INVESTIGATION OF PHYSICAL METALLURGY CHARACTERISTICS OF TWO-WAY SHAPE MEMORY EFFECT IN TiNi ALLOY

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The two-way shape memory effect (TWSME) represents a behaviour in which a reversible temperature change of a "memory alloy" is accompanied with spontaneous reversible macroscopic deformations. It was generally accepted that internal defects, which are introduced during the so called training procedure, are responsible for this phenomenon. The formation of ghost martensite may contribute to the enhanced reversibility of binary TiNi system without R-phase formation. The aim of this study is to investigate TiNi materials in which R-phase formation occurs. The trained specimens contain dislocation array, stabilised martensite and ghost martensite. It is expected, owing to the specific crystallographic relation, that ghost martensite formation can facilitate both the R-phase formation as well as B 19′ martensite formation and in this way support the reversible memory of TiNi alloys.

VÝZKUM FYZIKÁLNĚ METALURGICKÝCH CHARAKTERISTIK VRATNÉHO TVAROVĚ PAMĚŤOVÉHO JEVU VE SLITINĚ TiNi

Vratný tvarově paměťový jev (TWSME) představuje odezvu, při níž je doprovázena vratná změna teploty „paměťové slitiny" spontánními vratnými makroskopickými deformacemi. Jako všeobecný princip bylo přijato, že defekty vyvolané v materiálu během tzv. tréninkového procesu zodpovídají za tento jev. Vznik tzv. martenzitického přízraku (ghost martensite) může přispět k zintenzívnění vratnosti v binární soustavě TiNi bez vzniku R-fáze. Cílem této studie byl výzkum materiálů typu TiNi, v nichž dochází k tvorbě R-fáze. Ve vzorcích po tréninkovém procesu jsou dislokace uspořádány do řad, dochází ke stabilizaci martenzitu a ke vzniku martenzitického přízraku. Předpokládá se, vzhledem ke specifickým krystalografickým vztahům, že vznik martenzitického přízraku může usnadnit jak tvorbu R-fáze, tak i vznik martenzitu B 19′. Tyto procesy podporují vratný paměťový jev ve slitinách TiNi.

Key words: shape memory alloy, two-way shape memory effect, ghost martensite, R-phase, B 19′ martensite, training procedure, hard, soft training

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1. Introduction

The two-way shape memory effect (TWSME) is a special kind of shape memory behaviour. It is characterised by a macroscopic shape change, which depends only on temperature. No external stress has to be applied on the material. The physical basis of TWSME is a reversible martensite transformation. Spontaneous macroscopic shape change is linked to the dominant formation of the preferential martensite variant (cold shape) and retransformation of martensite to high temperature phase (hot shape). The TWSME is not an inherent property of shape memory alloys (SMA). The dominant and spontaneous formation of a preferential martensite variant during the cooling process accompanied with transformation plasticity (cold shape) can only be induced after a particular thermomechanical training procedure [1–4]. The training generates some kinds of microstructural asymmetry [2]. The transformation of martensite and a recovery of a hot shape during heating to the high temperature phase should not destroy this asymmetry. The two main structural changes responsible for the TWSME are either based on i) generation of dislocation arrays or ii) presence of stabilised martensite [1, 2].

The most widely accepted mechanism is based on the observation of dislocation arrays generated during training routes. These dislocation arrangements are produced by thermomechanical treatment [1, 2, 5] or by thermal cycling [1, 2, 6]. Based on these observations, the TWSME has been attributed to the oriented residual stresses accompanying the dislocation arrangements. They favour the nucleation and growth of the preferential variant of martensite. Since the formation of martensite is accompanied by shear-like deformation, the residual stresses are relaxed by a shape change [1]. The preferentially formed variant of martensite grows without any external assistance during cooling. Heating and the realised reverse transformation of martensite to high temperature phase (austenite) leads again to the generation of oriented residual stresses in matrix. This process can be repeated during following thermal cycles.

The second mechanism is based on the stabilisation of preferentially oriented martensite variants which are retained after the heating above the original transformation temperature A_f. Only the most favourable oriented variants of martensite grow during applying an external load [1]. However, if the applied load is high enough or repeated, the deformation process is also accompanied by generation of dislocations. According to the assumption of stabilised martensite formation, the generated dislocations do not allow the martensite to shrink and disappear completely after heating to transformation temperature A_f. During cooling the stabilised martensite grows preferentially. The internal stress related to the growth of preferentially oriented martensite modifies the arrangement of further variants, which are also formed in preferential orientation during subsequent cooling. At heating, the less stable variants disappear, however, those originally stabilised by presence of dislocations remain in the matrix.

Authors [1, 7] tried to distinguish between so called intrinsic and extrinsic TWSME. They disproved two previous explanations. Following their assumption, the most important influence of training procedure is not the development of internal oriented stresses, but rather a microstructural anisotropy inducing a thermodynamic anisotropy. The presence of "ghost martensite" was also discussed as a possible reason for TWSME [8, 9]. Different opinions were presented about the effect of R-phase formation in TiNi based alloys on the stability of TWSME [4, 10].

The stability of TWSME represents a very important parameter of this effect in SMA. The complex degradation mechanisms occur in TiNi alloys during repeated heating and/or loading cycles [11]. The accompanied generation of dislocations (work-hardening process) strongly influences the maximum level of generated stress and the extent of reversible strain [12–14]. The aim of this paper is to contribute to the elucidation of the physical metallurgy of two different training procedures and the influence of structural parameters on the TWSME.

The work is a part of the set of studies devoted to the analysis of the SMA-response to the different loading conditions [8, 11] as well as to the investigation of ways resulting in a higher level of the SMA surface properties [15, 16].

2. Experimental material and technique

The experimental material used in this study was a commercial Ti-50.4at.%Ni alloy supplied by Fibra Ltd. in the form of wire with diameter $d = 5$ mm produced by several cold drawing steps with intermediate annealing in vacuum at 800 °C/30 min/water [17]. The wires were deformed with the constant bending strain of 4%. The transformation temperatures, T_{R} (the temperature at which the rhombohedral R-phase starts to form), M_{s} (the temperature of the B 19′ martensite start) and A_{f} (the temperature at which austenite B2 phase finishes), were established by use of measurements of electric resistance versus temperature [18]. The microstructure of specimens was studied by a TEM Jeol 200 CX and Hitachi H7100. Thin foils were finished by two different methods: i) spark cutting (thickness ≈ 400 μm), grinding (≈ 100 μm) and polishing using a twin jet polisher in an electrolyte of $HClO_4$ and CH_3COOH at ≈ 15 V and temperature $T = 0$ °C; ii) diamond saw (thickness ≈ 200 μm), prethinning in dimpler D 500 (≈ 50 μm), and atomic milling (Maxmill 360 B) in order to avoid the influence of liquid environment with H^+. Mechanical properties were tested using Instron 1196 machine equipped with a heating element. Temperature of the TiNi samples was measured by Ni-NiCr thermocouples, which were spark-welded to the central part of specimens. Stability of trained specimens was tested using a specially designed testing device in which the specimens were working against biasing spring with stiffness of 15 N$\cdot$mm^{-1}. This device enabled to measure the extent of reversible bending strain in dependence on the number of performed working cycles. The critical extent of reversible strain $\varepsilon = 2\%$ was defined as a measure of functional element. Mechanical properties, transformation temperatures and microstructure were inspected after performing 10^4 working cycles.

The thermomechanical training consisted of bending of the samples ($\varepsilon = 4\%$) at room temperature and following 20 thermal sequences, each of them composed of heating the material to 135 °C and subsequent cooling to room temperature. Two training procedures were applied: i) so-called "soft training" in which TiNi elements were constrained by a biasing spring with a stiffness of 100 $\mathrm{N \cdot mm^{-1}}$ (specimens are further referred to as A type specimens). ii) "Hard training" in which samples were totally constrained by a rigid frame without a possibility to change their shape during heating (specimens B) [8, 9].

3. Results

The transformation temperatures T_{R}, M_{s} and A_{f} of investigated material variants are summarised in Table 1. The determined changes of transformation temperatures correspond to previously stated principles [11–13].

Table 1. Transformation temperatures of investigated alloys

Specimen	T_{R} [°C]	M_{s}[°C]	A_{f} [°C]
As-received material	43	39	70
After soft training, samples A	50	31	85
After hard training, samples B	60	30	90
After 10^4 working cycles, samples A	53	34	75
After 10^4 working cycles, samples B	70	36	78

The temperature M_{s} decreased after the training. Both soft and hard training procedures are linked to increasing dislocation density leading to the work hardening of investigated material. The decrease of M_{s} is attributed to the lowering of the interface mobility [1, 12, 13] and to the increase of transformation enthalpy as well as entropy, whereby the entropy changes are more pronounced and the equilibrium temperature between austenitic and martensitic phase decreases [19].

The increase of temperature A_{f} after training is due to the lowering of the interface mobility during recovery at heating. In accordance with earlier presented results, the sweeping effect occurs during repeating of the transformation cycles [11]. Contrary to the training procedures, the movement of interfaces becomes easier with increasing number of working cycles and this is connected with the subsequent increase of M_{s} and lowering of the temperature A_{f}. Besides this influence, the effect of the elastic energy stored upon thermoelastic transformation plays an important role [20]. The elastic energy resists the forward transformation and assists in the reverse transformation. Thus, the temperature A_f is lowered with increase of the elastic stored energy during the sweeping effect [11]. The dependence of the reversible deformation (transformation plasticity) on the number of the performed working cycles is plotted in Fig. 1. After some initial cycles (approximately 100 cycles), the extent of TWSME is stabilised, and a degradation of TWSME accompanied with lowering of transformation plasticity follows afterwards. The specimens B exhibit better performance after application of hard training procedure. The reversible strain exceeded the critical value of $\varepsilon = 2\%$ during the entire testing period (up to 10^4 working cycles).

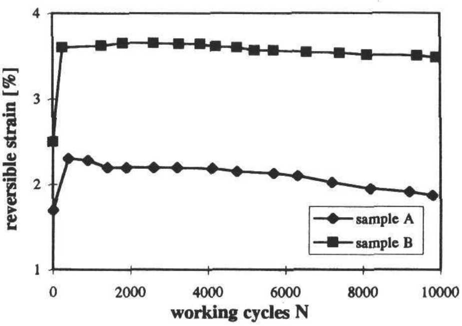

Fig. 1. Reversible strain ε vs. number of working cycles N.

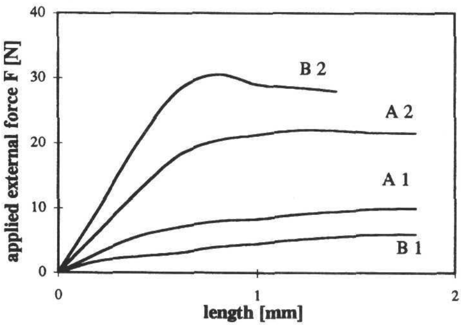

Fig. 2. Force F vs. change of length l plots of trained specimens as detected at room temperature (A_1, B_1 in martensitic state) and at 135 °C (A_2, B_2 in austenitic state).

In the case of A specimens (soft training), the observed number of stable cycles ($\varepsilon > 2\%$) ranged between 3×10^3 and 5×10^3 working cycles. The differences between A and B samples can be ascribed to the higher stability of the transformation process in more work hardened B samples. The results are in good correlation with the results reported in [11]. The more work hardened material (B specimen) prevents generation of new dislocations and subsequent decrease of reversible strain. The higher work hardening rate in the case of trained B specimens compared to the A samples was confirmed by the evaluation of mechanical properties. The applied forces vs. length plots as obtained in bending tests performed at room temperature (below M_s) and at 135 °C (above A_f) are presented in Fig. 2.

Higher strength of high temperature phase indicates that B-type specimens are not only more stable and show higher reversible deformation, but are also able to generate greater forces if compared to the A-type samples. In the case of martensite deformation (testing at room temperature), the B specimens are typified by lower force necessary to the martensite reorientation or for stress induced martensite formation. To obtain the same strain in A and B specimens, a lower force is necessary for B specimens deformation if compared to the A ones. The summary effects of internal stresses generated in the matrix during training sequences and the external stresses applied during the bending test play an important role. The second reason is the easier growth of preferentially oriented martensite variants in material B in which the sweeping effect is more pronounced during training in comparison with A [11].

The results of mechanical tests were correlated with the substructure observations. The substructure of the investigated material in as-received conditions is predominantly formed of B 19′ martensite at room temperature. The martensite is internally twinned and this twinning morphology is conserved after soft training procedure (Fig. 3 – specimen A after 20 training sequences). The substructure after hard training (specimen B) changes dramatically after 20 training sequences (Fig. 4). The martensite plates have preferential orientation, they are finer compared to the as-received state, and typical internal twinning was not observed. The individual martensite plates seem to be single variants with a similar relationship to the matrix. It means that during repeating working cycles, the preferentially oriented martensite variants are formed directly and the reorientation based on the movement of twin boundaries is lacking.

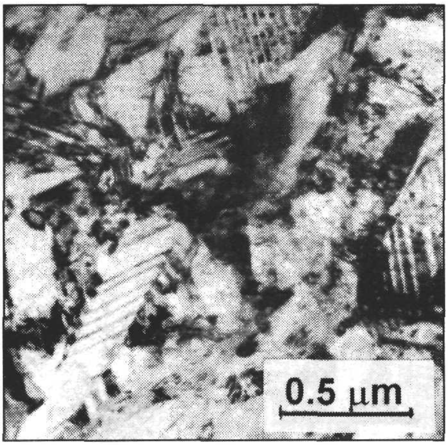

Fig. 3. Substructure of specimen A after soft training.

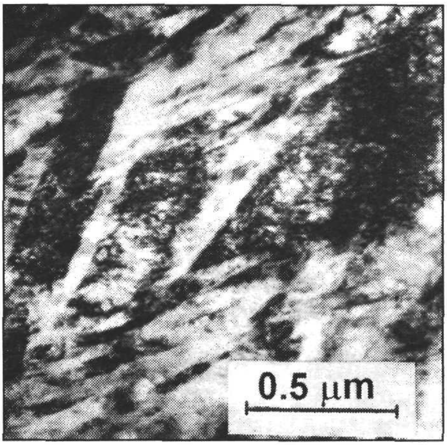

Fig. 4. Substructure of specimen B after hard training (20 training sequences).

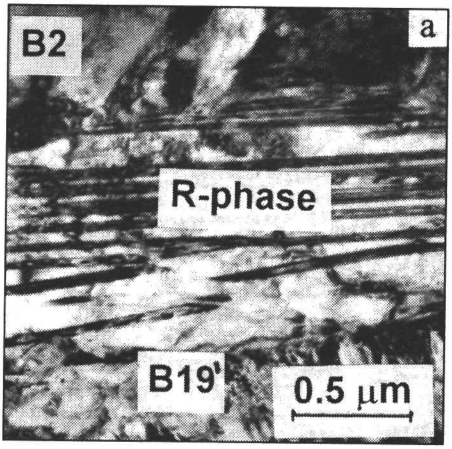

Fig. 5a. Morphology of R-phase – specimen B.

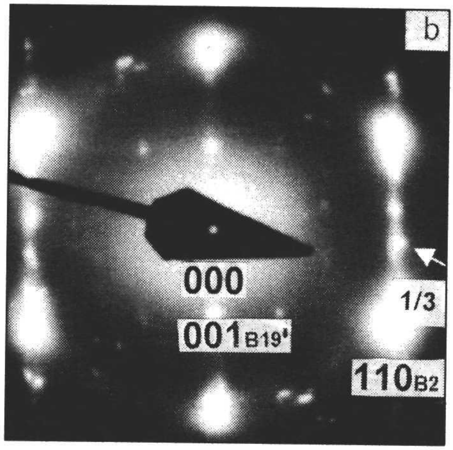

Fig. 5b. Related diffraction pattern (zone axis – [111] B_2).

4. Discussion

The very important difference between specimens A and B, observed in the microstructure, is given by a lower content of R-phase in A specimens and its more frequent occurrence in the B ones after working cycles. The morphology of R-phase and corresponding diffraction spots characterised by typical $\{033\}_{B2}$ diffraction pattern are presented in Fig. 5a,b. In the hard trained specimens B, the increase of transformation temperature T_R was found. This tendency is observed even after working cycles. On the other hand, the temperature T_R in specimens A practically does not change after working cycle (Table 1).

The R-phase formation is often considered as the prerequisite (premartensitic phase) of B 19′ martensite formation [1, 21]. It has been found that higher internal stresses assist in the R-phase formation at given chemical composition of TiNi [1, 13].

A very important character of trained specimens is the formation of so called ghost martensite having a special contrast observed using TEM. The structure of ghost martensite is given in Fig. 6a. Ghost martensite was not observed in as-received samples without training procedure. The structure shown in Fig. 6a is formed of high temperature B2-phase as it results from the diffraction pattern presented in Fig. 6b.

Ghost martensite was reported in several systems. The occurrence of this special form of martensite is related to structural defects (dislocation debris) which remain in the structure after reverse transformation of martensite to austenite [22].

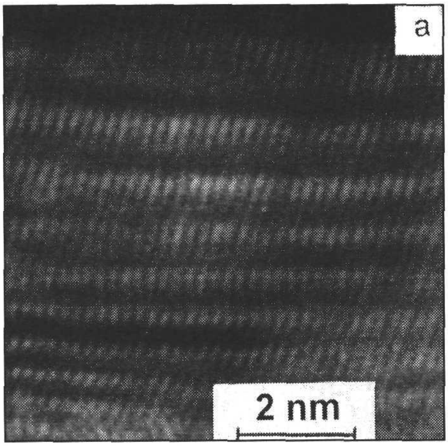

Fig. 6a. Ghost martensite – hard training after 10^4 working cycles (specimen B).

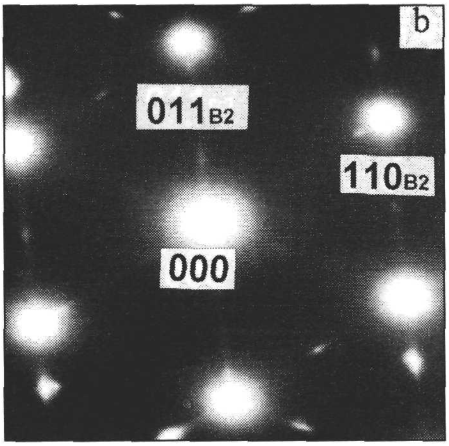

Fig. 6b. Corresponding diffraction pattern.

On the contrary, Olson et al. [23] and also Lee [24] related ghost martensite to the periodic microsegregation of interstitials. The dislocations were visible between alternate bands of TiNi. In the case of TiNi alloys, we suppose that the several changes of the atomic substructure level may occur in a similar way like in the premartensitic "commensurate to incommensurate" transition [21]. These changes could interact with applied mechanical effect as it is in the premartensitic stage. We also expect, that similarly as in CuZn type shape memory alloys, the B 19′ martensite and R-phase are formed preferentially in orientation related to the alternate bands of ghost martensite. It seems that the suggestions made by [2, 8] are supported by these results. However, parameters of TWSME are apparently also related to the presence of oriented stress fields connected with the specific dislocation arrays or stabilised martensite. It is true that the influence of stabilised retained martensite on the TWSME can not be discussed more in detail because the martensite is stable at room temperature in investigated samples. Nevertheless, it is apparent that the applied training procedures led to the stabilisation of the martensite phase. Stabilisation of martensite is accompanied by an increase of temperature A_f and also by an increase of transformation hysteresis (difference between temperatures M_s and A_f) in investigated TiNi alloy.

5. Conclusions

The strong influence of training procedure on TWSME was confirmed. Work hardening of TiNi alloys influences both the extent of reversible strains as well as the stability of TWSME. The morphology of B 19′ martensite changes, temperature

M_s decreases, A_s increases and mechanical properties of B2 and B 19′ phases vary in work hardened specimens. These changes were also detected after working cycles. The stability of TWSME is higher in samples which are more intensely work hardened in the training process. It corresponds to hard training. The formation of R-phase before the phase transformation (B2 → B 19′) contributes to the increase of TWSME stability. TWSME is accompanied with the presence of specific arrays of internal defects. These involve dislocation arrangements, presence of stabilised martensite and ghost martensite. These internal defects favour the formation of specific, preferentially oriented martensitic variants.

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