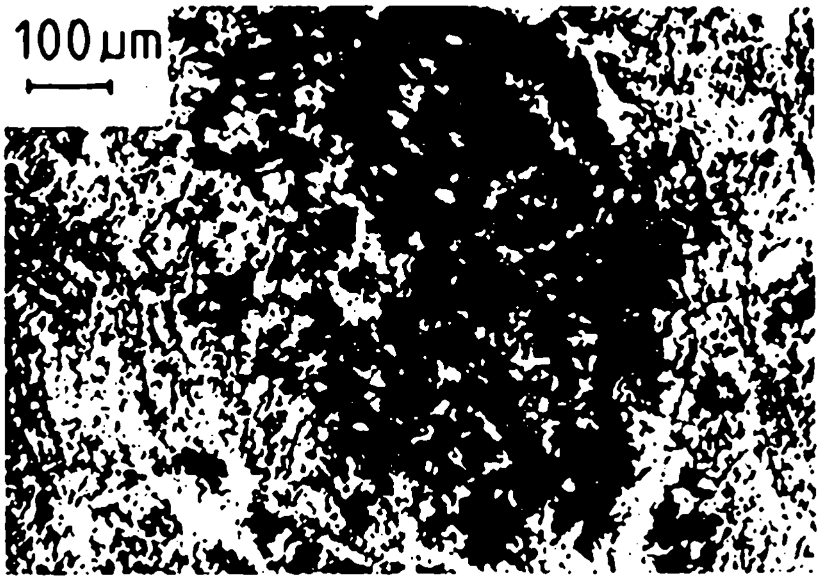

Fig. 2b: Microstructure of alloy I with 70 % prior deformation, (10h/600 °C → −196 °C → RT), discontinuous precipitation of stable η–phase especially at grain–boundaries and shear–bands (LM)

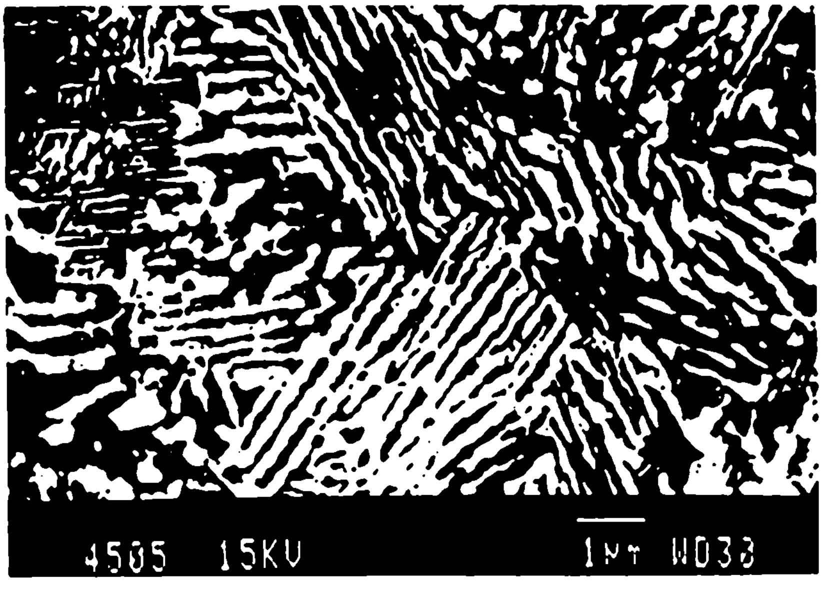

Fig. 2c: Microstructure of alloy I with 70 % prior deformation and 50 h aging at 600 °C, complete transformation into a lamellar structure due to the discontinuous precipitation of η–phase (SEM)

These results can be explained by the change in microstructure with aging time and degree of prior deformation. In Fig. 2 some examples of optical micrographs are given. It is evident that the specimens with a small hysteresis exhibit the typical thin plate martensite (Fig. 2a). As it was reported earlier, this is the result of a dispersion of small coherent and ordered γ'-$(Ni,Co)_3Ti$ precipitates which lead to a very high value of austenite hardness (4,5). If the diameter of the precipitates is lower than a critical value ($d<d_c$), the particles will be sheared with the martensite into a metastable structure. Thereby elastic energy is stored, which lowers the required overheating (i.e. A_s and A_f) and thus the thermal hysteresis.

High amounts of deformation produce large shear bands. Subsequent aging leads to a combined continuous and, especially at deformed grain boundaries and shear bands, discontinuous precipitation. The discontinuous precipitates can be analyzed as the stable η-Phase Ni_3Ti which implies an overaged condition (Fig. 2b). With aging time these precipitates grow very rapidly into the austenite grain so that amount of transformable residual austenite and thus the dilatation decreases. At the same time this austenite becomes more and more metastable due to the lower constituent of Ni in the matrix. In this condition M_s and ΔT_h increase. After an aging time of 50 h of the 70% deformed specimen no residual austenite can be observed. The specimen is completely transformed into a lamellar structure due to the discontinuous precipitation of η-phase (Fig. 2c).

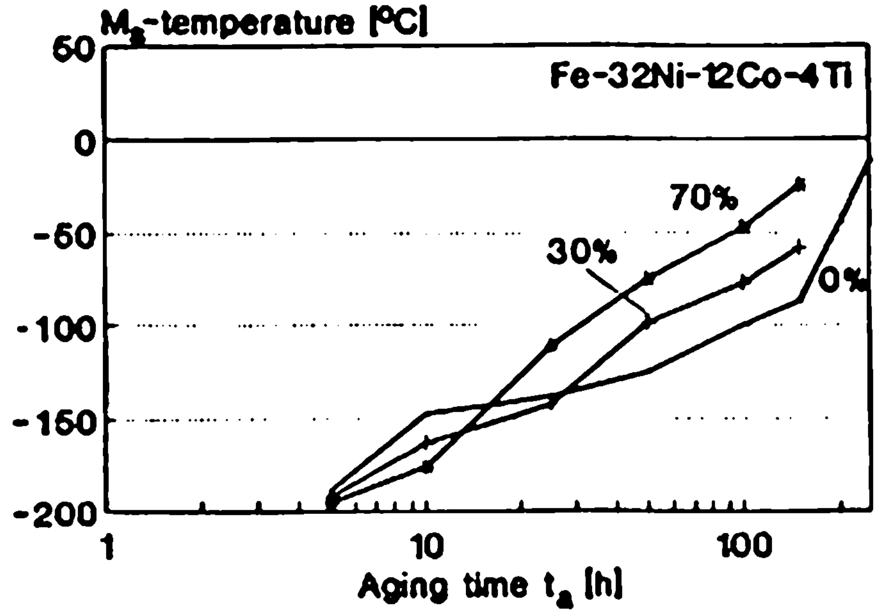

Fig. 3a: M_s-temperatures of alloy II after different amounts of prior deformation and aging times

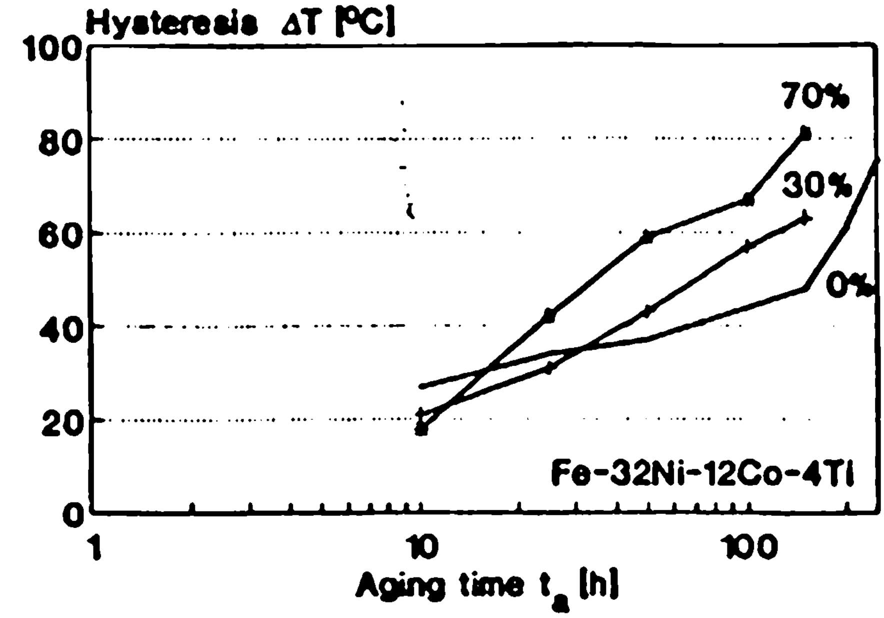

Fig. 3b: Hysteresis of alloy II after different amounts of prior deformation and aging times

Fig. 3 shows the results of alloy II. M_s of the unaged specimens is below −196 °C because of its higher Ni–content, and longer aging is necessary to lower the Ni–content in the matrix so that a martensitic transformation can be observed above −196 °C. Aging for 10 h leads to quite a low M_s–temperature of about −150 °C. It should be noted that the influence of the prior deformation is of the same degree of order as in alloy I. With further aging M_s and ΔT_h increases. In aggreement with alloy I, the smallest hysteresis is observed at the lowest M_s–temperature. This implies that the primarily mechanism to obtain a small hysteresis is a effective austenite hardening by coherent and ordered particles which are able to store elastic energy by shearing with the martensite into a metastable structure.

b) Thermal fatigue

It could be shown in some earlier investigations that Fe–Ni–Co–Ti–alloys exhibit a shape—memory effect related to thermoelastic martensite after an ausaging treatment (3–5). One important criterion for the applicability of these alloys is the transformation behaviour after thermal fatigue. Fig. 4 shows the results of undeformed but aged specimens of alloy II after different numbers of thermal cycles. Alloy II was chosen because of its nearly complete forward transformation (M_s = − 100 °C, $M_f \approx$ − 196 °C) and a very small temperature hysteresis of ΔT_h = 42 °C after 100 h aging at 600 °C.

As it can be seen from Fig. 4a, thermal cycling leads to a remarkable change of the whole transformation characteristic. In Fig. 4b–e the measurements of the transformation temperatures, dilatation, thermal–hysteresis and hardness are summarized. Most remarkable is the considerable decrease of M_s and dilatation and the simultaneously strong increase of ΔT_h and the austenite hardness. Up to 50 thermal cycles A_s and A_f first decrease. After 50 thermal cycles no further change in A_s and A_f can be observed.

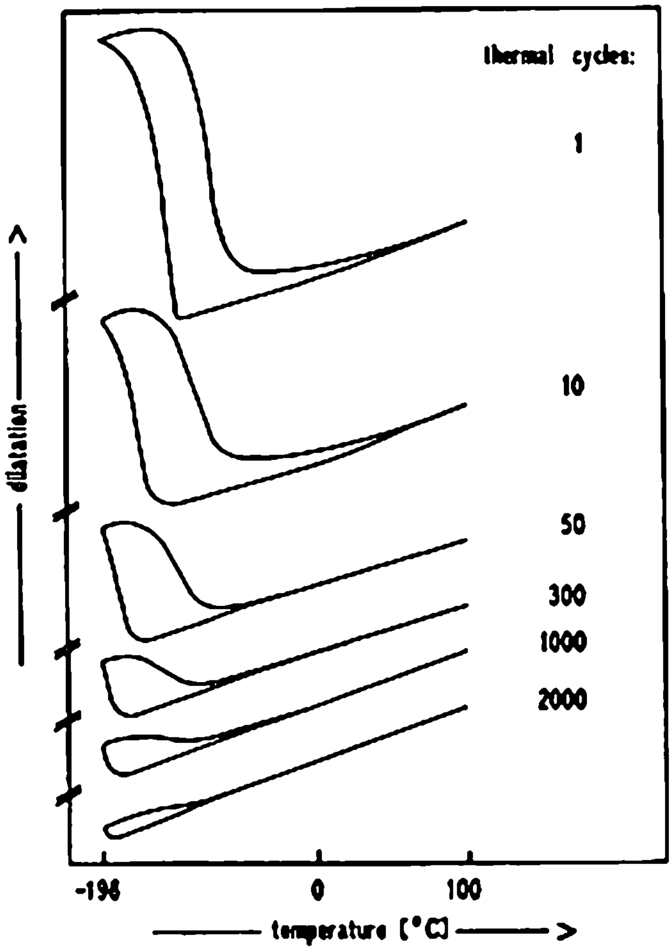

Fig. 4a: Transformation loops after different numbers of thermal cycles (dilatometric measurements, alloy II, 100 h/600 °C)

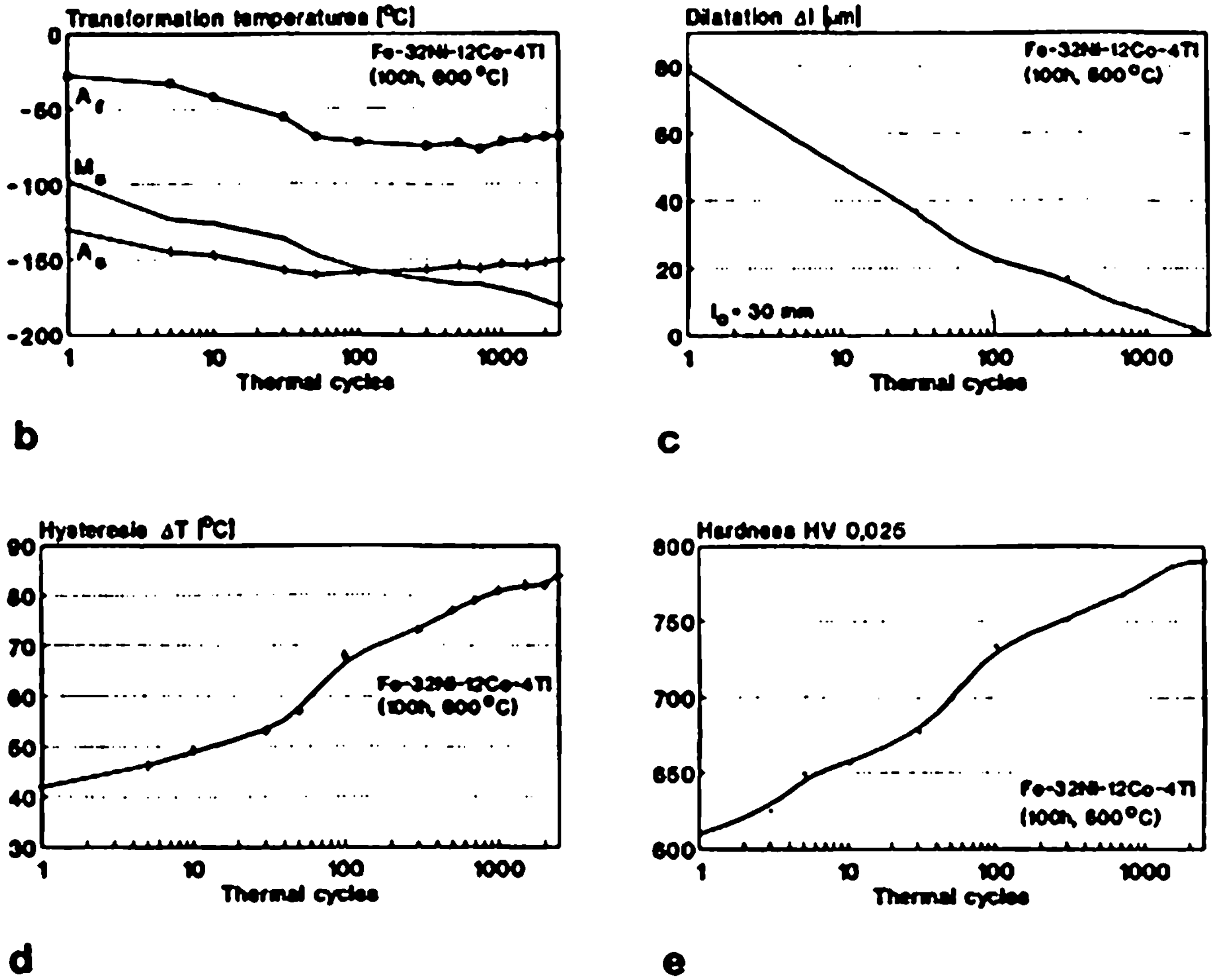

Fig. 4b–e: Measurements of transformation temperatures, dilatation, hysteresis and austenite hardness after different numbers of thermal cycles (alloy II)

For an analysis of the effect of cycling the martensite morphology and the observation of work hardening can be used for an interpretation. As it was said above, the forward transformation is nearly complete. This means that there is nucleation of quite large martensite (first nucleated) as well as very small martensite plates (last nucleated). In addition, the high austenite hardness of about HV 600 for the uncycled state has to be taken into account. Lattice defects such as dislocatons and stacking faults will primarily be produced by the nucleation and growth of the first martensite plates. The dislocations impede the motion of the transformation interface with the result that this martensite becomes very rapidly irreversible. As a consequence, the amount of residual austenite and, thereby, the dilatation decreases. Simultaneously the austenite hardness increases which, in turn, leads to a steady decrease of M_s. As a further consequence, only the small martensite plates will nucleate and grow after the first thermal cycles. A_s and A_f show a strong decrease because this martensite needs a much lower overheating, compared to the first nucleated large martensite plates. After 100 cycles this effect is compensated. Although the transformation loops are still complete, the dislocation density increases and more and more martensite becomes irreversible. Complete irreversibility can be observed after about 2500 cycles. In this condition the microstructure is fully martensitic, whereby the martensite seems to be strictly orientated in the grains (Fig. 5).

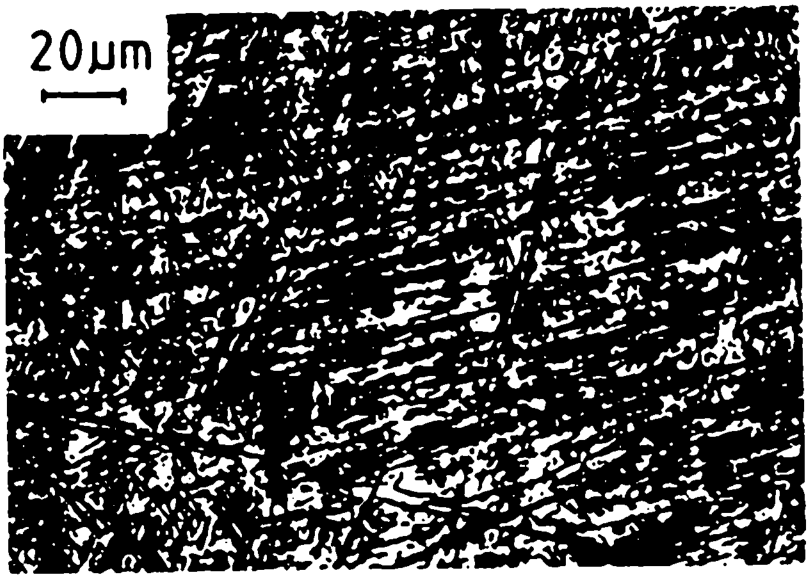

Fig. 5: Microstructure of alloy II after 2500 thermal cycles, strictly orientated martensite (LM)

Conclusions

1. The prerequisite condition for introducing thermoelasticity of the martensite and, thereby, shape memory in the investigated alloy system is a precipitation hardening with coherent and ordered γ'–$(Ni,Co)_3Ti$–particles.
2. Aging leads to a strong decrease of ΔT_h. This is due to the decrease of A_s and A_f.
3. Thermo–mechanical treatment results in a very rapid growth of stable η–phase, so that the amount of residual austenite decreases and the metastability increases.
4. The smallest hysteresis can be observed at the lowest M_s–temperatures.
5. Thermal cycling leads to an increase of austenite hardness and thermal hysteresis because of the introduction of lattice defects. Simultaneously M_s and dilatation decrease.
6. After about 2500 thermal cycles the alloy is completely thermal fatigued. In this condition the whole specimen is martensitic.

Acknowledgement

Financial support of the German Science Foundation (DFG HO 325/20) is gratefully acknowledged.

References

(1) E. Hornbogen, Acta Met. 32 (1984) 615–627
(2) N. Jost, E. Hornbogen, in: Proc. Int. Conf. Phase Transformations 1987, Cambridge, England, The Insitute of Metals, G. W. Lorimer (ed.), 1988, p. 405–407
(3) Y. U. Koval, V. V. Kokorin, L. G. Khandros, Fiz. metal. metalloved. 48 (1979) 1309–1311
(4) T. Maki, K. Kobayashi, I. Tamura, in: Proc. ICOMAT '82, Leuven, Belgium, Journal de Physique, 1982, p. 541–546
(5) N. Jost, M. Hühner, Pract. Met. 26 (1989) in print