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Relationship between thermomechanical treatment, microstructure and α' martensite in stainless Fe-based shape memory alloys

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Abstract

This work presents some preliminary results relating training treatment, training temperature and the formation of α' martensite to the shape recovery effect of stainless shape memory alloys. For the composition tested, the sample shows some mechanical memory (constant tensile stress at 4% strain and constant yield stress throughout the training cycles) with a very good shape recovery (95% after 4% tensile strain) at a training temperature of 873 K. Its residual strain is related to the generation of perfect dislocations only. For the sample trained at 723 K, the residual strain could be attributed to incomplete reversion of stress-induced ε martensite, in part due to the blocking effect of α' martensite and also to the generation of perfect dislocations. The influence of α' martensite on shape recovery is relative and is dependent on training temperature, and the preferential growth of α' martensite is shown to occur for large grain size. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Shape memory alloys; Stainless alloys; Thermomechanical treatments; Microstructure

1. Introduction

In the 1990s, it was observed that Fe–Mn–Si–Cr–Ni–(Co)-type stainless alloys [1–6] have a shape memory effect (SME) associated with the non thermoelastic γ(fcc) to ε(hcp) martensitic transformation, and that near the M_S (martensitic transformation starting temperature) temperature martensite could also be stress-induced. Reversion of this stress-induced ε martensite by heating promotes shape recovery. In addition to the factors such as high mechanical resistance and the low stacking fault energy of the austenitic phase, the training technique also enhances the SME [3,4,6,7]. It consists of deformation of the sample (e.g. by tensile stress at room temperature), heating to a temperature above A_F (the reverse martensitic transformation temperature) to recover the shape and final cooling to the temperature of the initial deformation. When repeated several times this operation can increase the total shape recovery up to 50%. However, this training technique can also induce the formation of a second α' martensite that according to some authors [5,8,10–12] can decrease the degree of shape recovery. α' Martensite can hinder the reversion of the stress-induced ε martensite to the γ austenite and can also revert directly to the γ phase, i.e. skipping the phase. This work will show some results for thermomechanical treatment (training), the degree of shape recovery, the appearance of α' martensite and the microstructure for a stainless shape memory alloy.

2. Experimental procedures

The material used in this work was melted in an vacuum induction furnace (VIM), hot forged at 1550 K in bar shape, solution treated at 1323 K for 1 h and then quenched in water at room temperature (300 K). The alloy presents the following composition: Fe (balance), 0.039% C, 13.41% Mn, 5.07% Si, 8.83% Cr and 4.54% Ni (in wt.%). The material was analyzed as: (a) solution treated; (b) solution treated and 4% tensile strained and (c) trained at 723 or 873 K (strained 4% in tension at room temperature, load released to zero, heated to 723 or 873 K, kept at this temperature for 600 s and then furnace cooled to room temperature). The recorded parameters of the tensile test were tensile

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stress at 4% strain ($\sigma_{4\%}$); yield stress at 0.2% strain ($\sigma_{0.2\%}$); shape recovery after unloading, R_e; shape recovery upon heating and cooling, R_{sm}; and total shape recovery, R_t ($= R_e + R_{SM}$). The effects of thermomechanical treatment were analyzed in terms of shape recovery and variation in tensile stress as a function of number of cycles. Complementary analyses were performed using optical metallography, hardness measurement and X-ray diffraction.

3. Results and discussion

The influence of training (five or six cycles) and of training temperature (723 or 873 K) on shape recovery can be seen in Fig. 1. The two samples present a large increase in total shape recovery in the first three cycles then practically levels off in the following cycles. Total shape recovery R_T, is 70% (2.8% of 4% strain) and 78% (3.1% of 4% strain) in the first cycle, 86% (3.4% of 4% strain) and 95% (3.8% of 4% strain) in the final cycles for training temperatures of 723 and 873 K, respectively, (100% means 4% strain recovery). For both temperatures, the largest contribution to the total shape recovery, R_T, comes from the term R_{SM} (shape memory effect). The contribution of shape recovery upon unloading, R_E, is more pronounced at 723 K. It presents an increase on the order of 4% throughout the cycles while, for the sample trained at 873 K, the R_E was practically constant. As shown above, another aspect that should be emphasized is the good total shape recovery of almost 80% presented by both samples in the first cycle, i.e. prior to the influence of the training process (the most common data is around 50% shape recovery after 4% strain). According to Ogawa and Kajiwara [13], who were the first to obtain 80% shape recovery after 4% strain in the first cycle, the sample presents a band structure, with a mixture of hcp and fcc phases of very fine thicknesses of 1–10 nm, which makes the reverse martensitic transformation easier.

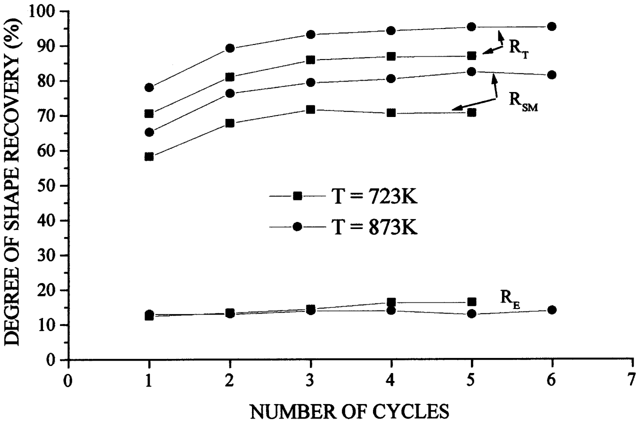

Fig. 1. Shape recovery as a function of number of cycles for the samples trained at 723 and 873 K.

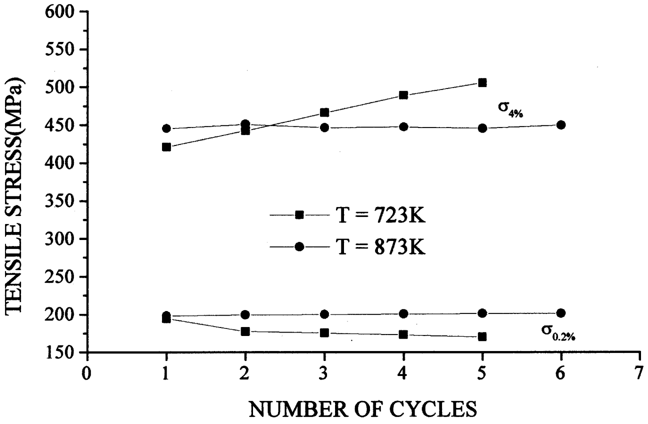

Fig. 2. Tensile stress as a function of number of cycles for the samples trained at 723 and 873 K.

The influence of training treatment and training temperature on the mechanical resistance can also be seen as shown in Fig. 2. While the sample trained at 723 K presents an increase in tensile stress at 4% strain, $\sigma_{4\%}$, and a decrease in tensile yield stress, $\sigma_{0.2\%}$, mainly in the initial cycles, these parameters remain almost constant with the cycling for the sample trained at 873 K. The improvement in shape recovery is very good and comparable to the best results published, especially in regards to the training at the highest temperature [3,4,6–9]. The improvement in the SME with training is attributed to the introduction of stacking faults (of an hcp structure) in the austenitic phase, which act as nucleation sites for the ε martensite and suppress deformation leading to the work hardening of the austenitic matrix. The consequence is a decrease in tensile yield stress and an increase in tensile stress at 4% strain with an increase in the number of cycles. This situation is always supposed to occur, regardless of the training temperature. However, this work showed that the assumption is true for the sample trained at 723 K but not for that one trained at 873 K, where both parameters are practically constant throughout the cycles. Therefore, complementary analyses should be performed in order to reach a better understanding of the shape recovery process in this alloy.

Table 1 summarizes some other results for the trained sample, the solution-treated sample and the 4% tensile-strained sample after solution treatment. The volume fraction of ε martensite for the solution-treated sample and for the 4% strained sample are, 5 and 9% and their hardnesses are 207HV and 249HV, respectively. This means that a tensile strain of 4% induces 4% ε martensite and an increase in hardness of about 40HV. At the end of five cycles at 723 K, the volume fraction of ε martensite is 20%; this means that 15% of the stress-induced ε martensite was retained, while the reversion was complete for the sample trained at 873 K. The presence of retained ε martensite would partially

Table 1
Volume fraction of ε martensite, α′ martensite and hardness as functions of the thermomechanical treatment

Thermomechanical treatment	α′ Appearance	$C_ε$ (%)	Vickers Hardness (HV)
1323 K/600 s/water	No	5.0 ± 1.0	207.4 ± 2.4
4% Tensile strained	No	9.2 ± 1.5	249.0 ± 0
Five cycles/723 K	Yes	20.6 ± 1.9	242.6 ± 2.9
Six cycles/873 K	Yes	4.7 ± 0.8	235.5 ± 7.0

justify the residual strain or incomplete shape recovery of the sample trained at 723 K. This can not be the reason for the sample trained at 873 K, which presents 5% residual strain in spite of the complete reversion of the stress-induced ε martensite. Observing only the tensile stress data, Fig. 2, one could conclude that the sample trained at 873 K does not show any work hardening, since the stress values of the 4% strain and yield stress throughout the cycles are almost constant. However, the hardness measurement indicates that the sample trained at 873K as well as that trained at 723 K presents a small increase in hardness, which is larger for the latter. The increase in hardness means a work hardening of the material and, therefore, the generation of perfect dislocations, which implies permanent plastic deformation. Working with a series of Fe–Mn–Si alloys, Sade et al. [14] showed that even thermal cycling (without deformation) between temperatures below M_S and above A_F resulted in an increase in hardness with the number of cycles. This increase in hardness was attributed to the introduction of sessile lattice defects that hinder the movement of partial dislocations. Working with Fe–17Mn and Fe–25Mn (in wt.%) alloys, Tsuzaki et al. [15] observed by TEM that the density of dislocations as well as the hardness increased considerably after some thermal cycles. These data corroborate the results obtained in this work, partially justifying the increase in hardness and the residual strain observed in the samples. Another fact that should be taken into account is the formation of α′ martensite. As shown in Table 1, α′ martensite was not seen for the solution-treated and the 4% strained samples. However, α′ martensite was present in the samples trained at 723 K and at 873 K. Its formation occurred preferentially on ε martensite plates with a rod like morphology, as shown in Fig. 3. Formation of α′ martensite on the ε martensite plates suggests that the precipitation sequence is $\gamma \rightarrow \varepsilon \rightarrow \alpha'$. According to Jang et al. [12], a larger deformation strain leads to larger α′ martensite rods. This is in agreement with the results of this work, where the sample trained at a lower temperature with a higher residual strain presents larger α′ martensite rods. However, some points are controversial: The first point refers to the influence of α′ martensite on the SME. According to some authors [8,12,16], α′ martensite has a blocking effect on the reversion of ε martensite and in addition reverts directly to the austenite, $\alpha' \rightarrow \gamma$. This causes a decrease in the SME. Tomota and Yamaguchi [11] showed that a volume fraction of α′ martensite below about 4% does not interfere with the extent of the SME. This is in agreement with the results of this work for the sample trained at 873 K, where the shape recovery is 95% and reversion of the stress-induced ε

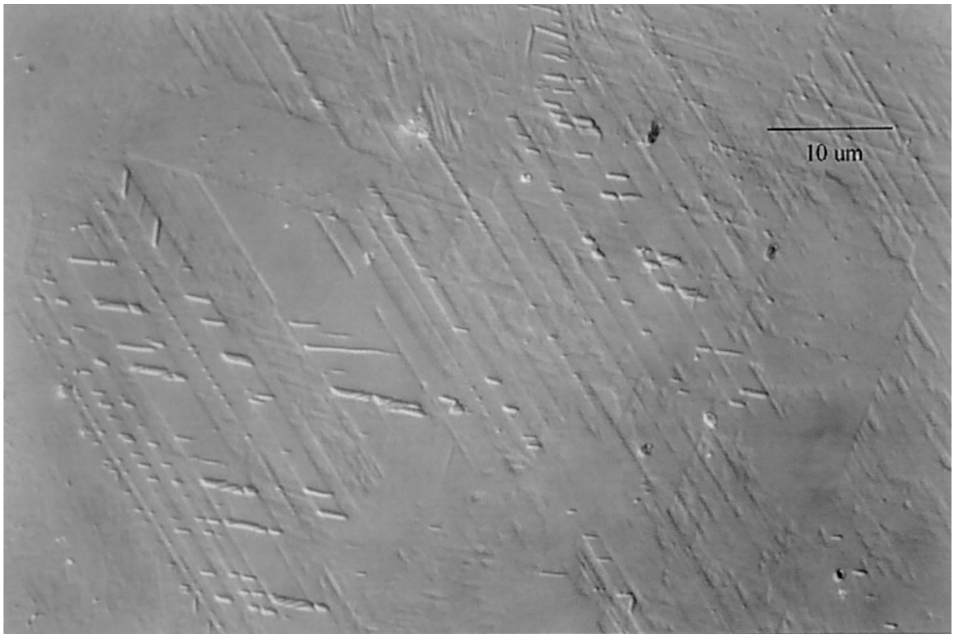

Fig. 3. Optical micrography of sample trained at 873 K showing α′ martensite (rod shaped).

Fig. 4. Optical micrography of the samples trained at 723 K showing precipitation of α′ martensite on large grains

martensite is complete, in spite of the existence of α′ martensite. However, for the sample trained at 723 K, the presence of α′ martensite could be one of the reasons for the incomplete reversion of stress-induced ε martensite. In any event, the volume fraction of α′ martensite for the samples tested must have been low since it was not detected by X-ray diffraction analysis. The second aspect that ought to be analyzed is the relationship between training cycles and the appearance of α′ martensite. According to Gu et al. [8], the α′ martensite disappears with an increase in number of training cycles. This is in disagreement with the observations in this work, where α′ martensite was observed only in the trained samples. Another aspect observed in this work, regardless of training temperature, is the precipitation of α′ martensite in localized areas where the grain size is large, as illustrated in Fig. 4. Areas with a small grain size such as those on lower left side of Fig. 4, do not show precipitation of α′ martensite. It seems probable that precipitation occurs in areas with a large grain sizes, since in these areas stress concentration is greater and consequently, it can generate a larger deformation, which is one of the conditions for precipitation of α′ martensite. In summary, the residual strain or incomplete shape recovery for the sample trained at 723 K can be attributed to the incomplete reversion of stress-induced ε martensite, partly due to the blocking effect of α′ martensite and also partly to the generation of perfect dislocations during cycling. For the sample trained at 873 K, the reason for the residual strain could be the generation of perfect dislocations.

These results are preliminary. More detailed studies linking parameters such as chemical composition, degree of deformation, volume fraction of α′ martensite, training temperature, grain size, etc. are in progress.

4. Conclusions

For the composition tested, the sample shows some mechanical memory (constant tensile stress at 4% strain and yield stress during the training cycles) with good shape recovery (95% after 4% tensile strained) at a training temperature of 873 K. Its residual strain is related to the generation of perfect dislocations only.

The residual strain, detected in the sample trained at 723K, can be attributed to an incomplete reversion of the stress-induced ε martensite, in part due to the blocking effect of α′ martensite and also due to the generation of perfect dislocations.

α′ Martensite could be seen by optical microscopy only in cycled samples, particularly in large grains and in larger amounts at the lower training temperature of 723 K.

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References

[1] H. Otsuka, H. Yamada, T. Maruyama, H. Tanahashi, S. Matsuda, M. Murakami, ISIJ Int. 30 (1990) 674.

[2] H. Otsuka, H. Yamada, H. Tanahashi, T. Maruyama, Mater. Sci. Forum 56/58 (1990) 655.

[3] Y. Moriya, H. Kimura, S. Hashizume, S. Suzuki, H. Suzuki, T. Sampei, J. Phys. France IV 1 (1991) C4–433.

[4] H. Inagaki, Z. Metall. 83 (1992) 90.

[5] J.H. Yang, H. Chen, C.M. Wayman, Metall. Trans. A 23 (1992) 1431.

[6] J. Otubo, P.R. Mei, S. Koshimizu, J. Phys. France IV 5 (1995) C8–427.

[7] Y. Watanabe, Y. Mori, A. Sato, J. Mater. Sci. 28 (1993) 1509.

[8] Q. Gu, J. Van Humbeeck, L. Delaey, Scripta Metall. Mater. 30 (1994) 1587.

[9] H. Otsuka, M. Murakami and S. Matsuda, Proceedings of the MRS International Meeting on Advanced Materials-Shape Memory Materials, Sunshine City, Tokyo, Japan, May 31–June 3, 1988, 9, p. 451.

[10] Q. Gu, J. Van Humbeeck, L. Delaey, L. Federzoni, G. Guénin, D. Gex, J. Phys. France IV 5 (1995) C2–311.

[11] Y. Tomota and K. Yamaguchi, J. Phys. France IV 5 (1995) C8–421.

[12] W.Y Jang, Q. Gu, J. Van Humbeeck, L. Delaey, Mater. Characterization 34 (1995) 67.

[13] K. Ogawa, S. Kajiwara:, Mater. Trans. JIM 34 (1993) 1169.

[14] M. Sade, K. Halter, E. Hornbogen, Z. Metall. 79 (1988) 487.

[15] K. Tsuzaki, M. Ikegami, Y. Tomota, T. Maki, ISIJ Int. 30 (1990) 666.

[16] J.H. Yang, C.M. Wayman, Metall. Trans. A 23 (1992) 1445.