Effect of Carbon on the Shape Memory Mechanism in FeMnSiCrNi SMAs

Nele Van CAENEGEM, Lode DUPREZ, Kim VERBEKEN, Bruno C. De COOMAN, Yvan HOUBAERT and Danny SEGERS

1) Department of Metallurgy and Materials Science, Ghent University (UGent), Technologiepark 903, B-9052 Ghent, Belgium. E-mail: Nele.VanCaenegem@UGent.be, Kim.Verbeken@UGent.be, decooman@Postech.ac.kr, Yvan.Houbaert@UGent.be
2) Industry Research Centre Ghent, Arcelor Group, J.F. Kennedylaan 3, B-9060 Zelzate, Belgium. E-mail: Lode.Duprez@arcelor.com
3) Department of Subatomic and Radiation Physics, Ghent University, Proeftuinstraat 86, B-9000 Ghent, Belgium. E-mail: Danny.Segers@UGent.be
4) The Fund for Scientific Research-Flanders (Belgium) (F.W.O.-Vlaanderen)

(Received on August 15, 2006; accepted on January 25, 2007)

Fe–Mn–Si–Cr–Ni alloys are Fe-based shape memory alloys (SMA), which make use of the γ→ε stress induced martensitic transformation. In the present study, the effect of C addition on the shape memory effect was reported. The characterization of the martensitic transformation and the phase components was carried out by using light optical microscopy, X-ray diffraction, internal friction measurements and transmission electron microscopy (TEM). C is often mentioned to improve the shape memory behaviour. Present results show, however, an opposite effect. It is believed that the relative position between the deformation temperature and the Ms temperature for the two alloys is of key importance when looking for an explanation for the presented experimental results. The lower Ms temperature for the high C alloy causes more slip and less transformation of the austenite. The microstructural characterization showed a lower amount of formed ε martensite during deformation for the high C alloy.

KEY WORDS: shape memory; C; ε martensite; FeMnSi.

1. Introduction

Fe–Mn alloys with 10–30% Mn are characterized by the reversible and self-accommodating face centred cubic (fcc) γ austenite to hexagonal close packed (hcp) ε martensite transformation.\(^1\) Ferrous shape memory alloys (SMAs) based on Fe–Mn alloy system have received much attention since the eighties and there are definite signals from the shape memory materials research community that they may become a new class of SMAs of great technical importance among others due to their high austenite yield strength, which makes them attractive for pseudoelastic applications, and due to their cost-effectiveness.\(^2\) The shape memory effect in FeMnSi alloys was first reported by Sato et al.\(^3\) They found that a single crystal of a Fe–30%Mn–1%Si alloy exhibited a complete shape memory effect when deformed in the (414) direction. Sato et al.\(^4\) and Murakami et al.\(^5\) also succeeded in developing polycrystalline FeMnSi shape memory alloys. Moriya et al.\(^6\) and Otsuka et al.\(^7\) developed FeCrNiMnSi and FeCrNiMnSiCo shape memory alloys, which are characterized by their corrosion resistance.

Different types of martensite are usually distinguished: thermal martensite, stress induced and strain induced martensite. Thermal martensite is formed by cooling the alloy below the Ms martensite start temperature. Stress induced martensite is obtained when the material is deformed between Ms and Mγ. Mγ is defined as the temperature at which the stress induced transformation changes into a strain induced transformation. Consequently, strain induced martensite is formed when the material is deformed between Mγ and Ms; Ms is the temperature above which there is no martensite transformation. In SMAs, only thermal and stress induced martensite should be present.

The large hysteresis and a poor shape recovery in the Fe–Mn binary system was addressed by making specific alloying additions of Si, C, Co, Ni, and Cr. In order to attain a complete shape memory effect, stress induced ε martensite must be formed without permanent deformation by slip. The latter is achieved when the yield stress of the γ matrix is high. In addition the γ/ε transformation interface must remain reversibly mobile at all times, i.e. formation of ε band intersections, ε to α’ transformation, etc. must be avoided. The required martensite morphology for ferrous SMA is of the thin plate type.

The shape memory effect in Fe–Mn–Si alloys strongly depends on the alloy composition. Alloying with Si lowers the stacking fault energy of the austenite. In addition, Si is a solid solution hardening element which increases the yield stress of the parent austenite phase and prevents the permanent deformation by slip. C strengthens the austenite and increases the stacking fault energy.\(^7,8\) Co also lowers the stacking fault energy of austenite. FeMnCo alloys\(^9\) only exhibit a small shape memory effect comparable to FeMn.
binary alloys. This is very likely due to the fact that Co does not sufficiently strengthen the austenite matrix. Ni lowers the Ms temperature. Ni is a γ stabilizer, which suppresses the formation of the ferrite and the σ phase precipitation. The presence of the intermetallic σ phase reduces the fracture toughness of the alloy. Otsuka et al. found evidence for the presence of the σ phase in a Fe–25%Mn–6%Si–9%Cr alloy which had an initial shape recovery of more than 60% after a 2.5% strain deformation, but which broke when the deformation and heating cycles were repeated. Cr is added to improve the corrosion resistance. The yield stress of the austenite increases by adding Cr. An increasing Cr content lowers the Ms temperature. Cr also lowers the stacking fault energy. Whereas the interstitial impurities C and N readily strengthen the parent austenite phase, they may also form carbides and nitrides. The presence of precipitates can cause the SME to occur incompletely by suppressing the mobility of the austenite/martensite interface, although others report an improvement of the SME by producing precipitates (e.g. NbC). The precipitates will provide a preferential nucleation site for the stress induced martensitic transformation through their large elastic strain field. Furthermore, being an obstacle for the martensitic growth, they generate a back stress acting on the martensite plate tip which helps the reverse movement of the Shockley partial dislocations, resulting in a good shape recovery. Interstitials also influence the stacking fault energy; whereas C increases the stacking fault energy, N decreases it. C and N are also known to influence the ordering of the substitutional elements. The nitrogen atoms favor short range ordering. In contrast, C atoms have a tendency to cluster.

Table 1 reviews a number of recently published results on the performance of ferrous SMAs based on alloy systems similar to the one used in the present study. These alloys have absolute recovery strains in the range of 2–4%. These recovery strains were obtained by deformation training of the Fe–Mn–Si alloys. The principle of the shape memory effect in ferrous SMAs is based on the γ→ε transformation which is obtained by the glide of isolated Shockley partial dislocations on the {111}γ planes during deformation. During subsequent heating, the reverse ε→γ transformation begins at a temperature Aγ and ends at a temperature Aε when all martensite has disappeared. It has to be mentioned that FeMnSi-type ferrous SMAs always contain some retained austenite at room temperature after deformation. The ε martensite forms dense transformed regions which still contain some amount of the parent γ phase. It is therefore unclear whether the Mf temperature is actually accurately known in these alloy systems.

In the present work, the deformation mechanism and the influence of C on the shape memory effect (SME) was investigated by testing two FeMnCrNiSi SMAs, containing 0.05% C and 0.18% C, respectively. The effect of C addition depends on the final heat treatment and the corresponding microstructure, in particular, if C exists at interstitial sites or as carbides is of importance. Interstitial C strengthens the austenite, thereby delaying the generation of dislocations during deformation, and thereby favoring the SME as the ε/γ interface preferably moves through a dislocation-free parent phase. Interstitial C is also mentioned to increase the stacking fault energy. It is called it reduces the Shockley partial dislocation separation. This is not a favorable condition to obtain a good SME. However, Bliznuk et al. refer to their TEM studies to say that the addition of about 1.0 at% of C to a Fe62Mn16Si10Cr9Ni4 alloy does not significantly affect the stacking fault energy. Consequently, the observed difference in the recovered strain when adding C cannot be ascribed to changes in the values of stacking fault energy.

In addition to solid solution strengthening, precipitation hardening is also an effective method to strengthen the austenite in order to improve the SME. Wen et al. mention that for their high C alloy that, during aging, car-

Table 1. Overview of the reported recovery strain of the different SMAs.

<table>
<thead>
<tr>
<th>Alloy (wt%)</th>
<th>Mode of deformation</th>
<th>Training</th>
<th>recovery</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMnSi</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30Mn-6.5Si</td>
<td>4 RT</td>
<td>Tensile</td>
<td>No</td>
<td>75%</td>
</tr>
<tr>
<td>32Mn-6Si</td>
<td>4 200-300</td>
<td>Tensile</td>
<td>No</td>
<td>80%</td>
</tr>
<tr>
<td>32Mn-6Si</td>
<td>2.5 RT</td>
<td>Tensile</td>
<td>5 cycles</td>
<td>600</td>
</tr>
<tr>
<td>17Mn-6Si-0.3C</td>
<td>4.5 RT</td>
<td>Tensile</td>
<td>1 cycle</td>
<td>600</td>
</tr>
<tr>
<td>14Mn-6Si-9Cr-6Ni</td>
<td>4 500</td>
<td>Tensile</td>
<td>Yes</td>
<td>600</td>
</tr>
<tr>
<td>14Mn-6Si-9Cr-5Ni</td>
<td>6 RT</td>
<td>Tensile</td>
<td>3 cycles</td>
<td>600</td>
</tr>
<tr>
<td>16Mn-5Ni-12Cr-7.5Ni</td>
<td>2.5 RT</td>
<td>Tensile</td>
<td>3 cycles</td>
<td>600</td>
</tr>
<tr>
<td>20Mn-5Ni-8Cr-5Ni</td>
<td>2.5 RT</td>
<td>Tensile</td>
<td>4 cycles</td>
<td>600</td>
</tr>
<tr>
<td>17Mn-4.5Si-1.5Cr-2Ni-0.25C</td>
<td>5 RT</td>
<td>Tensile</td>
<td>3 cycles</td>
<td>70%</td>
</tr>
<tr>
<td>12.5Mn-6Si-9Cr-5Ni</td>
<td>3.4 RT</td>
<td>Bending</td>
<td>No</td>
<td>270</td>
</tr>
<tr>
<td>12.5Mn-6Si-9Cr-5Ni-0.2C</td>
<td>3.4 RT</td>
<td>Bending</td>
<td>No</td>
<td>330</td>
</tr>
<tr>
<td>25.6Mn-5.1Si-4.1Ni-1.8Co</td>
<td>3-8 RT</td>
<td>Tensile</td>
<td>No</td>
<td>66-25%</td>
</tr>
<tr>
<td>29.0Mn-3.5Si-4.3Cr-2.0Ni-3.5Co</td>
<td>8 196</td>
<td>Bending</td>
<td>No</td>
<td>65%</td>
</tr>
<tr>
<td>14.5Mn-5.3Si-13Cr-5Ni-4.8Co</td>
<td>6-10 RT</td>
<td>Tensile</td>
<td>No</td>
<td>33-20%</td>
</tr>
<tr>
<td>8.8Mn-6Si-13Cr-6Ni-12Co</td>
<td>4 RT</td>
<td>Tensile</td>
<td>4 cycles</td>
<td>600</td>
</tr>
</tbody>
</table>

* = present work
bides continuously precipitate. The precipitated carbides strengthen the austenitic matrix and suppress the occurrence of permanent slip, thereby improving the SME. However, when the aging time was too long, the M<sub>s</sub> temperature would rise since the austenite is gradually depleted of C. Consequently, the critical stress for the stress induced aging, making Shockley partials slip more readily.

### 2. Experimental

Two ferrous SMAs with different compositions were prepared for the present study. The material was cast in an air furnace, air cooled, reheated to 1 200°C and hot rolled on a laboratory mill from 20 to 2 mm and air cooled. Their chemical composition is listed in Table 2.

The identification of the phase components, the distinction between ε martensite and twins, the study of a morphology evolution of the ε martensite during deformation were carried out by optical microscopy (OM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). Internal friction and dilatometry was done in order to determine the transformation temperatures of both alloys. Finally, the effect of C on the shape memory effect was evaluated by means of a bending test.

The specimens, examined by optical microscopy, were first mechanically polished. They were then electrolytically polished in a solution of 20% perchloric acid and 80% butylcellosolve. Afterwards, the specimens were color etched in an aqueous solution of 1.2% K₂S₂O₅ and 0.5% NH₄HF₂. Such phase could clearly be distinguished on the basis of its color and morphology. The change in color, when a thin layer of etchant is deposited on a metallographic specimen to reveal the microstructure, is related to the thickness of the film depending on the degree of corrosion reaction between phase and etchant. Whereas the ε martensite plates always appeared as long thin plates with a white contrast, the γ matrix was brown.

Thin foil TEM analysis was carried out on a Philips EM420, operated at 120 kV. Samples were prepared through electrolytical polishing with a solution of 95%CH₃COOH+5%HClO₄ at a temperature of 12.5°C and a voltage of 50 V.

X-Ray diffraction was used to determine the different phases and their volume fraction. The measurements were done using a Siemens D5000 diffractometer with Mo (λ<sub>Mo</sub>=0.071 nm) in the 2θ range of 18–55°. The undeformed alloys did not contain the ε phase; some α phase was however present. The formulas proposed by Cullity were used to determine V<sub>ε</sub> and V<sub>α</sub>. Note that this approach neglected the possible influence of pronounced crystallographic texture in the phases.

The internal friction was measured by an automated ultrasonic piezoelectric resonant composite oscillator operating at a vibration frequency of 40 kHz. The internal friction peaks were obtained at very low strain amplitude (10⁻⁸), which is typical for a truly anelastic relaxation phenomenon. The specimens (1 mm×3 mm×62.5 mm) were prepared along the rolling direction of the rolled and annealed sheet material. The internal friction was measured by monitoring the drive voltage required to keep the gauge voltage constant during the heating and cooling of the specimen. The heating was done by means of infrared heaters; the heating rate was 100°C/min.

The specimens for dilatometry (3.5 mm diameter and 5 mm in length) were machined from the hot rolled sheets. The specimens were austenitised at 1 200°C, cooled to room temperature and tested in an automated dilatometer. The temperature cycle imposed to the dilatometer specimens consisted in a heating with a rate of 1°C/s to 1 200°C followed by a cooling with a rate of 1°C/s.

The shape memory effect was evaluated by means of a bending test. Samples of 150×15×1.7 mm and 100×15×1.7 mm were bent to a 50 mm or 10 mm diameter which caused a strain of 3.4% or 17%, respectively. After deformation the samples were heated in an oil bath (T<200°C) or a salt bath (200°C<T<450°C). The samples partly recovered their initial shape.

### 2.1. Initial Microstructure

After rolling, the two SMAs were annealed at 1 100°C for 15 min and water quenched to room temperature in order to austenitize the microstructure. The microstructural analysis, Fig. 1, revealed the presence of large austenitic grains, large coherent twins as sharp parallel lines with dark contrast within the austenite. The thin lines are visible in 3 directions in most of the austenite grains. Ferrite was still present in the microstructure of the FeMnSiCrNi+0.2%C alloy. Figure 2 represents the XRD pattern of both alloys. Only the 2θ<sub>α</sub> range which contains the {100}, {002}, and {101} peaks is shown. It also shows the presence of ferrite in the alloy with C. The ε martensite phase is not detected with the XRD. Table 3 lists the volume percent of ferrite and austenite calculated from the XRD measurement, in the undeformed samples, before and after the heat treatment. It is clear that the annealing and water quenching reduces the amount of ferrite phase. The difference in microstructure between the two alloys means that there is a different thermodynamic mechanism active for both alloys.

Samples were also cooled to liquid nitrogen temperature (−196°C) in order to obtain a large volume fraction of ε phase. After quenching a widening of the plates, i.e. ε martensite formation, became visible.

Figure 3(a) shows TEM bright fields of a FeMnSiCrNi sample in the undeformed state. TEM analysis revealed a microstructure with a high density of planar faults on the (111)E planes. The lines indicated as A and B are stacking faults on resp. the (111)E plane and the (111)E plane.

### Table 2. Composition of the FeMnSiCrNi and FeMnSiCrNi+C SMAs.

<table>
<thead>
<tr>
<th>alloy</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeMnSiCrNi</td>
<td>12.60</td>
<td>6.00</td>
<td>0.27</td>
<td>9.27</td>
<td>4.74</td>
<td>0.13</td>
<td>0.05</td>
</tr>
<tr>
<td>FeMnSiCrNi+0.2%C</td>
<td>12.56</td>
<td>6.09</td>
<td>0.44</td>
<td>9.44</td>
<td>4.89</td>
<td>0.13</td>
<td>0.18</td>
</tr>
</tbody>
</table>

© 2007 ISIJ
Figures 3(c) and 3(d) show bright field and dark field micrographs of a FeMnSiCrNi+0.2%C sample in the undeformed state. The parent fcc crystal is oriented in the [11\bar{2}] beam direction. There are additional diffraction spots. It is not clear yet whether they are \(\varepsilon\) martensite diffraction spots or if they are due to double diffraction. These spots can be spots of higher order Laue zone. One can see, by selecting the undefined spot for dark field, a band in contrast and a dislocation structure in it.

Since no \(\varepsilon\) martensite is observed with TEM and XRD at room temperature, the thin lines visible in the optical microscopy in Fig. 1 are characterized as a sequence of stacking faults. Since the absence of thermally induced \(\varepsilon\) martensite at room temperature, the \(M_s\) temperature for both alloys has to be below room temperature. Because of the growth of the \(\varepsilon\) martensite during cooling to the liquid nitrogen temperature, the \(M_s\) temperature is between room temperature and the liquid nitrogen temperature (\(-196^\circ\text{C}\)).

| Table 3. | Austenite and ferrite volume percentage in the as-prepared SMAs, the lattice parameters \(a_g\), \(a_e\), \(c_e\) and the atomic density of the fcc and hcp phase of the two alloys. |
|----------|--------------------|--------------------|
|          | FeMnSiCrNi         | FeMnSiCrNi+0.2%C   |
| \(\alpha\) phase (%) | HR+AC              | 7.0                | 20.4                |
|          | HR+AC+A+WQ         | 3.7                | 13.3                |
| \(\gamma\) phase (%) | HR+AC              | 92.9               | 79.7                |
|          | HR+AC+A+WQ         | 96.3               | 86.7                |
| \(a_g\) (nm) | HR+AC              | 0.3594             | 0.3600              |
|          | HR+AC+A+WQ         | 0.3592             | 0.3593              |
|          | HR+AC+A+WQ+c\(\varepsilon\) | 0.3586             | 0.3597              |
| \(a_e\) (nm) | using \{100\}_a  | 0.2553             | 0.2556              |
|          | using \{101\}_a   | 0.2475             | 0.2476              |
| \(c_e\) (nm) | using \{002\}_a  | 0.4105             | 0.4105              |
|          | using \{101\}_a   | 0.3186             | 0.317               |
|          | using \{100\}_e+\{002\}_e | 1.608              | 1.606               |
|          | using \{101\}_e   | 1.287              | 1.280               |
| Atomic density (at/nm\(^3\)) of the fcc unit cell | HR+AC              | 86.171             | 85.762              |
|          | HR+AC+A+WQ        | 86.337             | 86.214              |
|          | HR+AC+A+WQ+c\(\varepsilon\) | 86.742             | 85.949              |
| Atomic density (at/nm\(^3\)) of the hcp unit cell | HR+AC              | 86.321             | 86.137              |

* HR: hot rolled, AC: air cooled, A: annealed, WQ: water quenched
2.2. Microstructure of the Deformed SMA

When the shape memory alloy is deformed, the austenite to ε martensite transformation takes place.

Figure 4 shows the microstructure after 15% tensile deformation. Broader, white ε martensite plates appear.28) The martensite plates had a preferred direction as a result of the tensile straining. TEM micrographs of the FeMnSiCrNi(C) alloys, in the deformed state clearly confirms the presence of thin plates of ε martensite (Fig. 5). Figure 6 shows a clear diffraction pattern in detail of ε and γ reflections in the [011]γ/[210]ε beam direction. The close-packed planes, (111)γ, are parallel to (0001)ε according to the transformation of the (111)γ planes to the (0001)ε planes.

In Fig. 5(a) the thin plates appear in two directions, indicating the presence of two ε variants. At the intersection of two variants of ε martensite, α′ martensite was often observed (Fig. 7). It is very likely that the formation of α′ martensite is the main cause for relatively low recovery of the ferrous SMAs. The α′ regions impede the reverse motion of the Shockley partial dislocations. In the diffraction pattern of α′ martensite, γ and ε martensite, one can see the orientation relationships: [0001]ε//[011]γ (Bogers–Burgers) and [011]γ//[111]γ (Kurdjumov–Sachs).

The comparison of the XRD of Fig. 8 and Fig. 2 confirms that there is more ε martensite present in the 5% deformed samples than in the undeformed ones. The deformed FeMnSiCrNi alloy had a higher intensity in the ε peaks or it seems to have formed more ε phase during the

![Fig. 3. TEM of (top) FeMnSiCrNi and (below) FeMnSiCrNi+0.2%C, hot rolled, air cooled, annealed at 1 100°C–15 min and water quenched at room temperature (top) [011] zone axis (below) bright field (left) and dark field (right) of the same area of [112] zone axis.](image)

![Fig. 4. OM microstructure of FeMnSiCrNi (left) and FeMnSiCrNi+0.2%C (right), hot rolled, air cooled, annealed at 1 100°C–15 min and water quenched at room temperature, tensile deformation: 15% (color etching) (left) γ grains with white martensite plates in one direction and others with fine black plates in 2 directions. (right) ferrite (black), martensite plates in austenite in two directions, or thicker white plates in one direction.](image)

![Fig. 5. TEM bright field of FeMnSiCrNi (top) and FeMnSiCrNi+0.2%C (below), hot rolled, air cooled, annealed at 1 100°C–15 min and water quenched at room temperature, bending deformation: 3.4%, [011], [210]ε, zone axis.](image)

![Fig. 6. TEM diffraction pattern of FeMnSiCrNi+0.2%C showing ε and γ reflections in the [011]γ/[210]ε beam direction.](image)
deformation than the alloy with C. This could confirm that the effect of C, lowering $M_s$, has a large influence on the formation during deformation.

2.3. Effect of Carbon on the Tensile Deformation

The solid solution strengthening of the parent $\gamma$ phase as a result of the C-alloying is clear from the stress–strain curves shown in Fig. 9a, obtained for the two alloys. The yield strength of the alloy without C was $R_{p0.2}/H11005259$ MPa. The yield strength of the C-alloyed SMA was 352 MPa. During deformation the transformation $\gamma \rightarrow e$ proceeds and $\alpha'$ martensite is formed at the intersection of the $e$ plates, which causes strain hardening as shown in Fig. 9(b). As shown by XRD measurement, the alloy without C forms much more $e$ martensite during deformation which results in a higher strain hardening compared to the alloy with C. The presence of C resulted in a lower tensile strength (755 MPa compared to 825 MPa, in eng strain–eng stress curve) due to a reduced strain hardening.

The uniform elongation $e_u$ and the true stress at the uniform elongation $e_u\sigma$, which is also the stress at necking, are larger for the C-free alloy. This might be correlated with the fact that due to the formation of the $e$ phase or twinning the microstructure is progressively subdivided in much smaller sized units in the C-added alloy; although this could not be quantitatively proven by the observed microstructures. Consequently, the effective grain size is reduced. In steel with a smaller grain size, more stress is needed for the movement and multiplication of dislocations. They are impeded by the grain boundaries which lead to a lower strain hardening and to a smaller uniform elongation. In both alloys, fracture occurred before the necking condition $e=n$ was met.

2.4. Transformation Temperature

Transformations associated with a volume change or change in thermal dilatation can be observed by means of dilatometry. The volume change during the fcc $\rightarrow$ bcc transformation of a pure fcc Fe (85.734 at/nm$^3$) and bcc Fe (83.160 at/nm$^3$) is usually clearly visible.

The atomic density of the fcc and hcp unit cell can be calculated by using the lattice constants measured with XRD. The lattice parameter $a_g$ was obtained for each of the diffraction peaks was plotted versus the function $\cos^2 \theta/\sin \theta + \cos^2 \theta/\theta$ following the Nelson–Riley method. The lattice parameter $a_g$ was obtained by the intersection of the line fitted through the data points and the $Y$-axis. The results obtained for $a_g, a_e$ and $c_e$ are given in Table 3. Lattice parameters for FeMnSiCrNi SMAs have been reported by Putaux et al.\textsuperscript{29} For a 15.92%Mn–0.04%W–5.06%Si–0.019%C–9.13%Cr–0.016%N–4.18%Ni alloy, a composi-
tion close to that of the FeMnSiCrNi alloy in the present research. They reported $a_{\gamma} = 0.359\,\text{nm}$, $a_{\varepsilon} = 0.253\,\text{nm}$ and $c_{\gamma} = 0.411\,\text{nm}$. The present results are in good agreement with their values: $a_{\gamma} = 0.3586\,\text{nm}$, $a_{\varepsilon} = 0.2553\,\text{nm}$ and $c_{\gamma} = 0.4105\,\text{nm}$. The results indicate that a very small specific volume decrease is associated with the $\gamma \rightarrow \varepsilon$ transformation. The specific volume ($\text{nm}^3/\text{atom}$) for the $\gamma$ phase in the deformed alloy was 0.011528 $\text{nm}^3$ for FeMnSiCrNi and 0.011635 $\text{nm}^3$ for FeMnSiCrNi$+0.2\%\text{C}$. The lattice parameter increase is an indication that the addition of C results in a lattice dilatation. Table 3 shows that there is not much difference for the fcc and hcp unit cell. The $\varepsilon \rightarrow \gamma$ transformation could therefore not be observed with the dilatometer. This is due to the absence of a volume change during the $\gamma \rightarrow \varepsilon$ transformation and to the small differences in the thermal dilatation coefficient for $\gamma$ and $\varepsilon$. During the fcc→hcp transition, the $\{111\}_\gamma$ planes are transformed to the $\{0001\}_\varepsilon$ planes. The distances between the $\{111\}_\gamma$ planes and the distance between the $\{0001\}_\varepsilon$ planes were calculated. The values obtained are reported in Table 4. There was a contraction of the interplanar spacing of 1.1% ($=(0.2075-0.2052)/0.2075$) associated with the $\gamma \rightarrow \varepsilon$ transformation.

As the transformation temperatures could not be determined with dilatometry, internal friction measurements were carried out between 20°C and 350°C (Fig. 10). On an austenitized specimen (annealed at 1100°C during 15 min and water quenched to room temperature), one could not observe IF peaks. On samples containing stress induced $\varepsilon$ martensite (deformed 15%), the internal friction spectrum had a maximum during heating over the temperature range where the $\varepsilon \rightarrow \gamma$ transformation took place. The elastic modulus also shows a change in slope due to the transformation. During cooling, one would expect a peak corresponding to the reverse transformation at a temperature lower than the peak temperature on heating. The internal friction peaks do not appear as could be expected thermodynamically (see Fig. 11). A possible reason is that the damping peak on cooling is not due to the movement of the $\varepsilon/\gamma$ interface. The internal friction is also affected by other phenomena, such as the movement of twin interfaces, dislocations, interstitials, anti-ferromagnetic transformation. Since no peaks were observed in DSC measurements, the anti-ferromagnetic transformation can be excluded. Also TEM observation revealed no presence of interstitials, which can exclude the movement of interstitials. To characterize this peak exactly, a supplementary method is still needed. The absence of supplementary peaks means that the peak of the $\gamma \rightarrow \varepsilon$ transformation is below room temperature and could thus not be measured in the internal friction experiment.

It is clear from Fig. 10 that C decreases damping; this is in accordance with the observation by Baik et al.\textsuperscript{30} The re-

| Table 4. (111) and (0002) interplanar spacing (nm) of FeMnSiCrNi(0.2% C). |
|--------------------------|--------------------------|--------------------------|
| $d_{111}$ (nm) | HR+AC | HR+AC+WQ | HR+AC+WQ+C |
| FeMnSiCrNi | 0.2075 | 0.2074 | 0.2070 |
| FeMnSiCrNi(0.2% C) | 0.2078 | 0.2074 | 0.2077 |

![Fig. 10. Internal friction of FeMnSiCrNi(0.2% C), deformed 15% (a) internal friction $Q^{-1}$ as a function of the temperature; (b) $\varepsilon$ modulus as a function of the temperature for the cooling cycle.](image)

![Fig. 11. Possible thermodynamic explanation of the internal friction measurement. $Q^{-1}$ theoretical (top), $Q^{-1}$ experimental (below).](image)
laxation peaks for the alloy with C appear at higher temperatures. It is well known that the \(M_s\) temperature is lowered by C; it is therefore very likely that the internal friction peaks are not due to the \(\gamma \rightarrow \varepsilon\) transformation. This also confirmed by the fact that the initial microstructure has no \(\varepsilon\) martensite because the \(M_s\) temperature is below room temperature.

The propagation of the \(\varepsilon/\gamma\) interface during the \(\gamma \leftrightarrow \varepsilon\) transformation is thermally activated. It is believed that the internal friction peaks are due to specific relaxation processes: the motion of a transformation interface. This transformation interface consists of Shockley partial dislocations trailing stacking faults. These partial dislocations move in to accommodate the transformation strains within the parent phase. Their back-motion results in the reversion to the parent austenite. The kinetics of this process were derived by using the kinetics for dislocation relaxation processes. It has to be stressed that this analysis still requires more experimental evidence of relaxation effects by measuring the frequency dependence at different temperatures. Dislocation-related relaxation processes can be represented by the Debye relaxation equation:

\[
Q^{-1} = \frac{\Delta \tau_0 \omega}{1 + (\tau_0 \omega)^2}
\]

where \(\omega = 2\pi f\) is the vibration frequency (rad/s), \(\Delta\) is the relaxation strength and \(\tau\) the kinetic parameter of the relaxation process. The activation energy \(\Delta H\) for the transformation process can then be obtained from the temperature-dependence of \(\tau\):

\[
\tau = \tau_0 \exp \left( \frac{\Delta H}{RT} \right)
\]

where \(\tau_0\) is the relaxation time at 0 K, \(R\) the gas constant (8.31 J/mol K) and \(T\) the absolute temperature in K. The kinetic parameter of the relaxation process, \(\tau\), can be calculated from the experimentally measured internal friction \(Q^{-1}(T)\) and the vibration frequency \(f(T)\) by the following equation:

\[
\tau(T, Q^{-1}) = \frac{1}{2\pi f(T)} \left\{ \frac{Q_{\text{max}}^{-1} \cdot T_{\text{max}}}{Q^{-1} \cdot T} + \left( \frac{Q_{\text{max}}^{-1} \cdot T_{\text{max}}}{Q^{-1} \cdot T} \right)^2 - 1 \right\}
\]

where \(Q^{-1}_{\text{max}}\) and \(T_{\text{max}}\) are the internal friction and the temperature at the peak. Hence, a plot of \(\ln(\tau)\) vs. \(1/T\) (Fig. 12) therefore results in a straight line and the relaxation parameters can be derived.\(^{25}\) Table 5 shows the results obtained for the relaxation peaks during heating and cooling for both alloys. The activation energy of the relaxation during cooling is higher than that of heating. The relaxation time is shorter when the activation energy is higher. From these results, it is clear that the addition of C results in a higher activation energy barrier for both transformations. C additions do not facilitate the transformation interface motion. This may be due to a higher lattice friction experienced by the transformation-related dislocations moving through a solution strengthened parent phase.

2.5. Shape Memory Evaluation

The recovery strain \(\varepsilon\) was calculated using Eq. 13:

\[
\varepsilon = \varepsilon_p \frac{\theta_0}{180 - \theta_e}
\]

where \(\varepsilon_p\) is the prestrain (= \(t/d\), thickness of the sample/diameter), \(\theta_0\) is the elastic spring-back angle after deformation and \(\theta_e\) is the remaining bending angle after the strain recovery annealing.

Table 5. The activation energy and the relaxation parameter for the relaxation processes in \(\text{FeMnSiCrNi}\) and \(\text{FeMnSiCrNi} + 0.2\%\text{C}\) during heating and cooling.
FeMnSiCrNi effect of training was not extensively examined in the case mostly reported to be in the range of 1 to 2.2% strain. The recovery strain for the Fe–Mn SMAs is indicated at higher strains such as 17%. The presence of dislocations will impede the back movement of the partials. In addition, the plastic deformation of the austenite will be initiated at interstitial sites or as carbides in the microstructure. The presence of dislocations in the parent phase prevents the free motion of the transformation interface.

The results of the bending test are given in Fig. 14. The recovery strain increased with increasing annealing temperature. Annealing at 50°C did not result in shape recovery. At 80°C, the recovery strain was limited. At 270°C the recovery strain was very large and reached its maximum. It is clear from the data that a higher prestrain reduces the shape recovery strain. If the deformation is small, the reverse movement of the Shockley partials is not impeded because only primary variants moved through the parent austenite under the influence of stress. When the strain is large, several variants will be activated and the intersection of variants will plate the back movement of the partials. In addition, the plastic deformation of the austenite will be initiated at higher strains such as 17%. The presence of dislocations in the parent phase prevents the free motion of the transformation interface.

The addition of C to the FeMnSiCrNi alloy lowers the recovery strain. The recovery strain for the Fe–Mn SMAs is mostly reported to be in the range of 1 to 2.2% strain. The effect of training was not extensively examined in the case of the present work. The FeMnSiCrNi + 0.2%C was tested in 3 training cycles consisting of a 3.4% deformation and a heating to 170°C. This heating temperature was too low since the recovery by heating to 170°C is incomplete (Fig. 14). During these cycles no improvement of the SME was observed. Cumulative strain during the training caused fracture during the 4th deformation cycle. It can be concluded that the addition of C results in a lower SME for a strain of 3.4%.

At first sight, this finding is contradictory with the fact that C addition has been reported to improve the shape memory behaviour. The effect of adding 0.3% C to a FeMnSiCrNi alloy was also studied by Gu et al. They reported an improvement the shape memory effect and the training effect. They compared the two following alloys: Fe–24.2%Mn–4.5%Si–2.1%Ni–1.2%Cr with Fe–17%Mn–4.5%Si–2%Ni–1.5%Cr–0.25%C. The alloy without C, with an Ms temperature of 302 K forms thermally induced martensite, while the alloy with C, with a lower Ms temperature 232 K, forms strain induced martensite, which resulted in a better shape memory effect. When looking for an explanation for this improvement, besides the effect of C, the absence of thermal martensite in one alloy must, however, also be taken into account. Moreover, it must also be stressed that both alloys have a different Mn content. In the present study only the effect of C is investigated, since the content of the other alloying elements was kept the same for both alloys. Similar remarks can be made for the work of Tsuzaki et al.,15) who compared two alloys with the same Ms temperature, but with different chemical composition of Mn. It is therefore not clear that the improvement they reported is due to effect of the C addition only.

The present work studies the effect of C on the shape memory behaviour of two FeMnCrNiSi SMAs, containing 0.05% C and 0.18% C, respectively. As already mentioned before, the influence of adding C depends on whether C exists at interstitial sites or as carbides in the microstructure that is deformed during the bending test. In-depth investigation of this microstructure showed, on the one hand, that, at the deformation temperature, i.e. room temperature, no thermal martensite was present, so deformation occurs, for both alloys, at a temperature above the Ms temperature. On the other hand, the absence of carbides in both alloys indicated that all C was present at interstitial sites. Consequently, precipitation hardening of the austenite, as described by Wen et al.,23) is not believed to influence the shape memory behaviour reported in the present work. In addition, the work of Bliznuk et al.22) would tend to suggest that differences in stacking fault energy do not explain the present observations.

The relative position of the deformation temperature with respect to the Ms temperature is also reported to be one of the key factors. For a deformation temperature that is much higher than the Ms, the austenite is too stable to obtain an easy martensitic transformation. When deformation occurs below Ms, there is some thermal martensite present in the matrix at the deformation temperature. This diminishes the amount of austenite and consequently also the amount of stress induced martensite. The result is a small SME. Therefore, the largest SME is obtained when the deformation occurs slightly above Ms.

Most probably, the less favorable SME observed when C is added, can be attributed to the relative position of the deformation temperature with respect to the martensite start temperature for this alloy. It is known that the addition of C lowers the Ms temperature and consequently also the Ms and Mf temperatures. For the alloy with 0.05% C, deformation will therefore occur closer to the Ms temperature, and the austenite will be less stable and more martensite will be formed. For the alloy with 0.18% C, the austenite is far more stable, because of the effect of the lower Mf temperature. Consequently, a greater part of the deformation energy will cause the austenite to slip instead of causing the
austenite to transform. Moreover, microstructural characterization showed a lower amount of formed ε martensite during deformation for the high C alloy. The solid solution strengthening by C appears not to be able to compensate for the lower \( M_\text{f} \) temperature. This is similar to what Wen et al.\textsuperscript{23} observed for their non-aged samples. A possible solution for the deterioration of the SME in the high C alloy might be lying in changing the amount of the other alloying elements in order to bring the \( M_\text{f} \) temperature of this alloy closer to the deformation temperature.

3. Conclusions

The main conclusions of the present study on the effect of C-additions on the shape memory effect in FeMnCrNiSi alloys are:

1. The initial microstructure of both alloys shows thin lines which are not identified as ε martensite. The alloy with C also contains ferrite.

2. After deformation, thin plate ε martensite, visible as broader lines in light optical microscopy and TEM, is formed in both C-free and C-alloyed SMAs. The presence of ε martensite was also observed by XRD. TEM analysis revealed the existence of \( \alpha \)’ martensite at intersections of two variants of ε martensite.

3. The addition of C to the FeMnSiCrNi alloy results in increased tensile strength, lower strain hardening and lower amount of ε martensite formed during deformation. It was shown that this is related to the fact that the alloy without C has a lower activation energy for transformations than the alloy with 0.2% C. This clearly suggests that C additions do not facilitate the transformation interface motion.

4. Bending tests show that the addition of C to the FeMnSiCrNi alloy lowers the recovery strain for a small deformation strain. Large strains deteriorate the shape memory effect. The detrimental effect of C on the shape memory behaviour of the two alloys is believed to be due mainly to the effect of C on the \( M_\text{f} \) temperature.

Acknowledgements

This work was supported by the grant of BOF (contract number 01108303). The authors also gratefully acknowledge the expert technical assistance of E. De Temmerman.

REFERENCES