

The hysteresis loop interior of the thermoelastic martensitic transformation

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Abstract: The hysteresis loop interior of thermoelastic martensitic transformations of TiNi-base shape memory alloys including the transformation with invariant plane is investigated in the partial transformation cycles and discussed. For the transformations with invariant plane the latent hysteresis is negligible small. The dependence of the measured heat on the martensite fraction transformed in the partial cycles is achieved and analyzed. The “invalidity” of the second rule of the thermodynamics is observed in partial cycles of the transformation with invariant plane: at the interrupt of the reverse transformation at a temperature in the interval $T_p^h < T < A_f$ the released heat of the forward transformation measured in the same partial cycle is larger as the absorbed heat of the reverse one. The stability of the two-phase system and connection between the observed energy effects and the dissipation of the elastic energy is analyzed.

Introduction

Through the partial transformation cycles of single crystals of Cu-based shape memory alloys the existence of two equilibrium lines was established, which build the internal loop of the latent hysteresis [1]. The analyze of the interior of the hysteresis shows, that the stored as well as the dissipated energy are of the same kind of elastic nature. Dependence of the dissipated energy on the martensitic fraction includes a parabolic term. The energy dissipated within the latent hysteresis is described by a linear term. Although various investigations of the thermoelastic hysteresis and even quantitative estimations of the stored elastic energy and the dissipated energy [2] the establishment of a direct correlation between stored and dissipated elastic energy or between the thermoelasticity and the hysteresis is unique. The extension to different kinds of

thermoelastic transformations in several alloys including polycrystals is necessary to generalize the thesis.

Several kinds of transformation and hysteresis were investigated by calorimetric measurements for TiNi based alloys. This includes the transformations with invariant plane and therefore minimal hysteresis [3]. This work examines the interior of the hysteresis loops for these transformations.

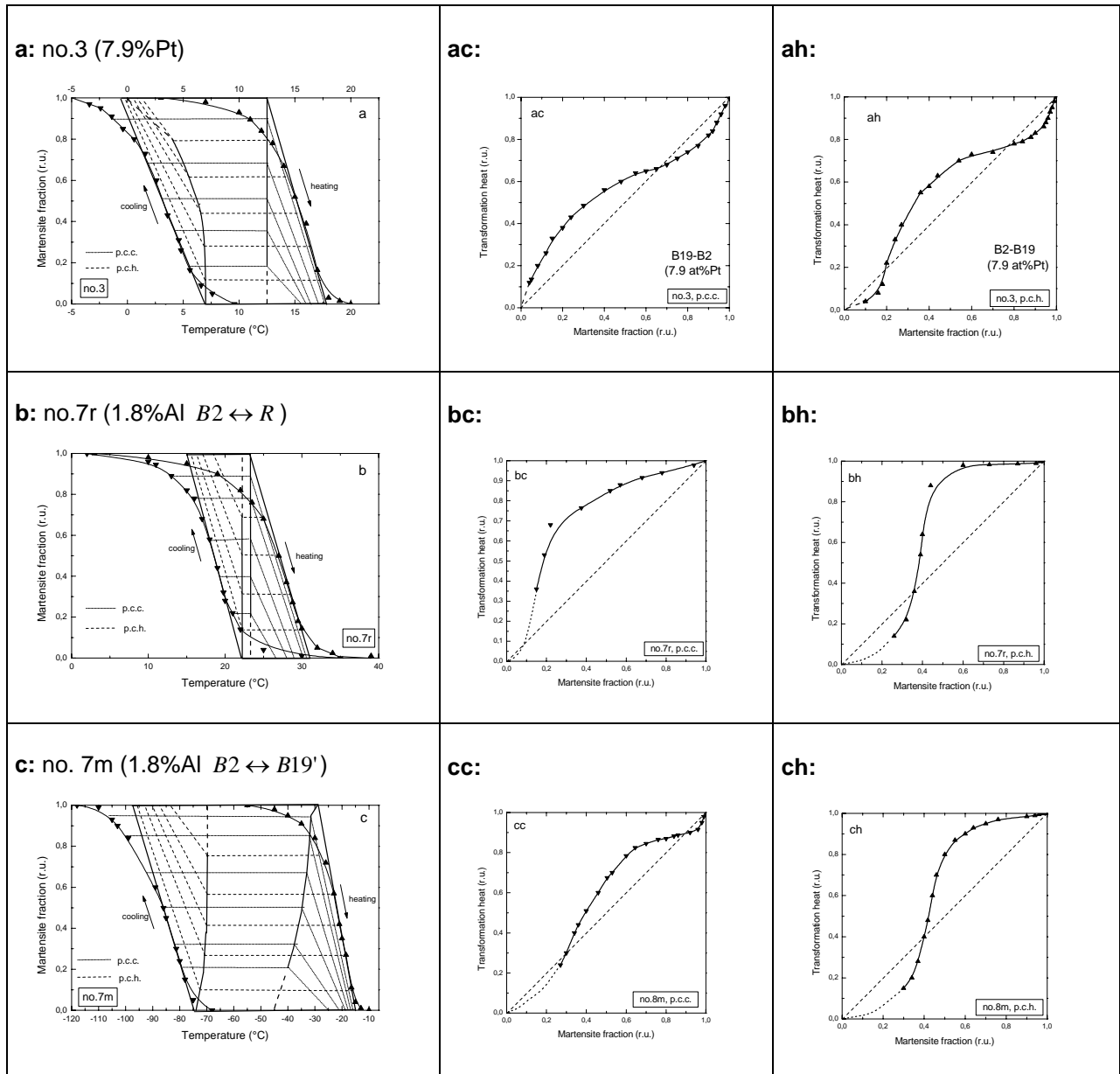
Experimental methods and results

The investigated alloys, the preparation of samples, the calorimetric measurements and their results are described in [3]. The algorithm to rebuild hysteresis loops from calorimetric curves using partial integration ("Partial Area"-program) is explained in [1].

The starting temperatures of the forward and reverse transformation lay along two lines, which are established inside of the hysteresis loop of every transformation (Abb. 1a-c). In general they are orthogonal to the temperature axis and parallel to each other ($B2 \leftrightarrow B19$ transformation of sample 5 and 6 and $B2 \leftrightarrow R$ one of sample 7 (fig. 1b)). At $B2 \leftrightarrow B19$ transformation of sample 3 is $A'_s(z) = const$, whereas $M'_s(z) = const$ is valid only in the range $0.4 > z > 0$ (fig. 1a). For higher values of z $M'_s(z)$ run along the main trajectory. The width of the latent hysteresis of the $B2 \leftrightarrow B19$ transformation of sample 2 and 5 is about 6°C, whereas the width can be ignored for the $B2 \leftrightarrow B19$ transformation of sample 6 and the $B2 \leftrightarrow R$ transformation of sample 7. A special course of $A'_s(z)$ at the maximal latent hysteresis of more than 35°C demonstrates the $R \leftrightarrow B19'$ transformation of sample 7 (fig. 1c). This line has a positive slope from $A'_s(1) - A'_s(0) > 10^\circ C$. The partial cycles of $B2 \leftrightarrow B19$ transformation with invariant plane of sample 5 and 6 and the $B2 \leftrightarrow R$ transformation of sample 7 (fig. 1bh) show a special behavior. Interrupting the reverse transformation at temperatures $A_f > T > T_p^h$ (T_p^h is temperature of the peak of the calorimetric heating curve) or for ca. $0 < z < 0.5$ neither the starting temperatures of

the partial forward transformation ($A'_s(z) = const$) nor the transformation heat ($q^{AM}(z) = const$) change.

Fig 1: Internal hysteresis loops and equilibrium lines in partial transformation cycling of investigated samples (a-c) and energy dissipation at the transformation arrested on the cooling (ac-cc) and on the heating (ah-ch) (nearly in the text).



For such values of z the radiated heat exceeds the absorbed one, what would contradict the second law of thermodynamics.

Discussion

The tensor of lattice deformation describing the transformation of the parent phase to martensite contains hydrostatic and deviatoric components. This components cause internal stress in the martensite and in the austenitic matrix, its value exceeds the limit of elasticity widely. One peculiarity of the thermoelastic martensitic transformation is the ability of martensite crystals to accommodate their form. This causes relaxation of this stress, so that it remains in the elastic range and does not produce any irreversible defects. In assuming that the modules of elasticity of both phases are equal, it is obvious that the stress at the boundaries including the so-called coherence energy should increase the Gibbs energy of both phases and not remove the equilibrium temperature. The temperature difference $T_0 - M_s$ arises only, if the energy of martensite increases more than the energy of austenite. The first mechanism of accommodation, which minimizes the distortion stress and the rotation moments at the habits plane, consists in building internal twins. The energy of such a martensite polydomain is higher than of a monodomain. The whole energy of the two-phase system is minimized and the transformation takes place. The energy of the twin boundaries can be regarded as barrier for nucleation and corresponds to one half area of the latent hysteresis. It is subtracted from transformation energy, so that the measured heat is lower. This assertion is confirmed by the small latent hysteresis of the transformation with invariant plane respectively with unstressed habits plane.

The second mechanism of accommodation consists in building of accommodated groups of several (3 or 4 in TiNi) growing martensite crystals. The elastic energy of these groups is lower than the one of the individual crystals added. This stabilizes the two-phase state and re-establishes the global equilibrium. The transformation passes as a lot of micro-jumps between local states of equilibrium. The breakdown of such stabile groups of martensite crystals during the reverse transformation requires additional energy. If forward or reverse transformation are interrupted not accommodated stress

forces the contradictory transformation, which doesn't start at the trajectory building the hysteresis loop, but at the equilibrium line $A'_s(z) = const$ respectively $M'_s(z) = const$, as emerges from the experiments. The stored elastic energy set free from this mechanism of accommodation is dissipated as heat and measured.

Such change of mechanisms of accommodation during the thermoelastic transformation should cause a not linear dependence of the measured heat on the fraction of martensite. This dependence is established in partial cycles as dependence of a dimensionless quantity $q_i^{f,r} / q^{f,r}$ of the fraction of martensite $z^{r,f} = q_i^{r,f} / q^{r,f}$ being formed by forward (f) respectively reverse transformation (r) (Fig. 1 ac, ah, bc, bh, cc and ch). The transition to fast growing or decrease of martensite requires overcoming the energy barriers.

The dependence of free transformation energy of the fraction of martensite reflects the dependence of the measured heat the opposite way: The maximum of heat corresponds to the minimum of free transformation energy and vice versa. The analyze of this quantities shows, that the mixture of two phases is stabile or meta-stabile in the range of fast martensite growing and instabile at the edge of the hysteresis loops. At the transformation with invariant plane the forward transformation takes place without any barrier just below the equilibrium temperature, what causes the very small latent hysteresis.

The here and in [3] presented experimental results $M'(z) = const$, $A'_s(z) = const$ and $(q_i^f(z) / q^f)_{z_p^h < z < 1} = const$) matches with other experimental results [4] essentially. A similar dependence of the heat measured in partial cycles on the fraction of martensite was published in [2] also.

The "contradiction" the second law of thermodynamics in investigated cases where the radiated heat exceeds the absorbed one can be traced back either to different contributions of dissipated and stored terms of elastic energy, which influence the measured heat, or to discrepancies between the transformation rate and heat removal

rate. The least means, that the gage measures only a heat trace of the very rapidly transformation. It means, that for this kind of transformation (with invariant plane) are invalid very important conditions:

$$z^{AM}(T) \neq \frac{\int_{M_s}^T h(T')dT'}{M_f} = \frac{q^{AM}(T)}{q^{AM}} \quad \text{und} \quad z^{MA}(T) \neq \frac{\int_{A_s}^T h(T')dT'}{A_f} = \frac{q^{MA}(T)}{q^{MA}}$$

for the determination of phase fraction of martensite. This situation must be taken into account by calorimetrically measurements of shape memory alloys.

Literature:

1. Prieb V., Link T., Feller-Kniepmeier M., Steckmann H. et all. Influence of the Structure and Orientation of the Parent Phase on the Hysteresis of Single-Crystal Shape Memory Alloys. //J. de Physique IV, Colloque C8 (ICOMAT'95). 51(995)913-918
2. Planes A., Macqueron J.L. and Ortin J. Energy contribution in the martensitic transformation of shape memory alloys.// Phil. Magazine Letters. 57(1988)291-298
3. Prieb V., Steckmann H. Thermoelasticity and hysteresis of martensitic transformation in shape memory alloys. Parts I-III. //Tech. Phys.. 41(1996)1132-1144
4. Madangopal K., Singh J.B. and Banerjee S. The Nature of Self-Accommodation in Ni-Ti Shape Memory Alloys.// Scr. Metallurgica. 29(1995)725-728