Recovery stress formation in FeMnSi based shape memory alloys: Impact of precipitates, texture and grain size

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Abstract

FeMnSi based shape memory alloys are considered for engineering applications such as prestressing of concrete or coupling devices. For this, a high recovery stress is desired which forms when the FeMnSi alloy is first elongated and then heated above the austenite transformation temperature under mechanical constraints. In this work, we study the impact of three different microstructural properties on the recovery stress of Fe₁₇Mn₅Si₁₀Cr₄Ni₁(V,C) shape memory alloys: Precipitates, texture and grain size. Precipitates allowed varying the recovery stress in a broad range between 255MPa and 564MPa. A recovery stress of 564MPa was achieved by a combination of a high materials yield strength $\sigma_{0.1}$ of 536MPa and a shape recovery of 14%. The [001] grain orientation with a low Schmid factor has a beneficial impact on the recovery stress due to a higher yield strength when compared with the [011] orientation. A decrease of the grain size caused a Hall-Petch strengthening but had no influence on the recovery stress. However the pseudo-elasticity increased for a decrease of grain size.

1. Introduction

The shape memory effect (SME) in FeMnSi based alloys was first discovered by Sato in 1982 [1-3]. Due to low costs, high recovery stresses and its damping capacity the material is considered for use in civil engineering as prestressing or damping element [4-9]. The SME is based on the stress-induced austenite fcc (γ) to martensite hcp (ϵ) transformation. After pre-straining and subsequent unloading the stress-induced hcp phase remains in the material due to a large transformation hysteresis. A back transformation to the austenite fcc phase takes place once the austenite start transformation temperature is reached. In most of the previous studies, it was tried to achieve the highest possible SME, i.e. the maximal recoverable strain, e.g. by tuning the alloy composition [10, 11], pre rolling [12], solution strengthening [13], training [14], annealing [15] or the introduction of stacking faults [16]. It was found that FeMnSi based alloys undergo a paramagnetic to antiferromagnetic transition. When the Néel transformation temperature of the austenite is above the martensite transformation temperature the austenite phase can be stabilized and thermally induced martensite can be suppressed [17, 18]. The formation of stress-induced hcp martensite is closely related to the stacking fault energy of the material [19, 20]. The fcc lattice transforms into a hcp lattice by the formation of stacking faults on every

second {111} layer. A major improvement of the SME was achieved in 2001 by the introduction of NbC precipitates [21]. These precipitates are supposed to act as nucleation sites for the hcp martensite. When the martensite is monopartial hcp martensite, i.e. single variant martensite, a pronounced SME can be achieved by using precipitates without the need of additional training.

The impact of precipitates, texture and grain size on the SME of FeMnSi based shape memory alloys was studied in recent years. It showed that precipitates improve the SME for sizes above around 50 nm [22]. The optimum SME in FeMnSi based alloys is achieved when straining along the [441] direction due to a high Schmid factor [23]. Reducing the grain size decreases the martensite start transformation temperature and thus stabilizes the austenite phase due to a hindered accommodation of stresses which are accompanied by the phase transformation [24]. During these studies the SME was characterized by heating a pre-strained specimen above the austenite transformation temperature without imposing any constraints on the shape change and measuring the recovered strain.

Constraining the shape change by keeping the length of the specimen constant leads to the formation of a recovery stress. Due to this constraint the formation of recovery stress turns into a more complex problem than the recovery strain formation without constraints. The current paper focuses on the formation of recovery stresses which are created during the back transformation from martensite hcp to austenite fcc under constraints. In previous studies effects like pre-strain, heating temperature or the amount of Carbon content on the formation of recovery stresses were studied [25-27]. Compared to the many studies about the SME relatively few systematic studies exist about recovery stress formation in FeMnSi based alloys.

Assuming an elastic modulus of 200GPa a transformation related strain of 0.5% is sufficient to create a recovery stress of 1GPa - a recovery stress which has not been achieved yet. This transformation related strain of 0.5% is far below typical achieved transformation related strains (under no constraints) in polycrystalline FeMnSi based alloys of around 4% [28]. This simple calculation shows that comparably small transformation related strains are sufficient to create huge recovery stresses. However recovery stresses as large as for example 1 GPa can only be achieved if the material shows a yield strength in the same range. Yield strength and transformation related strains are closely related. Both phenomena depend on the interaction of dislocations and defects. Thus in order to achieve a high recovery stress a high materials yield strength and a moderate SME are required.

In this study the formation of recovery stresses is investigated in FeMnSi based alloys by changing three microstructural properties which are known to have an impact on the SME and on the strength of the material and thus are assumed to have an impact on the recovery stress: i) precipitates ii) texture and iii) grain size. The associated strengthening mechanisms are precipitation strengthening, strengthening due to Schmid factor reduction and Hall-Petch strengthening.

Precipitates have a beneficial effect on the SME when exceeding a size of roughly 50 nm [22]. For Fe₂₈Mn₆SiCr₁NbC it was shown that the optimum precipitation aging temperature to obtain a high SME was around 800°C [21]. In another study using Fe₂₀Mn₂Si based shape memory alloys with different amounts of V,C a high strength and a moderate SME was achieved by using a low temperature aging process at 650°C [29]. In this work the effects of an aging at 630°C and at 830°C on the recovery stress will be studied.

It was shown already in 1983 for FeMnSi single crystals that the crystal orientation has a pronounced impact on the shape memory behavior [2]. Tension along the [441] axis resulted in a perfect SME due to a high Schmid factor of 0.5. A strongly suppressed SME was observed when tension was applied along [001] due to a low Schmid factor of 0.24. There exist many studies about the impact of texture on the SME [30-32]. Here we investigate the effect of texture on the formation of recovery stresses in hot rolled polycrystalline specimen. For this purpose dogbone specimens are orientated parallel and transversal to the rolling direction.

Beneficial effects on the recovery stress formation by grain refinement (Hall-Petch strengthening) are highly desirable from an industrial point of view due to the easy adaption into an industrial process, for example by changing the hot rolling temperature. Here we study the recovery stress of two different alloys with different grain sizes.

2. Experimental

Three different batches of the same material were produced. Table 1 summarizes the batches used and their heat treatments.

Section	Batch	Material	Width x thickness	Solution treatment	Aging temp.
3.1 Precipitates	B1	Hot rolled at 1100°C	100mm x 1.5mm		
		Cold rolled to final thickness		2h 1130°C	630°C
				2h 1130°C	830°C
3.2 Texture	B1	Hot rolled at 1100°C	100mm x 1.5mm		
		Cold rolled to final thickness		No heat treatment applied	
3.3 Grain size	B2	Hot rolled at 1040°C	150mm x 15mm	No heat treatment applied	
	B3	Hot rolled at 1000°C	150mm x 15mm	No heat treatment applied	

Table 1: Batches of Fe17Mn5Si10Cr4Ni1(V,C) used and their heat treatments.

While batch B1 was used to study the effects of precipitates and texture on the formation of recovery stresses (Section 3.1 and 3.2), batches B2 and B3 were used to study the impact of grain size on the recovery stress (Section 3.3). B1 is a hot rolled sheet material with a final cold rolling treatment from a thickness of 1.7 mm to 1.5 mm and a width of 100mm. The material is studied in the as received state in Section 3.2 where we make use of the rolling texture in the as received state. B1 was produced in an industrial hot-rolling environment from an ingot of 1t. B2 and B3 were produced for research purposes on a laboratory scale and have a length of around 1m. B2 and B3 were produced from an induction-melted 95kg batch which was cast into a cylindrical mold with a diameter of 160mm. Then, the alloy was hot forged at 1150°C to a rectangular bar with a cross section of 100 x 100mm². After the forging, 1m long plates with a final cross section of 150mm x 15mm were produced in several hot rolling steps. The final hot rolling temperature was 1040°C for B2 and 1000°C for B3.

All alloys used in the present study have a nominal composition of Fe17Mn5Si10Cr4Ni1(V,C) ma.%. Here, 1(V,C) means that the amount of V and C in the material is in sum 1ma.%. Whether V and C are dissolved in the matrix or precipitates form depends on the final heat treatment. In Section 3.1 the final heat treatment is a solution treatment followed by an aging treatment at 630°C and 830°C, respectively. Thus in Section 3.1 the aging treatment creates precipitates. These precipitates are assumed to be MC type precipitates where M is primarily Vanadium but other elements might be present. In Section 3.2 and 3.3 the final heat treatments were done at 1100°C, 1040°C and 1000°C, respectively. Due to these high temperatures it is assumed that V and C are dissolved in the matrix and no precipitates are present.

To study the role of precipitates on the recovery stress formation, dogbone specimens were cut using electrical discharge machining (EDM). These specimens had their tensile axis parallel to the rolling direction (RD). They were solution treated for 2h at a temperature of 1130°C and water quenched. Different aging treatments were applied in order to create precipitates. The specimens were aged at 630°C and 830°C, respectively. Aging times were 2h, 6h, 9h, 24h, 48h, 72h and 144h for the specimens aged at 630°C and 0.2h, 1h and 2h for the specimens aged at 830°C. Batch B1 was also used to study the effect of texture on the recovery stress (Section 3.2.). For this, dogbone specimens were cut by EDM along the rolling direction (RD) and along the transverse direction (TD). These specimens were not solution treated in order to maintain the rolling textures of the as prepared specimens. The XRD pattern and the microstructure presented in Figure 5 shows the batch B1 in the as received state.

B2 and B3 were hot rolled to a final dimension of 15 mm. Different hot rolling temperatures were applied to modify the grain size of the material. For B2 a hot rolling temperature of 1040°C was used while for B3 the final hot rolling temperature was 1000°C. Dogbone specimens which had their tensile axis parallel to the rolling direction were cut by using EDM. The XRD pattern and the microstructures shown in Figure 8 show the batches B2 and B3 in the as received state.

Thermomechanical tests, i.e. stress-strain and recovery stress measurements were performed using a Zwick/Roell Z020 tensile testing machine equipped with a climate chamber (please see [33] for a detailed view of the used setup). The geometry of the dogbone specimens was published recently ((see Figure 2 a) of [34]). In Section 3.1 and 3.2 the used dogbones had a thickness of 1.5 mm while in Section 3.3 the thickness of the dogbone specimens was 0.8 mm. In general we use a thickness of the dogbone specimens of 0.8 mm so that rapid temperature changes in the material during heating and cooling are ensured. However for Batch B1 it was difficult to prepare a 0.8 mm thick dogbone specimen out of the initial 1.5 mm thick sheet material. Therefore, we used a thickness of 1.5 mm for batch B1. A clip-on extensometer was used to measure changes in strain along a gauge length of 20 mm. A relative experimental error of $\pm 5\%$ for all values of stress and pseudo-elasticity can be assumed due to uncertainties in the determination of the exact cross section of the dogbone specimens. In 3.2 and 3.3 specimens were pre-strained to 4% in order to stress-induce the hcp martensite phase. Due to the high strength of the specimens containing precipitates and a maximum loading capacity of the load cell of 2.5kN, specimens were only pre-strained to 2% in Section 3.1. Loading and unloading of the specimens was performed under strain-controlled conditions at a deformation rate of $0.2\text{mm}\cdot\text{min}^{-1}$. Once the final strain was reached specimens were unloaded. These pre deformed specimen were heated and cooled with a rate of $2^\circ\text{C}\cdot\text{min}^{-1}$ under constraints to study the formation of recovery stresses.

The constraint was applied in a way that the dogbone specimens were not able to change their length. For this, the position of the tensile specimen was fixed by keeping the position of the crosshead of the tensile testing machine constant during the test. The maximum heating temperature was 160°C. This temperature was selected with regard to the application of the Fe-SMA in civil engineering, e.g. for pre-stressing of concrete [35, 36]. This upper temperature guarantees that the concrete beam is not damaged during heating above the austenite transformation temperature. The temperature was kept constant for 20 minutes once the final temperature of 160°C was reached. The specimens were subsequently cooled to room temperature and the final recovery stress was measured. As will be seen in Section 3.1 some recovery tests failed when the recovery stress became negative because the dogbone specimens were not stable in the mounting bracket and started slipping when the stress exceeded a value of around -25MPa. The pseudo-elasticity ε_{pse} is defined as the reversible strain upon unloading which cannot be attributed to linear elastic unloading [37]. It was obtained by measuring the total change of strain upon unloading $\Delta\varepsilon_t$ and subtracting the strain related to the linear elastic behavior ε_{el} :

$$\varepsilon_{pse} = \Delta\varepsilon_t - \varepsilon_{el} = (\varepsilon_{max} - \varepsilon_{min}) - \frac{\varepsilon_{max}}{E}$$

Here ε_{max} and ε_{min} denote the strains prior to and after unloading, respectively. E is the elastic modulus. An elastic modulus of 200 GPa was used for the calculation of pseudo-elasticities and yield strengths. This value was obtained from the linear elastic behavior of the 2h solution treated specimen B1. The same value was obtained in a previous study on the same material [37]. Phase analysis prior to pre-straining of all materials was performed using x-ray diffraction (XRD) on a Bruker D8 diffractometer with Cu K α radiation using a 0.012mm thick Ni filter. A FEI NanoSEM230 scanning electron microscope was used for imaging with back scattered electrons. Textures were studied on a Zeiss DSM96 using electron backscatter diffraction (EBSD) with 20keV electrons and a tilting angle of the specimen surface of 70°. Surfaces of the specimens were ground and polished prior to analysis using standard metallography preparation techniques. The final grinding paper used was P4000. Subsequently polishing was done using 6 μ m, 3 μ m, and 1 μ m Al₂O₃ suspension. As the final polishing step a 50nm SiO₂ suspension was used. No chemical etching was applied. In order to observe precipitates differently heat treated specimens B1 were ion milled for 5 minutes using 6 keV Kr-ions and an inclination angle of 30° on a Hitachi IM4000 machine.

3. Results and discussion

3.1 Impact of precipitates on the recovery stress

The reference state of all materials studied in this Section is the solution treated state of batch B1 (Figure 1). Solution treatment creates a fully austenitic structure with large grains of several 100 μ m as

confirmed by austenite peaks in the XRD pattern and the absence of hcp bands on SEM images (Figure 1 a) and b)).

Figure 1: a) XRD measurement and b) SEM micrograph (backscatter electrons) show a fully austenitic structure after 2h solution treatment at 1130°C of batch B1.

After the solution treatment the specimens were aged under different temperatures and for different durations to create carbide precipitates with different sizes and in different densities. In Figure 2 precipitates are exemplarily shown for aging for 48h and 144h at 630°C and for 2h at 830°C. For all aging conditions elongated precipitates are observed. The number of precipitates per area was obtained for these three aging conditions by counting the number of precipitates on minimum five different SEM images (each image 750 μm^2). For these three aging conditions, the area density of precipitates is higher by a factor of 8 for the specimens aged at 630°C when compared with aging at 830°C. An area density of $(0.9 \pm 0.5) \times 10^{10}$ precipitates/ m^2 was obtained for an aging condition of 2.0h at 830°C. Aging for 48h at 630°C and 144h at 630°C both resulted in $(8 \pm 2) \times 10^{10}$ precipitates/ m^2 . Precipitation can be explained by nucleation and growth. The energy barrier to form a stable nucleus and the diffusion of atoms are functions of the temperature and typically result in a maximum of the nucleation rate at a certain temperature. For high temperatures with a large energy barrier to form a precipitate and for very low temperatures where no diffusion takes place, a vanishing nucleation rate is expected. We attribute the increased density of precipitates for aging at 630°C to a sufficiently high diffusion and a low energy barrier when compared to aging at 830°C. At 830°C the nucleation rate is reduced but the diffusion of atoms is faster. This results in a reduced density of precipitates but an increase of the growth rate. Thus, for aging at 630°C in general a high density of small precipitates and for aging at 830°C a low density of large precipitates is expected.

The deformation behavior of FeMnSi alloys is governed by full dislocations and Shockley partial dislocations (SPD's). The latter are associated with the hcp phase. The interaction mechanism of these dislocations with precipitates is determined by the coherent properties of the precipitates. It can be expected that in the beginning of the growth process coherent or semi-coherent precipitates are present

and the interaction of precipitates with dislocations can be explained by cutting and bowing. In the later stages coherency might get lost and the interaction of dislocations and precipitates can be explained by dislocation pinning. The detailed analysis of dislocation interactions with differently sized precipitates which might be coherent or incoherent is beyond the scope of this work. In this Section we study the impact of precipitates on the recovery stress by systematically merging two different known concepts: Increasing the SME by precipitates and precipitation strengthening.

Figure 2: SEM micrographs (backscattered electrons) showing precipitates for aging of a) 48h at 630°C (564MPa recovery stress) b) 144h at 630°C (break at 1.3% strain) and c) 2.0h at 830°C (recovery stress 255MPa). The inset in a) shows a magnification of an area where a precipitate fell out of the matrix revealing the detailed shape of the precipitate. The precipitates are embedded in the matrix material which shows a rough surface caused by ion milling. d) The sample which was only solution treated for 2h at 1130°C does not show precipitates.

Differently aged specimens were pre-strained to 2% in order to stress-induce hcp martensite as shown in Figure 3. The aging treatment has an impact on the strength and the pseudo-elasticity of the material (Figure 3 c) and d)). Aging at 630°C caused higher $\sigma_{0.1}$ yield strengths when compared to aging at 830°C. The increase of strength for the specimens aged at 630°C compared to aging at 830°C is attributed to the higher density of precipitates for aging at 630°C. The highest applied aging times of 72h and 144h at 630°C caused the material to break at 1.3%.

For 24h of aging at 630°C the $\sigma_{0.1}$ yield strength decreases from 637MPa to 573MPa. The decrease of strength is caused by a coarsening of precipitates. Due to the coarsening effect, the precipitates reached the critical size to act as nucleation sites for the stress-induced hcp martensite which is reflected in the increase of pseudo-elasticity as shown in Figure 3 d). Stresses around precipitates shift the hcp martensite transformation temperature to higher temperatures and thus facilitate the growth of the hcp phase by acting as nucleation sites [21].

The specimen which was only solution treated and not aged shows the lowest yield strength of $\sigma_{0.1}=219\text{MPa}$ and the lowest pseudo-elasticity of 0.07%. This low yield strength is caused by the fcc to hcp transformation. The underlying stress strain curves show a strong nonlinearity for low strains [27, 37]. This strong nonlinear behavior for low strains results in a low yield strength. In the subsequent course of loading the material shows a strong strain hardening behavior which is a typical feature of the fcc to hcp transformation. An increase of the yield strength of the aged specimens is caused by precipitation strengthening. For aging of 1.0h and 2.0h at 830°C pseudo-elasticity reaches a plateau value of $\epsilon_{\text{pse}}=0.29\%$. For the samples aged at 630°C a plateau value of pseudo-elasticity is almost reached ($\epsilon_{\text{pse}}=0.20\%$ and $\epsilon_{\text{pse}}=0.22\%$ for aging of 24h and 48h, respectively). It is assumed that the pseudo-elasticity is correlated with the amount of stress-induced hcp martensite. This has been confirmed by the present authors in a recent Neutron diffraction study where upon unloading pseudo-elasticity is attributed to a back transformation from hcp to fcc for small strains in the range of around 3% [38]. Thus, we can conclude that the amount of stress-induced martensite does not change once the plateau value of pseudo-elasticity is reached.

Figure 3: Pre-straining of specimens aged at a) 830°C and b) 630°C. The aged specimens are compared with a specimen which has undergone no aging treatment but was only solution treated (reference state). For increasing aging times the pseudo-elasticity increases when aging at c) 830°C and d) 630°C. The maximum observed pseudo-elasticity is higher when aging at 830°C than at 630°C. Please note that after aging for 1.0h and 2.0h at 830°C the stress strain curves overlap upon unloading. c) and d) show the $\sigma_{0.1}$ yield strength. Peak aging is observed for aging of 9h at 630°C. For aging of 72h and 144h at 630°C pre-straining failed due to fracture below 2% strain.

The pre-strained specimens were heated to 160°C and cooled to room temperature under constraints to measure the recovery stress for differently aged specimens as shown in Figure 4. A prestress of 50MPa was applied in order to avoid compressive (negative) stresses acting on the specimen during heating to 160°C which are caused by thermal expansion [37, 39]. When the thermal expansion during heating is larger than the contraction due to transformation related strains, negative stresses will build up. At a negative stress of around -25MPa the measurements failed because the dogbone specimen slips out of the mounting bracket. This happened to two of the specimens as shown in Figure 4: the specimen which was only solution treated and the specimen aged for 9h at 630°C. These two specimens show low transformation related strains when heated. The solution treated specimen does not contain precipitates. Precipitates act as nucleation sites for hcp martensite [21]. The absence of these precipitates leads to a reduced amount of stress-induced hcp martensite during pre-straining. Due to the low amount of stress-induced martensite, the thermal expansion related strains are larger than

transformation related strains upon heating under constraints. A similar argument is valid for the specimen aged for 9h at 630°C. This alloy shows the highest yield strength of the present study of $\sigma_{0.1} = 637\text{MPa}$. The strengthening curve shown in Figure 3 d) shows a peak after aging for 9h at 630°C which can be explained by a high density of finely distributed precipitates. The size of precipitates is too small in order to provide nucleation sites for the stress-induced hcp martensite. Small precipitates showed to even have detrimental effects on the shape recovery strain [22].

The formation of recovery stress can be divided into two branches (Figure 4). During the first branch the specimen is heated to 160°C. In the second branch the specimen is cooled to room temperature. During heating to 160°C a back transformation from hcp to fcc takes place once the austenite start transformation temperature is reached. In this part a large amount of back transformation is desired to achieve a large recovery stress at 160°C. Under constraints these transformation related strains are smaller when compared with the recovery strain without constraints [37]. During cooling from 160°C to room temperature thermal contraction causes further increase of the recovery stress. Plastic deformation, i.e. bending of the recovery stress vs temperature curve during cooling from 160°C to room temperature, is expected once the yield strength of the material is reached. Therefore the yield strength of the material can be understood as the upper limit of the achievable recovery stress. In an ideal case the recovery stress curve will not bend upon cooling and the recovery stress will linearly increase due to thermal contraction and the absence of plastic deformation. This can be achieved by increasing the yield strength of the material.

Figure 4: Recovery stress formation of materials aged at a) 830°C and b) 630°C. The measurement of the solution treated specimen and the specimen aged for 9h at 630°C failed at around 83°C due to too large compressive stresses. The specimen aged for 48h at 630°C showed the largest recovery stress of the pre-sent study of 564MPa. High aging times above 72h at 630°C caused the material to break before 2% strain was reached. c) and d) show the final recovery stress and the recovery stress at 160°C for aging at 830°C and 630°C, respectively. For low and high aging times no recovery stress is observed. The range of aging times for which a recovery stress is measurable is marked by vertical bars.

Aging for 0.2 h at 830°C is sufficient to create precipitates which have a beneficial effect on the SME when compared to the solution treated specimen. The short aging treatment of 0.2 h leads to a recovery stress of 5 MPa at 160°C which is below the prestress of 50 MPa. Thus transformation related strains at 160°C are smaller than strains related to thermal expansion. This recovery stress of 5 MPa is below the recovery stress at 160°C for the samples aged for 1.0 h and 2.0 h at 830°C of about 90 MPa. The stress increase to 90MPa is caused by an increase of SME under constraints. However all samples aged at 830°C show a similar final recovery stress at room temperature in the range of 258MPa to 281MPa. An increase of the SME did not increase the recovery stress when comparing the sample aged for 0.2h with the samples aged for 1.0 and 2.0h at 830°C. The increase of SME is associated with a decrease of strength which causes a stronger bending during cooling of the stress vs temperature curve of the alloys aged for 1.0h and 2.0h at 830°C when compared with aging for 0.2h at 830°C.

For the specimen aged at 630°C the highest recovery stress within this study was observed after aging for 48 h at 630°C of 564 MPa. When aging for 24 h at 630°C a slightly reduced recovery stress at room temperature of 523 MPa is observed which can be attributed to a reduction of recovery strain at 160°C as can be seen in Figure 4 b). For the specimen aged for 24 h at 630°C the recovery stress at 160°C is 37 MPa while for the specimen aged for 48h at 630°C the recovery stress at 160°C is 101MPa. For these two aging conditions an increase of SME slightly increased the recovery stress. The increase of the SME is attributed to the reduction of the A_s temperature as can be seen Figure 4 b). A_s is around 32°C for the sample aged for 48h at 630°C while it is around 43°C for the sample aged for 24h at 630°C. The reduction of A_s might be explained by a reduction of force acting on the Austenite-Martensite interface or on back stresses due to the interaction of the hcp phase with precipitates. For the samples aged at 630°C an increase of SME showed an increase of the final recovery stress. However an increase of SME does not necessarily increase the recovery stress as discussed for samples aged at 830°C.

Strains related to the back transformation from hcp to fcc were calculated by dividing the final recovery stress with the elastic modulus of 200 GPa (Figure 4 c) and d)). The recovery strains calculated in the present study have to be understood as effective recovery strains. They are the sum of strains related to the back transformation from hcp to fcc and of strains related to plastic deformation. These plastic strains occur once the yield strength of the material is reached and diminish the effective recovery strain. Increasing the yield strength of the material by precipitates will reduce yielding and thus will increase the effective recovery strain. For a thorough understanding of transformation related strains under constrained conditions the reader is referred to [27]. In the same sense the shape recoveries calculated here are effective shape recoveries. For the specimens aged at 830°C recovery strains are in average 0.14%, while for the specimens aged at 630°C recovery strains are around 0.27%. Considering the pre-strain of 2% the relative amount of recovered shape is around 7% for the samples aged at 830°C and 14% for the samples aged at 630°C.

The amount of stress-induced hcp martensite depends on the aging treatment. Since samples which were only solution treated and not aged and samples which were aged for 9h at 630°C did not show sufficient shape recovery, as discussed above, we assume that the amount of formed hcp martensite is reduced when compared with samples aged for 24h or 48h at 630°C. The amount of stress-induced martensite also depends on the alloy composition, the pre-straining temperature and the final strain [10]. In addition due to the isothermal behavior of the fcc to hcp transformation also time has an impact on the amount of formed martensite [40]. In this recent study about creep phenomena in Fe17Mn5Si10Cr4Ni1(V,C) the amount of stress-induced hcp martensite was about 12% for a final strain of 2.5% achieved at 0°C. The sample was aged for 2h at 830°C. Since aging for 2h at 830°C shows the highest pseudo-elasticity within the present study and as discussed above the pseudo-elasticity is linked with the amount of stress-induced martensite, the maximum amount of stress-induced martensite after pre-straining to 2% should be in the range of 12%. However the exact value is not known and the value should only be considered as an approximate value.

When comparing the specimens aged at 630°C and 830°C the maximum observed recovery stress at 160°C was similar (88 MPa for 830°C and 101 MPa for 630°C). This indicates that the amount of recoverable strain under constraints is independent of the aging temperature once the plateau value of pseudo-elasticity is reached. However during cooling the recovery stress curves for specimens aged at

630°C bended at higher stresses due to an increase of yield strength. For this reason aging at 630°C leads to significant higher recovery stresses than aging at 830°C.

3.2 Orientation dependence of recovery stress

The diffraction pattern of B1 in the as received state shows four austenite peaks (Figure 5 a)). In general the fcc (111), (220) and (311) peaks overlap with the hcp (002), (110) and (112) peaks, respectively. An asymmetry of the fcc peaks was not observed and thus it is assumed that the hcp phase is absent. The microstructure shown in Figure 5 b) does not confirm the results of the XRD measurements since a relief profile is visible for many grains. This relief profile is caused by martensite hcp bands. These martensite bands are assumed to be created during the manufacturing process of the sheet material where a cold deformation takes place.

Figure 5: a) XRD pattern of B1 before pre-straining. The normal direction of the rolled material was parallel to the diffraction vector. b) SEM micrographs (backscattered electrons) of B3 before pre-straining. The relief profile indicates the martensite phase in many grains in the as received specimen.

Specimens were pre-strained to 4% in order to stress-induce the hcp phase (Figure 6 a)). The $\sigma_{0.1}$ yield strength reduces when the orientation of the tensile directions is changed from TD to RD. While the $\sigma_{0.1}$ yield strength along the RD is 368MPa, the yield strength for the TD is significantly higher with 468MPa. The measurements show that pseudo-elasticity is slightly more pronounced along the RD.

During the recovery stress formation the stress decreases for RD and TD due to thermal expansion of the specimens (Figure 6 b)) as already observed in Section 3.1. For the RD the slope starts to change at around 39°C while for the TD this point is shifted to a higher temperature of 46°C. At 160°C the maximum temperature is reached. The RD specimen shows at 160°C a positive recovery stress of around 33MPa (tensile stress) while the TD shows a negative recovery stress of -35MPa (compressive stress). The recovery stress at 160°C depends on the recoverable strain. Therefore, the SME is clearly reduced for the TD orientated specimen when compared with the SME along the RD. During cooling from

160°C to room temperature the change of the slope of the curve of the TD is less pronounced than for the RD and thus cuts the curve of the RD at around 51°C at a recovery stress of 374MPa. Due to the reduced bending of the stress vs. temperature curve upon cooling a similar but slightly higher final recovery stress for the TD specimen of 437MPa is achieved when compared to the final recovery stress of the RD specimen of 416MPa. These measurements demonstrate that increasing the SME can be detrimental for the recovery stress when the increase of SME is accompanied with a decrease of strength.

Figure 6: a) Pre-straining to 4% and unloading of specimens aligned with the RD and TD parallel to the tensile direction. b) Formation of recovery stress for both differently orientated specimens.

	Recovery stress [MPa]	Recovered strain [%]	Yield strength $\sigma_{0.1}$ [MPa]	Yield strength $\sigma_{0.2}$ [MPa]	Pseudo-elasticity [%]
Transverse direction (TD)	438±22	0.22±0.01	468±24	577±29	0.44±0.03
Rolling direction (RD)	418±21	0.21±0.01	368±19	461±24	0.53±0.03

Table 2: Recovery stress and strain, yield strength and pseudo-elasticity of material B3 in the as received state. Specimens had their rolling and transverse direction parallel to the loading direction.

Pole figures were obtained from EBSD measurements as shown in Figure 7. These measurements reveal which grains orientations are aligned along the RD and TD directions. In principle the pole figures shown in a), b) and c) can be transformed into the pole figures shown in d), e) and f) by a rotation of 90° around the normal direction (ND). However the current pole figures were measured using two differently aligned specimens (RD and TD). The reduction of the $\sigma_{0.1}$ yield strength of 100MPa for specimens strained along the RD compared to the TD is explained by differences in texture. The mechanical

response of the material is governed by the predominant crystal orientation parallel to the rolling direction. As can be seen in Figure 7 the RD shows an increased amount of (011) orientated grains (here the normal vector of the plane [0-11] is orientated parallel to the RD) and a decreased amount of (001) orientated grains. The transverse direction shows a complementary distribution, i.e. an increased amount of (001) grains and a decreased amount of (011) grains. Experiments on FeMnSi based single crystal showed that the yield strength along the [001] direction is five times as large as the yield strength along the [441] direction [2]. The [011] direction is rotated against the [441] direction by 10° and has also a high Schmid factor of 0.47. Therefore we assume that the mechanical behavior will be similar along the directions [441] and [011]. While along the [441] direction the formation of monopartial hcp martensite is observed, straining along [001] creates hcp martensite variants on differently aligned (111) planes [2]. These differently aligned martensite variants intersect which causes a large flow stress. Due to the intersection of martensite bands a higher driving force is needed to cause the back transformation from hcp to fcc. Therefore as mentioned earlier the A_s temperature for the specimen strained along the TD (texture: (001)) is around 7°C above the specimen strained along the RD (texture: (011)). (111) orientated grains are predominately aligned along the TD but also the RD shows a certain amount of (111) orientated grains. The Schmid factor for tensile strain along the [111] direction is 0.31. Therefore, [111] orientated grains are assumed to have a yield strength which is in between [001] and [011] orientated grains with a Schmid factor of 0.24 and 0.47, respectively. For the RD and TD the mechanical behavior can well be explained with the [001] and [011] texture components. In fact, recent Neutron diffraction experiments on the same material showed a softening behavior for the [111] direction which is in between the behavior of [001] and [011] directions [38]. Thus we assume that the (111) orientated grains have no significant impact on the mechanical behavior of the RD and the TD.

Figure 7: (001), (011) and (111) pole figures (stereographic projections) obtained from two differently aligned dogbone specimens. In a), b) and c) the center of the pole figure is orientated parallel to the RD while in d), e) and f) the center of the pole figure is directed along the TD.

3.3 Impact of grain size on the recovery stress

In this Section the impact of grain size on the recovery stress is studied. Due to different temperatures during the final hot rolling treatment (Table 1) the alloy B2 has an average grain size of $(17 \pm 2) \mu\text{m}$ (Figure 8 b)) while alloy B3 has an average grain size of $(8 \pm 2) \mu\text{m}$ (Figure 8 c)). XRD measurements show peaks of the austenite fcc phase for both batches B2 and B3 (Figure 8 a)). The appearance of all four peaks indicates randomly orientated fcc grains. Pole figure measurements for both materials (shown in the appendix) confirmed the absence of texture.

Figure 8: a) XRD pattern of B2 and B3 prior to pre-straining to 4% shows austenite fcc peaks both alloys. Electron micrographs (Backscattered electrons) of batches b) B2 and c) B3 show that the grain size of alloy B2 is larger than of alloy B3.

The stress-strain characteristics are nearly identical for low strains (Figure 9 a)). At a stress of 360MPa the stress-strain curves of B2 and B3 start to deviate from each other. The fine grained batch B3 shows an increase of yield strength which is attributed to a Hall-Petch strengthening (see Table 3). The Hall-Petch effect is frequently observed for twinning induced plasticity (TWIP) and transformation induced plasticity (TRIP) steels [41]. For strains above 1% the stress-strain curves are parallel while the curve belonging to B3 is shifted to higher stresses. The gap between the two curves in this region is around 60MPa. After the final strain of 4% is reached specimens were unloaded. B2 and B3 show a pseudo-elastic behavior. For B3 a pseudo-elastic effect of 0.57% is observed which is larger than the pseudo-elastic effect of 0.47% observed for B2 (Figure 9 a) and Table 3). The formation of recovery stress for materials B2 and B3 is nearly identical for heating to 160°C and cooling to room temperature. Both stress-temperature curves overlap and show within the experimental error identical values. At 160°C B3 shows a recovery stress of 86MPa while for B2 a value of 96MPa is obtained at 160°C. During cooling the recovery stress increases and reaches its maximum values of 447MPa (B3) and 443MPa (B2) at room temperature. Thus the increase of yield strength due to grain refinement does not have a significant impact on the recovery stress. It is expected that the amount of martensite after unloading is very similar for both batches B2 and B3 causing a very similar stress vs. temperature behavior.

Figure 9: Left: Pre-straining to 4% and unloading of materials with differently sized grains. A more pronounced strain hardening and pseudo-elasticity is observed for B3 compared to B2. Right: Recovery stress measurements show an almost identical behavior for materials with different grain sizes.

The differences in pseudo-elasticity between B2 and B3 are caused by differences in the interaction of hcp bands with grain boundaries. The length of one martensite band is limited by the grain size. Decreasing the grain size increases the amount of martensite hcp bands interacting with grain boundaries. Grain boundaries are known to exert back stresses on the tip of hcp bands which causes an increased pseudo-elasticity for decreasing grain sizes (0.57% for B3 compared to 0.47% for B2) [42].

	Recovery stress [MPa]	Recovery strain [%]	Yield strength $\sigma_{0.1}$ [MPa]	Yield strength $\sigma_{0.2}$ [MPa]	Pseudo-elasticity [%]
B2 (Large grains)	444±23	0.22±0.01	452±23	494±25	0.47±0.03
B3 (Small grains)	448±23	0.24±0.01	500±25	551±28	0.57±0.03

Table 3: Recovery stress and strain, yield strength and pseudo-elasticity of B2 and B3.

4. Conclusions

The impact of precipitates, texture and grain size on the recovery stress was studied. Precipitates have a large impact on the recovery stress by affecting the materials yield strength and the shape memory properties. Within this study an optimum of recovery stress was obtained by applying an overaging treatment at 630°C. Overaging at 630°C causes a high materials yield strength and a sufficient recovery strain which leads to the highest recovery stress obtained in this study of 564 MPa. 564 MPa were achieved by a recovery strain of 0.27%. This gives a shape recovery of 14% considering the pre-strain of 2%. The value is small compared to 80% of shape recovery achieved for a material with a similar alloy composition and a heat treatment applied to maximize the shape recovery by using NbC precipitates [21]. Thus in our study the observed shape recoveries are comparably small. Precipitates allow modifying the recovery stress according to the applications needs. This can be interesting for applications where the recovery stress has to be carefully selected. In the present study the amount of (V,C) was 1 ma.%. Even higher recovery stresses than 564 MPa might be achieved by increasing the amount of (V,C) due to an increase of yield strength. The yield strength was the limiting factor of the recovery stress throughout the whole study.

Texture has an impact on the formation of recovery stresses. The RD shows an increased amount of [011] orientated grains which are prone to the fcc to hcp transformation due to a high Schmid factor of 0.47. The TD shows opposing characteristics. The increased amount of [001] grains shows a weak SME due to a low Schmid factor of 0.24. As a consequence the transformation related strains and thus the recovery stress at 160°C is larger for the RD. However the decrease of strength of the RD leads to an increased recovery stress at room temperature for the TD. This shows that increasing the SME can be detrimental for the recovery stress, when the increase of SME is associated with a decrease of yield strength.

The grain size of FeMnSi based SMA had no significant impact on the recovery stress. The observed Hall-Petch strengthening had no influence on the recovery stress. Decreasing the grain size increased the pseudo-elastic effect which is explained by an increased amount of martensite hcp bands interacting with grain boundaries for decreasing grain sizes.

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