Influence of Thermomechanical Treatments and Cycling on the Martensitic Transformation and Shape Recovery of Fe-Mn-Si Alloys

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Abstract

The influence of different parameters on the shape memory effect and the transformation temperatures has been determined. In this respect it has been found that annealing at an intermediate temperature, after hot rolling, yields a maximum shape recovery. It is believed that partial removal of the work hardened structure is necessary while prevention of permanent slip in the matrix is essential, to obtain good shape recovery.
Also the influence of strain cycling and thermal cycling is determined. The shape memory effect increased after each strain cycle and the amount of martensite formed increased after each thermal cycle. Both observations can be accounted for by an increased nucleation rate. Also the heating and cooling rate are important parameters in this respect.

Introduction

In addition to the classical, non-ferrous Ni-Ti and Cu-based shape memory alloys, shape memory has also been observed in at least six different Fe-based alloys: Fe-Pt (1,2), Fe-Pd (3), Fe-Mn (4), Fe-Mn-Si (5-13), Fe-Ni-C (14,15) and Fe-Ni-Ti-Co (16). Among these the Fe-Mn-Si alloys appear to have commercial significance. Recently a nearly perfect shape memory effect has been reported in a Fe-30wt% Mn-1wt% Si single crystal (5,7) as well as in polycrystalline Fe-32wt% Mn-6wt% Si alloys (8).
The objectives of the present investigation are:
a) to study the effect of thermo-mechanical treatments
b) to study the effect of strain cycling
c) to study the effect of thermal cycling and aging
on the martensitic transformation and shape recovery.

Experimental procedures

An ingot of Fe-32wt% Mn-5.5wt% Si was melted and casted at the Raychem Corporation, USA in a plasma furnace using high purity metals. After homogenisation, annealing at 1473 K during 1 hour, hot rolling was carried out at 1473 K to obtain 0.4 mm thick sheets.
Tensile tests were done on 140 mm x 6.25 mm x 0.4 mm specimens by means of an Instron tensile machine, 250 kN, low temperature extensometer (25 mm-100%), 1 mm/min deformation rate.
Bending tests were done on 60 mm x 3 mm x 0.4 mm specimens which were sealed in evacuated quartz tubes and annealed at different temperatures for 1 hour and subsequently air cooled.
Following pickling and chemical polishing, these specimens were bent at room temperature to introduce 5% strain (ϵ_i), taking into account the exact thickness and the elastic spring back. The strain was calculated from $\epsilon_i = t/2r$, where t is the thickness and r is the bend radius of the sample.

The shape recovery R was calculated from $R = (\epsilon_i - \epsilon_r)/\epsilon_i$, where ϵ_r is the unrecovered strain at room temperature after heating the sample to 573 K.
Electrical resistance measurements, caloric measurements and positron annihilation Doppler broadening measurements were carried out on respectively 100 mm x 5 mm x 0.4 mm, 5 mm x 5 mm x 0.4 mm and 10 mm x 10 mm x 0.4 mm specimens, which were sealed in evacuated quartz tubes, annealed at 1373 K for 1 hour, quenched in liquid nitrogen and finally pickled and chemical polished. Vickers hardness of the samples was measured using a load of 2 kg.

Results

Effect of thermo-mechanical treatment

Samples following the hot rolling, were annealed at different temperatures and air cooled. As shown in figure 1, the hardness of the samples was found to decrease with increasing annealing temperatures. The shape recovery of the as-annealed samples was measured and is shown in figure 2. It may be noted

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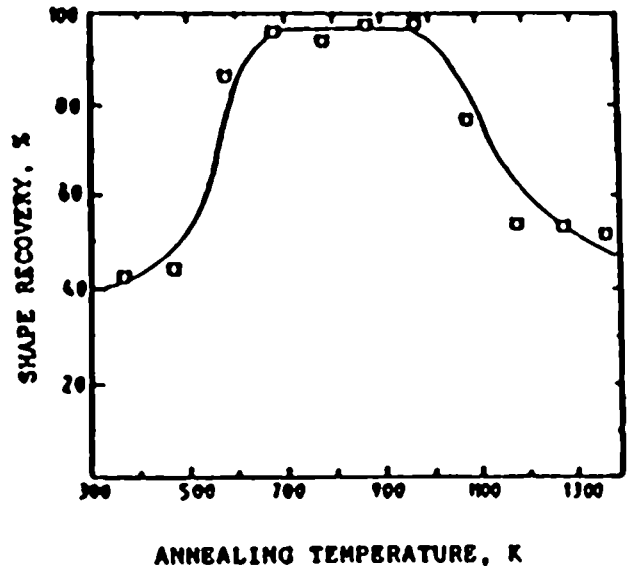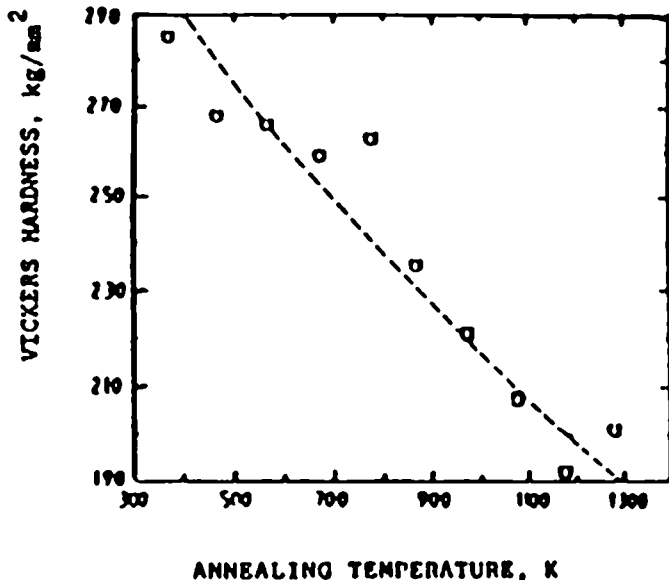

ANNEALING TEMPERATURE, K

Figure 1 : the hardness as function of annealing temperature after hot rolling

Figure 2 : the shape recovery after 5% bending as function of the annealing temperature

that the shape recovery first increases and then decreases with increasing annealing temperature. A maximum recovery of 5% is observed over a broad temperature range from 673 to 1073 K. Also by means of caloric measurements a maximum transformation heat was noticed on heating (10 K/min) in samples annealed in the temperature range from 673 to 1073 K (and quenched in liquid nitrogen). The retransformation temperatures both decrease as a function of higher annealing temperatures. As can be seen in table 1 the transformation temperatures and the shape memory effect are also highly influenced by the amount of plastic strain input (in a tensile test).

Strain Input	Shape Recovery (%)	Retransformation temperatures (K)
0	-	383 - 425
1	70	367 - 495
2	55	343 - 613
3	37	339 - 653

Table 1: Results of tensile tests with recorded retransformation curves (samples are sandblasted and subsequently annealed at 623 K for 1 hour).

Effect of thermo-mechanical cycling

Samples following the hot rolling were sandblasted and annealed at 623 K during 1 hour. The average grain size of this polychrystalline material was approximately 50 μm. The strain cycle consisting of annealing at 623 K during 1 hour, applying 2% strain in a tensile test at room temperature and heating to 623 K is repeated a few times. As can be seen in table 2, the shape memory effect $R = \epsilon_i - \epsilon_f)/\epsilon_i$ increases with the number of cycles. The retransformation temperatures remain almost constant with strain cycling. By transmission electron microscopy an increasing number of dislocations could be seen in the cycled samples. Finally it has to be noticed that a low but significant two-way memory in the order of 0.1% has been observed on cooling.

N	r%
1	55
2	61
3	81
4	91

Table 2: Shape memory effect (R) as a function of the number of strain cycles (N).

General observations on the electrical resistance-temperature curve

Typical electrical resistance-temperature curves obtained on heating/cooling are shown in figure 3. The Y-axis in those plots denotes the quantity $(R_T - R_{298})/R_{298}$, where R_T is the electrical resistance at temperature T and R_{298} is the electrical resistance in the austenitic state on extrapolating to 298 K. On heating the sample from room temperature a change in slope of the elctrical resistance curve is observed at T_N which represents the antiferromagnetic to paramagnetic transition of the austenite. During cooling, the continued increase in the electrical resistance below this temperature T_N (upto about 77 K) is similar to the behaviour exhibited by several metals (17,18) and is not attributed to the martensitic transformation, because it is believed that below T_N the austenite is more stable due to antiferromagnetic ordening. The nominal values of the transformation temperatures are $T_N = 293$ K, $M_s = 325$ K, $A_s = 393$ K and $A_f = 435$ K.

Effects of thermal cycling

The as-quenched samples exhibited a partially transformed microstructure. The effect of thermal cycling between 473 K and 77 K (5 K/min) on the transformation behaviour is shown in figure 3.
As a function of the number of cycles it can be seen that :
1) A_s remains constant, A_f increases
2) R_{298} increases
3) amount of martensite formed increases
Also by caloric measurements it was shown that the transformation heat increases with an increasing number of annealing and quenching cycles. It should be added that the time of holding at the upper temperature limit of the cycle does not have any significant influence on the transformation behaviour or the hysteresis.
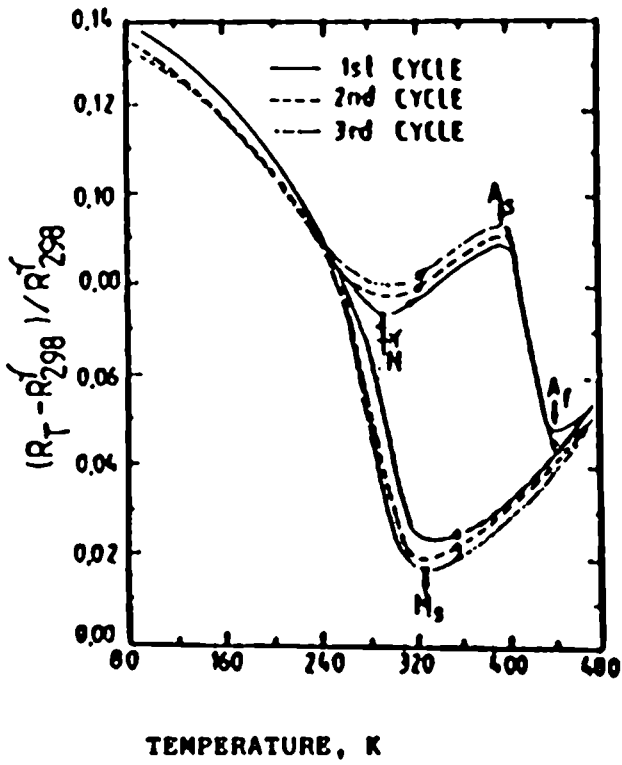
Figure 3 : the electrical resistance as
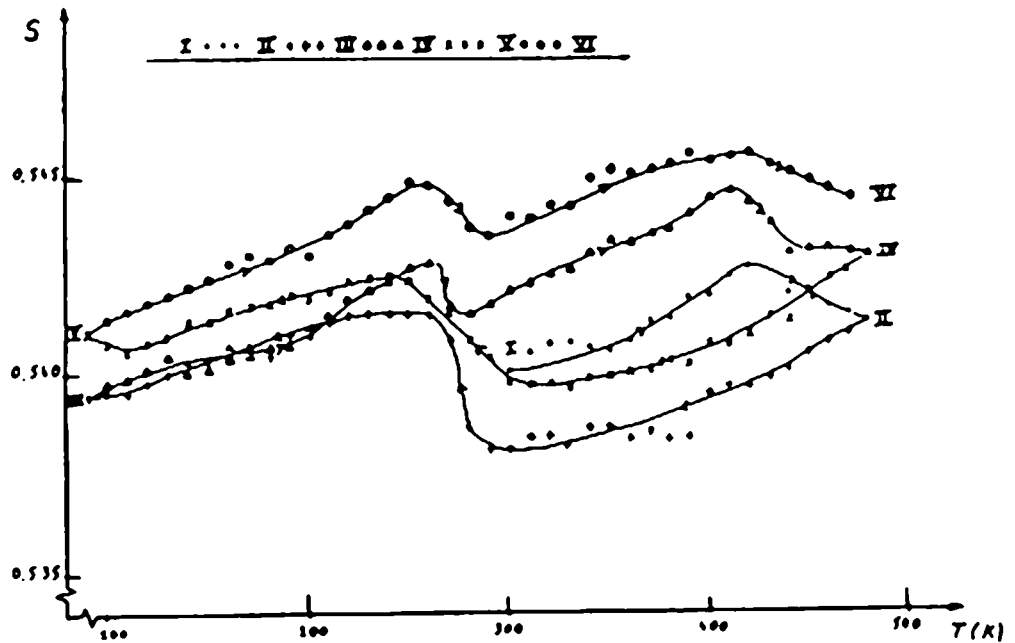function of temperature with indication
of the transition temperatures

Figure 4 : the line-shape parameter S measured by positron-
annealing during three heating and cooling runs.
S can be seen as proportional to the defect concentration.

Figure 4 shows the S-parameter as a function of temperature during cycling between 90 K and 500 K. This S-parameter is proportional to the amount of annihilation of positrons and thus to the defect structure of the material. It can be seen that

1) the curve shifts completely to higher values during cycling
2) the S-value increases during cooling starting at M_s until M_f
3) a similar increase occurs during heating starting at A_s; here the S-value goes through a maximum. This can be explained by the fact that the particular defect concentration of the martensite disappears. Also the defects remaining in the austenitic phase can disappear since recovery annealing is possible. As a consequence the rate of heating and cooling through this temperature zone is important with respect to the defect structure.
4) a change in slope occurs around T_N. This can be related to the change of the linear expansion coëfficient around T_N (19). Consequently the formation energy for defects in the paramagnetic state is different from the energy in the antiferromagnetic state.

It was also measured that both the yield stress and the hardness increase due to cycling, which is in agreement with the fact that more and more martensite is formed. However the shape memory effect was found to deteriorate with each cycle. The results are given in table 3.

Heat Treatment	Yield Stress (MPa)	Shape Recovery (%)
1. Annealed at 1373 K and cooled to 77 K	270	59
2 1 + heated and hold at 573 K for 5 mins and cooled to 77 K	254	42
3. 2 + heated and hold at 573 K for 5 Mins and cooled to 77 K and this step was repeated 3 times	299	39

Table 3: Results of thermal cycling.

The deformation temperature of the bending tests was always room temperature. Moreover the shape memory effect also decreases from 46% (as-rolled) to 33% (cycled) when the bending is done, after cooling from A_f to an intermediate temperature between M_s and M_d.

Discussion

The shape recovery in Fe-Mn-Si alloys has been associated with the reverse transformation of stress induced martensite. The largest shape recovery will be obtained when 100% martensite is stress induced from austenite during deformation of the sample. The presence of any martensite, thermal or stress induced, prior to this deformation is liable to produce irrecoverable rather than recoverable plastic deformation. This will consequently reduce the extent of shape recovery. For the same amount of initial martensite such a deterioration will be more pronounced the larger the deformation is. Also the retransformation temperatures (martensite to austenite) are influenced by the amount of deformation : by deformation, stresses are built which firstly help the retransformation but finally resist the retransformation.

The as-hot rolled samples will always contain some stress induced martensite. Annealing after-hot rolling will not only remove this martensite but will also remove the work hardened structure and affect the grain size of the austenite. All these processes will contribute to the decrease in hardness with increase in annealing temperature as seen in figure 1. The extent to which these processes take place can in principle influence the subsequent deformation behaviour of the austenite and thus the shape recovery. However, increase in grain size by an order of magnitude has been reported to have no influence on the shape recovery (12). A more complete removal of the work hardened structure by annealing the samples at higher temperatures will make the austenitic matrix softer so as to cause the deformation to take place by conventional slip rather than by transformation. On the other hand, very low annealing temperatures might be associated with an incomplete reversion of the stress induced martensite from rolling. A maximum shape recovery is thus expected after annealing at an intermediate temperature which is consistent with the results shown in figure 2.

It is clear from the obtained results that the amount of stress induced martensite respectively thermal martensite increases with respectively strain cycling and thermal cycling. As could be seen in transmission electron microscope observations of strain cycled samples more (partial) dislocations are formed with the number of cycles. In other words, by strain cycling a structure is built which gives rise to an increased nucleation density and thus increased nucleation rate.

By means of positron annihilation measurements it could be seen that a defect structure is built with an increasing number of thermal cycles. Also here, since the defects (particularly dislocations) left behind in the austenite after the reverse transformation are more likely to favour the nucleation rate than the growth rate of martensite, the increase in martensite content with each thermal cycle is related to the increased nucleation rate. The present results are also in accordance with the findings of Bogachev et al (19) who studied the effect of addition of C and Si on the transformation behaviour of an Fe-20wt% Mn alloy by means of magnetic susceptibility, dilatometry etc. These authors reported that the addition of Si enhances the formation of martensite during the first few cycles, since the binary Fe-Mn alloy did not exhibit such behaviour. An attempt may be made to understand further the role of Si in this respect. It is believed that Si lowers the stacking fault energy of austenite in Fe-Mn-Si alloys (6,8). This will enhance the extension of the stacking faults enclosed between the partial dislocations obtained from the dissociation of perfect dislocations produced by the reverse transfor mation. Since the formation of martensite in these alloys would seem to depend on the extension of such faults in the austenite (20), it would explain the role Si plays in enhancing the thermal martensite content after each cycle.

Moreover the increasing dislocation density accounts for the increase of R_{2}s and A_f (more thermal activation is needed for the complete retransformation). Finally the influence of thermal cycling on the shape memory effect has to be considered. As already mentioned, more deterioration in shape recovery can occur, for a fixed amount of deformation, with more martensite before this deformation. This can partly explain the decrease of shape memory effect in cycled samples. But because of the fact that the shape recovery also decreases at a deformation temperature above M_s (after cooling from A_f) with cycling, also the defect structure built by thermal cycling has to be taken into account to explain this decrease.

Conclusions

1. The shape recovery and the retransformation temperatures are highly influenced by the amount of plastic strain input and the annealing temperature. Maximum shape recovery is obtained in samples annealed at an intermediate temperature after hot rolling.
2. By strain cycling, the shape memory effect improves progressively. The increasing amount of stress induced martensite can be explained by a favourable defect structure, which is introduced and which accounts for an increasing nucleation rate.
3. The amount of thermal martensite increases with transformation cycles. Also here a defect structure is built and accounts for the increased nucleation rate after each cycle. However cycled samples show less shape recovery.
4. The rate of heating and cooling through the higher temperature zone is important with respect to the defect structure, built by thermal cycling. Recovery annealing is possible.
5. A nearly perfect shape recovery of 5% can be obtained through an appropriate choice of composition and heat treatment (combination of thermo-mechanical cycling and annealing in an "intermediate temperature range"). A low two-way memory in the order of 0.1% has been noticed.

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