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On the Effect of Volume Change and γ' -Precipitation Hardening on the Reversibility of Martensitic Transformation in Fe-Ni-Co-Ti-Alloy

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Abstract: Martensitic transformation in Fe-Ni-based alloys is accompanied with an increase of volume ($\Delta V_{\gamma-\alpha} \approx 3\%$). Lattice invariant shear leads to additional dilatometric changes for non-random transformations. As the result of predominantly $\Delta V_{\gamma-\alpha}$ a large thermal hysteresis (ΔT_H) originates. This leads to a diffusion-controlled $\alpha \rightarrow \gamma$ -transformation, i.e. the reverse reaction becomes crystallographically irreversible ($\alpha \neq \gamma$).

In the case of an aged Fe-Ni-Co-Ti alloy, $\Delta V_{\gamma-\alpha}$ depends on the magnetic state of the austenite and on the volume fraction of the precipitated γ' -particles. With increasing the volume fraction of γ' , $\Delta V_{\gamma-\alpha}$ is reduced. Dislocations at the former martensite/austenite interfaces indicate incomplete reversibility of the transformation cycles, even in the ausaged condition. However, drastic reduction of ΔT_H is observed during an ausaging sequence for conditions close to maximum volume fraction and minimum size of γ' .

1. INTRODUCTION

It is well known that the occurrence of shape memory effect (SME) is accompanied with a reversible transformation behaviour. In prior reports connected with the established shape-memory alloys NiTi and Cu-Zn, prerequisites are proposed which provide complete reversibility [1]. These can be concluded by:

1. diffusionless $\alpha \rightleftharpoons \gamma$ reaction. This implies that the retransformation is completed in a temperature range where aging effects of martensite do not occur and, additionally a small temperature hysteresis between the austenite and martensite temperatures.
2. creation of mobile lattice defects which annihilate during the reverse reaction. Thus, interactions of dislocation and/or intersections of martensite plates have to be avoided. This is supported by a small volume change accompanied with the martensitic transformation and a high resistance against true plastic deformation of the alloy.
3. ordered structure of the high temperature phase or ordered γ' -particles of small size which do not lose their coherency during $\gamma \rightleftharpoons \alpha$ transformations.

Usually, alloys of iron do not fulfill these requirements and as a consequence, their transformation behaviour is irreversible. But in some Fe-based alloy systems, e.g. Fe-Ni-(X), Fe-Mn-(X), the shape memory effect occurs. In contrast to the established shape-memory alloys (SMA) Fe-based SMA do not show complete reversibility and therefore the SME is limited drastically.

In the present work the attempt is done to apply the most favourable parameters in order to obtain complete reversibility of the Fe-Ni-Co-Ti-alloy by ausaging. In this case, the effect of volume change and γ' -precipitation hardening on the reversibility of martensitic transformation is of special interest.

2. EXPERIMENTAL METHODS

The investigated alloy (Tab.1) is melted in a vacuum induction furnace under argon atmosphere. The casted specimen is hot rolled ($T=900^{\circ}\text{C}$, $\epsilon = 0.8$) and vacuum homogenized at 1200°C for 24 h. To explore the influence of γ' - precipitates on the transformation behavior, the Fe-Ni-Co-Ti-alloy is ausaged at 600°C for 0.1 to 8 h . Due to this treatment fine precipitates are formed in austenite with a $L1_2$ structure.

Dilatometric measurements are conducted with a constant heating and cooling rate ($5^{\circ}\text{C}/\text{min}$) to determine the volume change, characteristic phase transformation temperatures and the Curie-temperature. Additional experiments are conducted with rapid heating rate ($300^{\circ}\text{C}/\text{min}$) to study the retransformation course of the alloy in the homogenized and ausaged condition.

Optical and transmission electron microscopy observations have been done to describe the changes in microstructure.

Tab. 1: Chemical composition of the investigated alloy (wt %)

Ni	Co	Ti	Fe
28	17	4	bal.

3. RESULTS

After homogenization and aging treatment the investigated samples are in austenitic phase, even at room temperature. During aging treatment, metastable $(\text{Ni,Fe,Co})_3\text{Ti}$ - particles with a $L1_2$ structure are observed which are homogeneously distributed in the matrix. The volume fraction of these γ' -precipitates increases with increasing aging time.

3.1 Microstructure of the martensite

To investigate the microstructure of the martensite the homogenized and ausaged specimens are cooled to liquid nitrogen temperature. In the case of the unausaged specimens, the martensite structure is characterized by lens shaped plates, with a clearly defined midrib indicating a $\{259\}$ habitus plane $/2/$. By TEM-investigations an arrangement of straight parallel dislocations is observed in the martensite (Fig. 1).

Aging treatment leads to a change in martensite microstructure. γ' -precipitates generated in austenite transform into martensite without losing their coherency and thus, these particles become α' .

Increasing the volume fraction of these coherent particles results a reduction of the width of the martensite plates and in addition, transformation twins are observed in the martensite plates (Fig. 2). The twin width of the martensite is reduced by increasing the aging time.

3.2 Microstructure of the retransformed austenite

After reheating in a temperature range $T > A_f$ three different types of microstructure can be distinguished. The first one is in homogenized sample by experiments conducted with a heating rate of $5^{\circ}\text{C}/\text{min}$. It is characterized by an increase of fraction of martensite and/or the additional appearance η - precipitates at grain boundaries. In contrast to the γ' these η - precipitates are hdp-packed and incoherent to the matrix. Additionally, both types of precipitates consist of an analogous chemical composition.

The second type of retransformed microstructure is obtained by rapid heating ($300^{\circ}\text{C}/\text{min}$) above $T > A_f$. In this case, the specimens are completely in austenitic single phase, even at RT. Their microstructure is characterized by the occurrence of an internal substructure (Fig. 3). This sub-

structure has a martensitic appearance and will be called "ghost martensite" in the following. Obviously, the ghost martensite consists of a high dislocation density at places of former martensite. The dislocations show a short length and are arranged straight and parallel to each other. Additionally, in the residual austenite which has not been transformed into martensite before retransformation dislocations are visible. These dislocations of the residual austenite accumulate at lattice defects of the "ghost martensite".

In contrast to this, retransformations do not cause a significant change in microstructure of the ausaged specimens (third type). Consequently, no change in grain size and microhardness is measured. However at high magnification dislocations are visible in the retransformed microstructure at places of the former martensite (Fig. 4).

3.3 Dilatrometric measurements

Variations in aging time lead to a change in phase transformation temperatures (Fig. 5). By short aging M_s , M_f is almost unaffected. Increasing the aging time results a drop of the martensite temperature and the minimum (-49°C) is observed at 8 h.

In contrast to the martensite temperatures, short ausaging leads to a drastical decrease of retransformation temperatures (Fig. 6). A_s , A_f are reduced from 510°C , 630°C (unausaged condition) to 110°C and 245°C ($t_a = 30$ min) respectively. A slight increase of the retransformation temperatures to an almost constant level is observed by further ausaging. Due to the fact that A_s and A_f decrease more significantly compared to M_s and M_f , the thermal hysteresis ΔT_h is lowered ($\Delta T_h = A_{50} - M_{50}$).

Simultaneously, the Curie temperature (θ_C) is affected by aging treatment (Fig. 5). Increasing the aging time first a slight shift of θ_C to lower temperatures is observed. Further aging results a continuous increase of θ_C . As a consequence of both (θ_C , M_s), the temperature difference of ($\theta_C - M_s$) approaches a maximum value at long aging times (Fig. 7).

In addition, the γ - α -volume change is influenced by ausaging treatment (Fig. 7). The highest value of $\Delta V_{\gamma-\alpha}$ is observed in the unausaged condition and it decreases continuously to a minimum with increasing aging time.

4. DISCUSSION

The investigated alloy shows a para $\rightarrow$ ferromagnetic transition in the austenitic phase before martensitic transformation. Due to the magnetovolume and magnetostrictive effects of the ferromagnetic austenite a small coefficient of thermal expansion is observed in the temperature range ($\theta_C - M_s$). Although, it is possible to reduce $\Delta V_{\gamma-\alpha}$ to a minimum ($<0.1\%$) by variation of the chemical composition, a small value of volume change seems not to be a sufficient condition to obtain a reversible retransformation course /3/. Main reason for this irreversibility is, the high value of the austenite start temperature (550°C). Due to this, a diffusion-controlled α - γ -transformation is favoured and a change in the retransformed microstructure is observed /4/.

If diffusion-controlled nucleation of new austenite grains is depressed by rapid heating the b.c.c. $\rightarrow$ f.c.c. transition by lattice shearing is preferred /4/. In the case of the unausaged alloy, lattice defects which are formed in the martensite are immobile and do not annihilate during the reverse shear process. The mechanism of the formation of these dislocation structures is still unclear. A possible explanation is proposed by Kajiwarra and Owen /5/. The dislocations are formed in the twinning shear plane of the martensite $\{211\}_\alpha$ by lattice invariant shear. According to Bain lattice correspondence $\{211\}_\alpha$ plane of the martensite is $\{202\}_\gamma$ of the austenite which is not a slip plane in the f.c.c. lattice. Therefore, the Burgers vector of the dislocations of austenite should be $\langle 101 \rangle_\gamma$ which is parallel to the twinning shear direction in martensite $\langle 111 \rangle_\alpha$. Thus, the occurrence of ghost martensite indicates that the reverse reaction is not completely reversible. In addition, this repre-

sents an intermediate state between complete reversibility and irreversibility.

By ausaging, metastable γ' -precipitates are formed which are coherent to the matrix. Due to this, the internal stress and as a consequence the microhardness of the austenite increases with increasing aging time. And as a result of the increasing internal stress, the magnetovolume and magnetostrictive effects of the ferromagnetic austenite become more evident (Fig. 7). Due to these effects the volume of the austenite increases related to the volume of the martensite. As a consequence the volume change accompanied with the martensitic transformation $\Delta V_{\gamma-\alpha}$ is reduced. This increase resulting from magnetovolume and magnetostrictive effects of the ferromagnetic austenite can be estimated indirectly by dilatometric measurements. If we assume that $\alpha_{\gamma,f}$ is composed of the coefficient of thermal expansion $\alpha_{\gamma,p}$ due to changes in temperature and a coefficient due to magnetic effects then ΔV_λ describes these magnetic effects in the temperature range Θ_c-M_s (Equ.1). A further requirement is a quasi-isotropic behaviour of the sample.

$$\Delta V_\lambda \approx 3 * (\alpha_{\gamma,p} - \alpha_{\gamma,f}) * (\Theta_c - M_s) \quad (1)$$

Thus, the theoretical volume change accompanying the martensitic transformation can be calculated by Equ.2. Here, $v_{A,\gamma}$ and $v_{A,\alpha}$ are the atomic volume of the austenite or martensite related to the unit cell. Deviations from this theoretical term characterize the residual austenite after martensitic transformation and can be used to describe the fatigue of shape memory effect.

$$\Delta V_{\gamma-\alpha} = \frac{v_{A,\alpha}}{v_{A,\gamma} * (\Delta V_\lambda + 1)} - 1 \quad (2)$$

Additionally, the formation of twins as lattice invariant shear is favoured by γ' -precipitates. These transformation twins have a higher mobility compared to the dislocations generated in the unausaged condition of this alloy. Pronounced by the easy motion of the twin interfaces, an almost defect-free restauration of the high temperature phase is received, even at low heating rates.

A further consequence of the γ' -precipitates is, that particles below a critical size ($d_c > d_i$) transform into the b.c.c. lattice of the low temperature phase without loosing their coherency during martensitic transformation [1]. Therefore, the metastability of the $\gamma' \rightarrow \alpha'$ transformed precipitates increases which contributes an additional energy for the retransformation. As a result, the thermal hysteresis is reduced and diffusion-controlled reactions are depressed.

5. CONCLUSIONS

The microstructure of the martensite in the unausaged specimen is characterized by a high density of parallelly arranged dislocations. After complete retransformation, conducted with rapid heating rate, "ghost martensite" occurs. In this case, a high defect density indicates partial reversibility.

By ausaging, the magnetovolume and magnetostrictive effects of the ferromagnetic austenite become more pronounced. Simultaneously, the volume change accompanied with the martensitic transformation, the temperature hysteresis as well as the austenite finish temperature are reduced, by γ' -precipitates. Furthermore, twinning of the martensite is favoured by ausaging. The twin width decreases with increasing ausaging time.

Thus, an almost complete crystallographic reversibility is obtained by ausaging and additionally by rapid heating rates.

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Fig. 1: Defect structure of the martensite (un-aused condition). High density of parallelly arranged dislocations (TEM- bright field).

Fig. 2: Microstructure of the martensite (aus-aged 600°C/4h→ 196°C). Due to α' -particles transformation stress is reduced by twinning of the martensite (TEM- bright field).

Fig. 3: Microstructure of the completely $\alpha \rightarrow \gamma$ retransformed specimen (heating rate: 300°C/min; $T > A_f$; un-aused condition). a) occurrence of "ghost martensite" (arrow) indicates partial crystallographic reversibility (optical micrograph); b) defect structure of "ghost martensite" (TEM- bright field).

Fig. 4: Microstructure of the completely retransformed specimen (ausaged condition: 600°C/4h). Dislocation density is reduced significantly, indicating almost complete crystallographic reversibility (TEM- bright field).

Fig.5: Martensite start temperature (M_s) and Curie-temperature (θ_c) versus ausaging time ($T_a=600^\circ\text{C}$).

Fig. 6: Retransformation temperatures (A_s , A_f) and temperature hysteresis (ΔT_H) versus ausaging time ($T_a=600^\circ\text{C}$).

Fig. 7: Volumen change ($\Delta V_{\gamma-\alpha}$) and temperature difference (θ_c-M_s) versus ausaging time ($T_a=600^\circ\text{C}$).