## Shape Memory Effect in Fe-Mn-Si Alloys

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### Introduction

Fe-Mn-Si alloys have recently received special attention due to their shape memory behavior (1,2,3). Shape recovery after deformation and reheating is explained here by the $\gamma$(fcc)$\rightarrow \epsilon$ (hexagonal) transformation. This can be obtained by a change in the stacking sequence ABCABC... $\longrightarrow$ABAB..., through a $(111)_\gamma [11\bar{2}]_\gamma$ shear on each second plane (4).

Concurrently with the $\gamma \rightarrow \epsilon$ transformation, the austenite can also transform into $\alpha$(bcc) martensite which inhibits the one way shape memory effect (1WSME) (5). The formation of $\alpha$ martensite can be suppressed if a proper selection of Mn content is chosen (Mn concentration > 20at%).

Another condition to improve the shape memory effect is that no diffusion occurs in the temperature range of the martensitic transformation. This can be achieved for Fe-Mn-Si alloys for which thermal hysteresis reaches values of about 100°C (6,7). A relevant factor which alters the shape memory effect in these alloys is a para-antiferromagnetic transition which affects the $\gamma$ phase, and which takes place at the Neel temperature ($T_N$). Both $T_N$ and Ms (the temperature at which the martensite forms) depend on the alloy composition. An increase in Mn content leads to a decrease in Ms as well as to an increase in $T_N$. On the other hand, an increase in Ms and a decrease in $T_N$ are found with the addition of Si (8,9,10). The martensitic transformation is inhibited or totally suppressed if the austenite is magnetically ordered before Ms has been reached. The dependence of $T_N$ and Ms with Mn and Si content sets the range of alloy compositions which are suitable for the study of the shape memory effect in these alloys (Mn concentration < 33 at% and Si concentration > 1at%). This fact together with the strengthening of the austenite and the lowering of the stacking fault energy explain the positive influence of Si on the shape memory effect of Fe-Mn based alloys.

It is the purpose of this work to present some results obtained with polycrystalline specimens of Fe-Mn-Si alloys, in the composition range where the one way shape memory effect is present and discuss some properties associated with this effect. The consequences of thermal cycling on the martensitic transformation will be considered, and compared with the effects of deformation-heating cycling..

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## Experimental methods

Alloys of different compositions were melted in an induction furnace (see table 1), homogeneized at 1000°C for 24 hours and hot rolled at 1000°C until sheets of 13 mm width were obtained. Cylindrical samples of 3 cm length and 3 mm diameter were used for dilatometric measurements and flat samples (30 mm length, square section 4 × 2 $mm^2$) for tensile experiments. The samples were tensile stressed in a temperature chamber at a crosshead speed of .5 mm/min. Strain gauges were used to measure the deformation. Optical and scanning electron microscopy observations were also performed. All the samples were thermally treated (1 hour at 1000°C and water quenched), before being used. Experiments of tensile deformation with subsequent heating to tempeatures higher than Af were performed to analyze the 1WSME. The distance between 2 indentation marks was used to measure the fraction of shape recovery. X-ray diffraction analysis was performed with Mo radiation, at different temperatures. Samples of several alloys were thermally cycled through the martensitic transformation between 320°C(>Af) and -196°C (<Mf). The samples were kept for 2 minutes at each temperature.

TABLE 1

| Alloy | Fe | Mn | Si | Ms | Mf | As | Af |
|---|---|---|---|---|---|---|---|
| 1 | 64.5 | 30.5 | 5.0 | 25 | -6 | 135 | 155 |
| 2 | 67.0 | 29.0 | 4.0 | 88 | 51 | 164 | 189 |
| 3 | 68.0 | 28.0 | 4.0 | 62 | 41 | 162 | 174 |

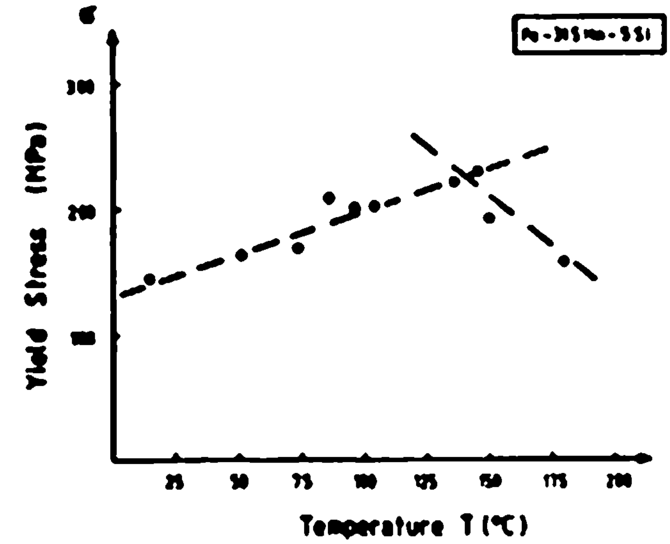
Alloy compositions in wt%, temperatures in °C.

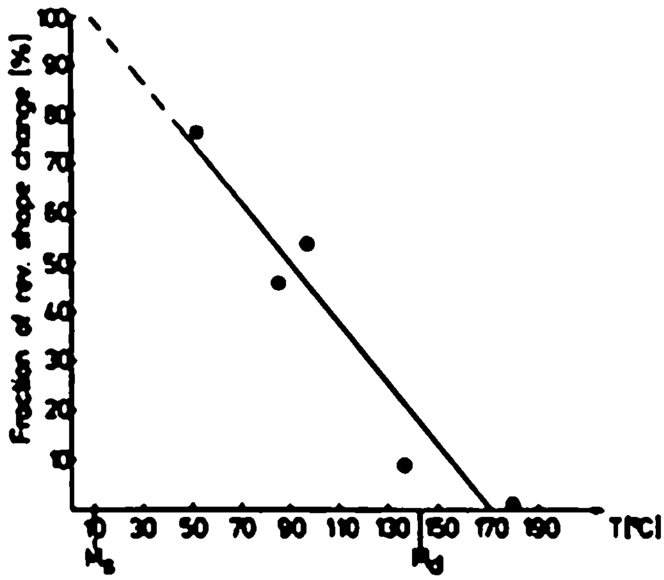
## Experimental results

The yield stress of alloy 1 is shown as a function of temperature in fig. 1a. For temperatures higher than Md = 140°C, a typical plastic deformation behavior is present. In the low temperature range an increase in yield stress at increasing temperatures implies the existence of a stress induced martensitic transformation.

The efficiency of the one way shape memory effect (1WSME) for samples deformed at different temperatures is seen in fig. 1b. Each sample was heated after deformation till 300°C. The amount of shape recovery increases when the temperature of deformation approaches Ms. For temperatures of deformation higher than 170°C, no shape recovery is obtained.

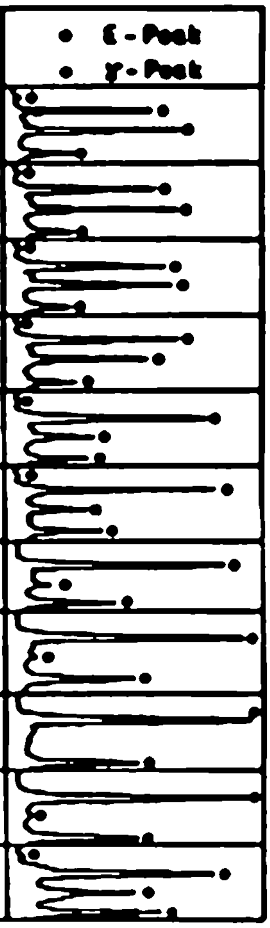
If the shape recovery of a deformed sample is desired the reverse transformation must be allowed to occur. It should be sufficient to heat the specimen to Af. Af as measured with dilatometry reaches values of about 155°C, for alloy 1. However X-ray measurements of diffraction peaks, performed at different temperatures have shown for the same alloy, that martensite peaks are still visible till 300°C (Fig.2).




<u>Fig. 1a</u>: (left) Temperature dependence of yield stress. <u>Fig. 1b (right)</u> One-way effect efficiency vs. temperature of deformation for 1,5% deformation.

| T (°C) | ε a (nm) | ε c (nm) | ε c/a | γ a (nm) |
|---|---|---|---|---|
| 25 | .2513 | .4087 | 1.6263 | .3560 |
| 100 | .2513 | .4087 | 1.6263 | .3561 |
| 140 | .2515 | .4086 | 1.6247 | .3562 |
| 170 | .2519 | .4082 | 1.6205 | .3563 |
| 200 | Dilatometric measurements $M_s$ = 25 °C, $M_f$ = -6 °C, $A_s$ = 135 °C, $A_f$ = 155 °C; Fe-30.5Mn-5Si | | | .3567 |
| 230 | | | | .3567 |
| 260 | | | | .3570 |
| 290 | | | | .3572 |
| 320 | | | | .3574 |
| 28 | | | | .3557 |
| 25 | .2512 | .4089 | 1.6270 | .3563 |




<u>Fig. 2</u>: X-ray diffraction patterns at different temperatures. Martensite is still found at temperatures higher than $A_f$ (dilatometrically measured).

The shape memory effect has been observed also in samples which were deformed at temperatures below Mf. This can be explained as the result of reorientation of martensitic variants as well as the transformation of residual austenite. A transformation of about 50% was determined from X-ray measurements for samples cooled to temperatures lower than the Mf which was determined dilatometrically. Samples cooled to liquid nitrogen temperature (T<<Mf) and tensile stressed at different temperatures show a negative slope of the yield stress vs. temperature (fig. 3).

The changes of transformation temperatures with cycling through the $\gamma \rightarrow \varepsilon$ transformation were measured. Dilatometric measurements were used for this purpose. An example can be seen in fig. 4 (alloy 3). An increase in As and Af are clearly visible. After 1000 cycles, the transformation temperatures stabilize. A small decrease in Ms is also observed (about 10°C after 1000 cycles). An increase of 15% in austenite hardness has been measured, after the same number of transformations. The amount of shape recovery decreases with cycling as it is shown in fig. 5. The stress strain curves for 2 samples of alloy 1 are seen, without cycling and after 1000 thermal cycles. The strain temperature curve as measured with strain gauge are plotted in the same figure for the subsequent heating.

## Discussion

The $\gamma \rightarrow \varepsilon$ martensitic transformation, which is responsible for the shape recovery in Fe-Mn-Si alloys, induces a positive slope in the dependence of yield stress vs. temperature. At temperatures of the order of Af, a classical plastic deformation behavior is found for the analysed alloy. The partial shape recovery found at deformation temperatures in the range between Ms and Md, can be explained by the existence of a mixture of martensitic

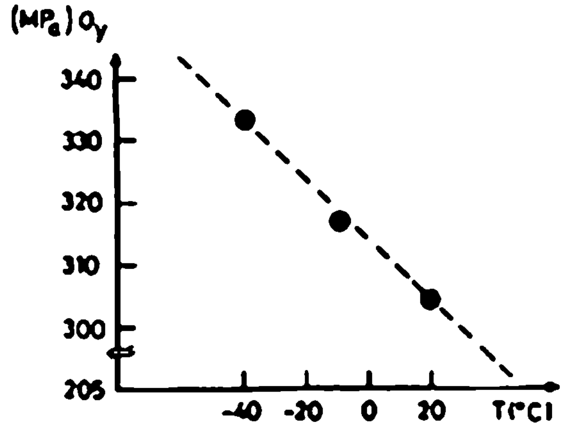



Fig. 3: Yield stress vs. temperature, for samples previously cooled to -196°C.

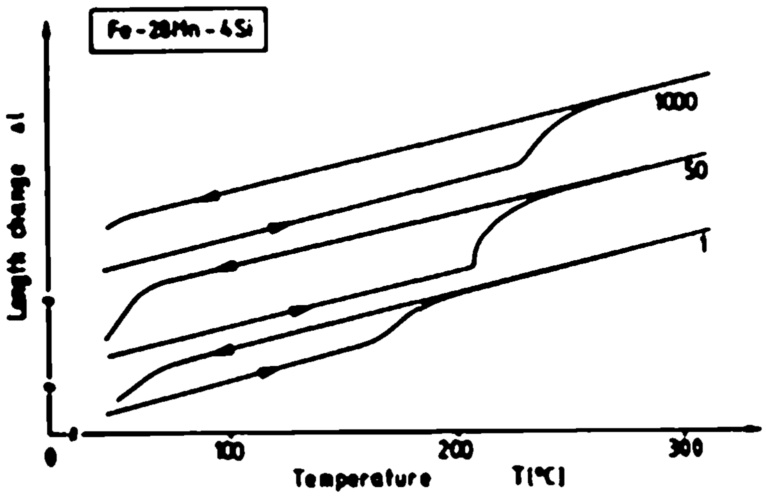



Fig. 4: Effect of thermal cycling on the dilatometrically hysteresis cycle for alloy 3.

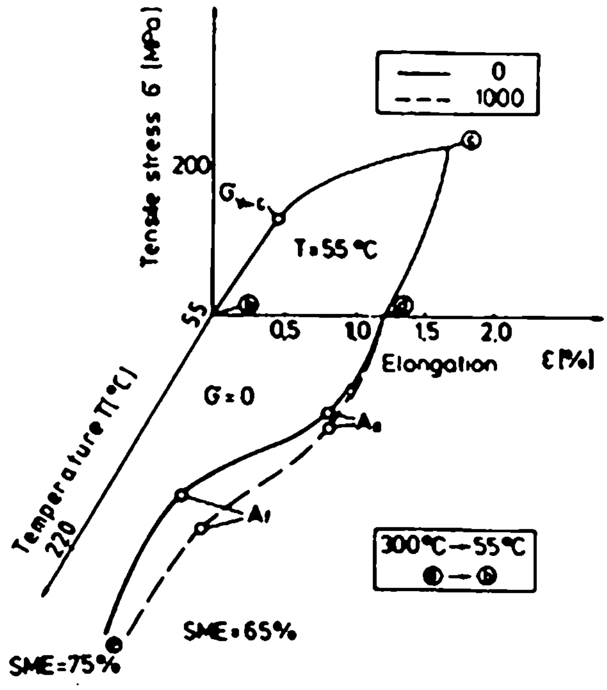



Fig.5: Stress strain temperature diagram showing the amount of strain recovery (one way effect, dotted curve N = 1000 cycles).

transformation and plastic deformation of the austenite or the induced martensite. It is interesting to notice here that deformation of samples which were previously cooled to -196°C have shown a shape recovery after heating. It is not clear whether reorientation of martensite variants or transformation of residual austenite is responsible for this effect. However, plastic deformation of martensite is also present, as was corroborated by the yield stress vs. temperature curve (fig. 3). A negative slope in the yield stress vs. temperature curve is also found in alloys where the hexagonal martensite is not thermally induced but only stress induced (2). This is not the case here since the transformation temperatures were clearly found with dilatometric measurements.

X-ray measurements have confirmed that an overheating respect to Af (dilatometrically measured) is necessary to remove all the martensite. This overheating can be related to the defects which are usually found after a transformation cycle in these alloys (11). The reason for their existence is the large volume change between the unit cells of both phases, of about 1,5%(12), which cannot be accommodated by an elastic movement of atoms. Plastic deformation arises in this way, stabilizing the martensite against the volume expansion necessary to recover the austenite. The volume contraction during the direct transformation, although small if compared with usual martensitic transformations in steels (fcc($\gamma$)$\longrightarrow$ bcc or bct ($\alpha$)), is high if compared with martensitic transformations of Cu based alloys and NiTi alloys.

The defects accumulated in each transformation cycle should affect the transformation. This can be made sufficiently noticeable if thermal cycling through the transformation is performed. The experiments with several alloys have shown that an increase in the hysteresis follows thermal cycling. This is due to a small decrease in Ms and a higher increase in As and Af.

The work hardening observed after thermal cycling can be used to interpret the lowering of Ms. Thermal cycling produces dislocations and stacking faults, which impede the motion of the partial dislocations in the interface during the $\gamma$ to $\epsilon$ transformation. A higher driving force is then necessary to activate the transformation. The conditions are different for the retransformation from $\epsilon$ to $\gamma$: the high amount of residual austenite which is found at temperatures below Mf indicates that the growth of existing austenite is the mechanism associated with the start of the retransformation. The residual austenite probably is plastically deformed due to the volume change, and since its yield strength is smaller compared to martensite. This impedes the motion of the martensite to austenite interface. A local intramartensitic deformation and defect accumulation in such martensite should account for the stabilization of the martensite against completion of the retransformation, leading to an increase in Af. The same mechanism should account for the unfavourable effect of thermal cycling on the shape recovery.

An unfavourable influence of thermal cycling on the shape recovery has also been reported recently (13). An increase in the amount of martensite formed after each cycle has been considered as the main cause for this effect, and the defects introduced by cycling were considered to favour the nucleation rate of martensite. An increase of martensitic formation after each cycle was not found in our case, instead a decrease in Ms has shown that work hardening which originated in induced defects does not favour the nucleation of martensite. On the other hand, the same behavior has been found if As and Af are considered, since both temperatures increase after thermal cycling.

Changes in As and Af have also been reported after deformation-heating cycles in Fe-Mn-Si alloys (3) of a composition close to alloy 1 of this work. However As was lowered and Af increased after this type of cycling. This suggests that defects introduced by thermal transformation or a stress induced transformation stabilize the martensite against completion of the $\epsilon \rightarrow \gamma$ transformation, in a similar way, i.e. increasing Af. On the other hand the opposite behavior in As can be explained by some directionality in the defects introduced when deformation is applied, which favours the onset of the retransformation. This agrees with the observation of a different density in partial dislocations of different Burgers vectors, as has been reported for stress induced hexagonal martensite (5).

It can be mentioned here that a decrease in To of about 30°C has been found after repeated deformation-heating cycles, if the heating temperature was raised to 430°C (3). The modification of the hysteresis after thermal cycling does not suggest a change in To. A lowering in Ms and As of the same amount has been found if the specimen is annealed at temperatures between 400°C and 600°C(10). A possible change in order or the formation of small coherent particles have been suggested as possible mechanisms to explain this shift. It should be further analyzed if this ageing effect is partially responsible for the shift in To reported after deforming-heating cycles.

The volume change and the associated plastic deformation is responsible for the degree of hysteresis (intermediate between the usual shape memory alloys and the steels), and the partial recovery. It should be expected that composition changes, which affect the amount of volume contraction should directly influence the shape memory effect. In which way the volume contraction affects the shape memory effect is also connected with the strength of the austenite against plastic deformation.

Acknowledgments

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