1. Introduction

The shape memory properties of the Fe–Mn–Si-based alloy system are well documented.1–3) The parent phase in these alloys is face centred cubic (FCC) austenite, and deformation produces a hexagonal (HCP) martensite known as ε. The transformation from FCC to HCP occurs by the formation and overlap of stacking faults.1) The stress-induced ε can be reversed to the parent phase by heating, and this imparts the shape memory effect (SME).

To maximise the reversible strain, ε martensite should form in preference to slip in response to applied stress. Therefore, material parameters that promote ε formation are likely to enhance the SME. Because ε forms by the proliferation of stacking faults, it has been suggested9) that lowering the stacking fault energy (SFE) promotes the formation of ε martensite. For this reason, it is expected that alloying additions that reduce the SFE of Fe–Mn–Si-based alloys will enhance the shape recovery through increased ε formation. Another property of the austenite that is known to affect ε formation is the Neél temperature (\(T_N\)).2,4–6) The \(T_N\) is the transition temperature between the higher temperature paramagnetic and the lower temperature antiferromagnetic states of the austenite. Antiferromagnetism is claimed to stabilise the austenite through ordering, hindering the formation of martensite, thereby reducing the SME.4,5) It is generally considered that the \(T_N\) must be below the \(M_s\) for optimum shape recovery.

Both the SFE and the Neél temperature can be manipulated through alloying, and there are a number of works that investigate the effect of substitutional alloying of elements such as Ni and Cr on the SME e.g. Refs. 4) and 7). However, the effect of carbon and nitrogen on SME has received less attention. These two interstitials have similar austenite stabilizing properties, and are both powerful austenite strengtheners. The effects of C and N on this alloy system have usually been studied with respect to their austenite strengthening capabilities9–14) and as yet there has not been an integrated investigation that considers the effects of SFE, \(T_N\) and composition on the SME. Moreover, of the available literature, there is no consensus as to whether interstitial elements have a beneficial or detrimental effect on SME. It is a major aim of this paper to investigate the effect of interstitial elements on SME in the Fe–Mn–Si-based system, taking into consideration the impact of \(T_N\) and SFE on the measured shape recovery.

In addition to interstitial alloying, alloys have also been produced in which 5% of the Mn content has been replaced by either Cr or Ni. These additions alter both SFE and \(T_N\), and provide benchmark alloys with which to compare the nitrogen- and carbon-containing alloys.

2. Method

The composition of the alloys investigated in this paper are detailed in Table 1. These alloys were prepared by arc-melting in 30–50 g buttons under an argon atmosphere. The alloys were made using high purity base components of Fe, Mn, Si, Cr and Ni. The carbon was added using a pre-prepared, high carbon content, Fe–Mn alloy. The nitrogen was added using high purity silicon nitride powder. Since the addition of carbon significantly depresses the \(A_s\) and \(M_s\) temperatures, Mn was reduced by an appropriate amount to maintain approximately the same transformation temperatures for each sample.

The arc-melted buttons were hot rolled at 1 000°C from a thickness of 6 to 1.5 mm in 6 passes. For X-ray diffraction and shape memory testing, sections from the hot rolled
strip with approximate dimensions of 20 × 15 mm were annealed at 1000°C for 1 h followed by a cold water quench. The shape memory of each alloy was also tested after annealing of the hot rolled strip at 600°C for 30 min.

The shape memory effect (SME) was measured at room temperature using the bend test technique. The strain of the sample at the outer edge of the bend radius is determined by the equation:

\[ \varepsilon = \frac{1}{(2R/h)+1} \] ..............................(1)

where \( \varepsilon \) = conventional strain

\( R \) = bend radius

\( h \) = sample thickness.

To produce a range of pre-strains, samples with a thickness of between 0.5 mm and 0.9 mm were bent around rods of different sized radii. The bent samples were photographed and then recovery annealed at 500°C for 15 min for shape recovery. After recovery annealing the residual strain (\( \varepsilon_r \)) remaining due to incomplete recovery was calculated using Eq. (1). The percentage recovery was determined by the equation:

\[ \% \text{ recovery} = (\varepsilon - \varepsilon_r) / \varepsilon \] ..............................(2)

The transformation temperatures were measured using a TA Q100 differential scanning calorimeter (DSC) equipped with a refrigerative cooling system. The transformation behaviour of each of the samples was measured in the as-quenched condition after annealing at 1000°C before testing in the DSC. The samples were immersed in liquid nitrogen to form thermal martensite, and then heated in the DSC to measure the reversion of martensite to austenite. The samples were then cooled to determine the Ms. The transformation temperatures for each alloy are shown in Table 2. The Neél temperature (\( T_N \)) was measured using a Quantum Design MPMS SQUID dc magnetometer at a cooling rate of 1.2°C/min, and these results are also shown in Table 2.

Transmission electron microscopy (TEM) was carried out at 200 kV using a JEOL JEM 2011 TEM equipped with a JEOL EDS composition analysis system. TEM samples were prepared with a Struers Tenupol jet-polisher using a solution of 5% perchloric acid in acetic acid at room temperature and a voltage of 30 V. A number of the TEM foils retained some electro-polishing residue, and this was removed using a Gatan plasma ion polishing system.

For X-ray diffraction (XRD), the oxide layer was mechanically removed by grinding, and then the deformed layer chemically removed using a solution of 15 mL \( \text{H}_2\text{O}_2 \) + 1 mL HF + 1 g \( \text{C}_{2}\text{H}_2\text{O}_4 \) for approximately 5 min. The X-ray radiation used was Cu K\( \alpha \), and the scan rate used was 0.2°/min. The peaks were analysed using Jade 5.0 software.

The Fe–Mn–Si-based alloy system has low stacking fault energy\(^{15}\) but it is difficult to measure this quantity accurately. Instead, the stacking fault energy was estimated by determining the stacking fault probability (SFP). The SFP was measured using the X-ray peak shift method, and this technique has been described in detail elsewhere.\(^{16}\) Briefly, the measurement is based on the shift of X-ray diffraction peaks that results from the presence of stacking faults in the microstructure. Stacking faults shift the \( \{111\} \) peak to larger \( 2\theta \) values, while the \( \{200\} \) peak moves to smaller values. The differential in \( 2\theta \) is used in conjunction with Bragg’s law to estimate the stacking fault probability.

For optical microscopy samples were polished to a 1 \( \mu \text{m} \) diamond finish, followed by 10 min polishing with colloidal silica (Struers OPS). Samples were then etched in either acid ferric chloride, or electrolytically etched in a solution of 10% oxalic acid and water at 4 volts for 60–90 s. This electro-etching procedure etches the austenite grain boundaries but was not successful on the Ni and Cr containing alloys.

3. Results

3.1. Microstructure

The microstructure of the alloys in the as-quenched condition were examined using optical microscopy. A typical example is shown in Fig. 1. The austenite grain size of the samples after austenitizing at 1000°C was \( \sim 15 \mu\text{m} \).

TEM was used to examine the microstructure of the alloys in the austenitized condition. This analysis confirmed

### Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Fe</th>
<th>Mn</th>
<th>Si</th>
<th>C</th>
<th>N</th>
<th>Cr</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>66.8</td>
<td>27.5</td>
<td>5.0</td>
<td>0.09</td>
<td>0.038</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C3</td>
<td>74.4</td>
<td>19.8</td>
<td>5.5</td>
<td>0.28</td>
<td>0.021</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C5</td>
<td>76.7</td>
<td>16.9</td>
<td>5.9</td>
<td>0.52</td>
<td>0.027</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>68.5</td>
<td>26.0</td>
<td>5.4</td>
<td>0.02</td>
<td>0.093</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5Mn</td>
<td>60.3</td>
<td>33.7</td>
<td>6.0</td>
<td>0.01</td>
<td>0.034</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5Ni</td>
<td>59.5</td>
<td>28.4</td>
<td>6.0</td>
<td>0.01</td>
<td>0.026</td>
<td>-</td>
<td>6.10</td>
</tr>
<tr>
<td>5Cr</td>
<td>59.5</td>
<td>29.9</td>
<td>6.0</td>
<td>0.01</td>
<td>0.038</td>
<td>4.6</td>
<td>-</td>
</tr>
</tbody>
</table>

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that the carbon-containing alloys were fully solution treated, and did not contain carbide particles at the grain boundaries or within grains.

3.2. Stacking Fault Probability

The X-ray peak shift method\(^{16}\) was used to measured the SFP of each sample. This measurement is closer to a measurement of the stacking fault density, rather than a measurement of the intrinsic stacking fault energy of the material. For a given alloy SFP is sensitive to the prior thermo-mechanical history, and as a consequence each sample must be prepared identically for the measurements to be comparable.

For the measurements made here the heat treatments were carried out in one batch to ensure each sample was subjected to an identical thermal history. The samples were then ground and polished, and the deformed layer removed chemically before XRD measurement. Typical examples of \{111\} and \{200\} peaks are shown in Fig. 2.

The SFP was examined in two conditions. Firstly, the SFP was measured on samples that were austenitized for 1 h followed by immediate cold water quenching. These results are labelled in Table 3 as SFP 1. These same samples were then re-annealed at 600°C for 1 h to relieve any quenched-in stresses, and the SFP measured again after removal of the outer oxidised layer. These have been labelled SFP 2 in Table 3.

For the substitutionally alloyed samples quenched from 1000°C (SFP 1), sample 5Cr had the highest SFP, with the value being lower for 5Ni and 5Mn. Recalling that SFP is expected to be inversely related to SFE, these results suggest that the high Mn alloy has the highest SFE of these three samples. Jiang et al.\(^{17}\) have also reported that increasing the Mn content in the range 26–32 wt% decreases the SFP, i.e., raises the SFE.

For the interstitially alloyed samples, the nitrogen-containing sample N1 had the lowest SFP, and C1 had the highest. C3 and C5 were similar. Further, the addition of C and N generally resulted in lower values of SFP than the substitutional alloys.

Annealing at 600°C did not have the same effect on the SFP of all alloys. The interstitially alloyed samples exhibited an increase in SFP after annealing, while the substitutionally alloyed samples showed a decrease in SFP. The change in SFP was moderate in all of the alloys except for 5Cr which showed a marked decrease in SFP after annealing at 600°C.

3.3. Shape Memory Behaviour

The shape memory behaviour of each of the alloys was measured in two conditions: after annealing at 1000°C for 1 h (Fig. 3); and after annealing of the hot rolled strip at 600°C for 30 min (Fig. 4). From Fig. 3 it is clear that carbon in solution has a detrimental effect on SME. It is also evident that of the substitutional alloying additions, Mn has the best effect on SME, followed by Ni, with Cr addition showing the lowest SME.

The SME of the samples after annealing of the hot rolled samples at 600°C is shown in Fig. 4. Annealing at 600°C for 30 min clearly effects a substantial improvement in SME for both the interstitially and substitutionally alloyed
samples. In this condition, sample C5 was too brittle to test for shape memory, and fractured above a strain of approximately 1%. Sample 5Cr was also brittle in this condition, and fractured above a strain of 2.5%. After annealing at 600°C, samples C1 and N1 exhibited very similar shape memories, as did 5Ni and 5Mn. The main outlier of the alloys was C3 which exhibited much lower SME than all the other alloys.

4. Discussion

4.1. Stacking Fault Probability and Shape Memory

Two SFP measurements were made. The first measurement, SFP 1, was made after each alloy was given an identical treatment of annealing at 1000°C for 1 h followed by water quenching. This is the same treatment given to alloys before the shape memory testing shown in Fig. 3 and Fig. 5(a). The SFP measurements were then repeated (SFP 2) after the samples were given an additional stress relieving heat treatment at 600°C for 1 h. There was only one sample in which this stress relieving treatment had a significant effect. Alloy 5Cr has a significantly lower SFP2 compared to SFP1. This dramatic change is likely to be the result of precipitation during the heat treatment, and this is further discussed in Sec. 4.2.

The measured SFP values for each sample are given in Table 3. Measurement of SFP on similar alloys has been carried out by Jiang et al.\textsuperscript{17) Jiang et al.\textsuperscript{17)} also used X-ray diffraction to estimate the SFP, but adopted a peak broadening method, rather than the peak shift method used here. As a consequence, the measured values from Jiang et al. were consistently smaller than the values obtained in this study.

The values obtained by Jiang et al.\textsuperscript{17)} are qualitatively consistent with the current result that increasing the Mn content decreases the SFP.

The peak shift method has been used to measure SFP in Fe–Mn–Si by Rong et al.\textsuperscript{16)} In that study too the SFP values were slightly lower than those measured here, being in the range of 2 to 7 (\(\times 10^{-3}\)). This difference is likely to be the result of the thermal history of the samples. Both methods\textsuperscript{16,17)} have been shown to be sensitive to the prior deformation and/or quench temperature that the samples have been subjected to, since these parameters affect the stacking fault density. It is likely that the elevated SFP measurements made here are due to the effects of quenching stresses that increase the SFP. For this reason care was taken to batch anneal the samples together to ensure that, at least within this group of samples, the SFP measurements are comparable.

The shape memory for each alloy after annealing at 1000°C and quenching is shown in Fig. 3. From these results, a line of best fit was used to estimate the shape recovery at a pre-strain of 4% for each alloy. These values for shape recovery are shown in Fig. 5 as a function of SFP. Both SFP values of SFP 1 and SFP 2 are shown in the figure. It is clear from Fig. 5 that there is no direct correlation between SFP and shape memory.

Of the 5 alloys used to examine the effect of C and N addition on SME (5Mn, C1, C3, C5, and N1) no clear trend was established between SFP and shape memory (Fig. 5). If samples C1 and N1 are compared, the SFP of the nitrogen-containing sample was significantly lower than C1. This is consistent with reports\textsuperscript{18)} that N increases SFE, and C decreases SFE for concentrations of approximately 0.1 wt%. Despite having significantly different values for SFP, samples C1 and N1 showed very similar SME (Figs. 3(a) and 4(a)).

No clear correlation was found in the current work between SFP and shape memory. There has been only a small
number of experimental investigations that measure the SFP in these alloys. Indeed, the current work appears to be the only study that systematically examines the SFP and shape memory for a range of alloy compositions. Jiang et al. measured the SFP of five Fe–Mn–Si-based alloys, and correlated SFP to composition, $M_s$, and strain hardening. However, this study only reported the shape memory of two of the five alloys examined, and therefore did not conclusively show that SFP directly affected the shape memory.

It is not disputed that the stacking fault energy plays an important role in promoting the formation of $\varepsilon$ martensite. Alloys with a higher SFE resulting from lower Mn concentrations have a propensity to form $\alpha'$ martensite instead of hexagonal $\varepsilon$, and these alloys do not exhibit good shape recovery. It is clearly important to have a low SFE to promote $\varepsilon$ martensite formation. However, it is possible that if an alloy is below the critical SFE for $\varepsilon$ martensite formation, further reduction in the SFE through alloying (such as replacing Mn with Cr) will not increase the shape recovery.

4.2. Shape Memory and Annealing Temperature

The best shape memory for these Fe–Mn–Si-based alloys is not obtained by fully recrystallizing the microstructure before testing. The best SME results are obtained by optimizing the thermo-mechanical treatments. For a wide range of alloys, it has been found that after hot rolling at 1000°C, a recovery anneal at 600°C for 30 min will give high shape recovery during subsequent bend testing. For this reason, after hot rolling, a sample of each of the alloys was annealed at 600°C and then tested for shape recovery, Fig. 4(b). Bend testing demonstrated that two of the alloys, 5Cr and C5, were too brittle to be tested. During annealing at 600°C, precipitation occurred in these samples at the grain boundaries (Fig. 6), resulting in embrittlement.

The measured shape memory in samples that were hot rolled followed by recovery annealing at 600°C is shown in Fig. 4. As can be seen the shape recoveries are basically the same for all samples except for one outlier. This one sample was alloy C3, which showed poor shape recovery compared to the other alloys. With a relatively high carbon content (0.3%) it is possible that carbide precipitates could form during hot rolling and annealing in this sample. However, TEM showed that there were no carbides formed. It is known that Si inhibits carbide formation, and the high Si content in these steels is probably the reason that carbide formation is inhibited during thermo-mechanical processing. It is likely that the lower SME in this sample is the result of higher carbon content, the carbon can segregate to the stacking faults and phase boundaries and inhibit their mobility and reversibility.

4.3. Effect of Interstitials on Shape Memory and SFP

The effect of carbon content on the measured SFP is shown in Fig. 7. It can be seen that the SME initially rises with increasing carbon content, and then after $\sim 0.1$ wt% carbon the SFP drops again. This is qualitatively consistent with previous work that has shown that carbon addition increases the SFP (decreases stacking fault energy) initially, the SFP reaches a maximum, and then drops again with increasing carbon concentration. However, the maximum SFP found here is approximately 0.1 wt%, whereas previous work on Fe–Mn–C has shown the point of inflection in that case to be closer to $\sim 0.4$ wt%.

Although there was no clear trend between SFP and shape memory, these experiments did show that the addition of interstitial elements was detrimental to shape memory when tested after annealing at 1000°C for 1 h. In Fig. 8, the SME after a pre-strain of 4% is shown as a function of total interstitial content (weight percentage nitrogen + weight percent carbon). This shows clearly that interstitial elements in solution are detrimental to shape memory. This result is at odds with a number of other reports from literature. For example, Tsuzaki et al. examined similar alloys to the ones studied here, and concluded that carbon addition improved SME. However, like many other reports, the $M_s$ of the alloys examined were quite different. In the case of Tsuzaki et al. the $M_s$ of the carbon-bearing alloy was well above room temperature, 50°C, resulting in one alloy
being tested with some thermal martensite already present in the microstructure. For this reason, the results do not conclusively show what effect carbon has on the shape memory. Dai\textsuperscript{21} investigated a 0.3% C alloy and compared it to a carbon-free equivalent. In that study the transformation temperatures were not reported, so the influence of these temperatures on shape recovery cannot be assessed. More importantly, Dai quenched the alloys from different temperatures, thus rendering the shape memory tests inconclusive. The thermal history of the alloys must be identical for valid comparisons to be made.

Wen et al.\textsuperscript{10,11} published 2 papers in 2004 after a solutionizing treatment (1 100°C) and immediate water quenching. They reported the same results as found here, that carbon in solution decreases the shape memory. However, these alloys show markedly different $M_s$ temperatures (< −85°C and 31°C). Ariapour et al.\textsuperscript{13,14} have shown that 0.26 wt% nitrogen in solution can markedly decrease the SME compared to a reference alloy with a much lower interstitial content. This is consistent with Fig. 8, where it can be seen that an interstitial content of 0.3% shows markedly decreased shape recovery compared to lower contents of ~0.01%. The inconsistent literature reports seem to be the result of comparing alloys with either dramatically different $M_s$ temperatures or different thermo-mechanical histories. When these two factors are kept the same, the results seem to be consistent with the current conclusion that interstitial carbon and nitrogen decrease shape memory when in solution. This too could explain further the improved shape memory properties found in alloys that contain NbC,\textsuperscript{21} the Nb addition ensures that the C and N are substantially removed from the parent phase during precipitation heat treatment.

Although Fig. 8 shows a clear correlation between interstitial content and shape memory, this trend is not repeated in alloys that have been thermo-mechanically processed for optimum SME. Figure 4 shows that samples that have been hot rolled and then recovery annealed at 600°C generally show much improved shape memory compared to the solution treated cases. These results suggest that the Fe–Mn–Si-based system can tolerate up to 0.1 wt% interstitial content without compromising the shape memory, provided that the alloy has been given an appropriate thermo-mechanical treatment.

4.4. Neél Temperature

The apparent absence of a relationship between the SFP and shape memory could be the result of Neél temperature differences between the alloys investigated. The Neél temperature has been reported to have a significant effect on $\varepsilon$ formation.\textsuperscript{5,6} Above the Neél temperature, in the paramagnetic condition, the austenite is reported to be unstable and is presumed to produce more stress-induced martensite—supposedly leading to better shape memory. To eliminate this magnetic transition as a potential cause of the anomalous relationship between SFP and SME, the Neél temperatures of each alloy were measured, and are shown in Table 2.

According to Murakami et al.,\textsuperscript{4} alloys should have a Neél temperature below the $M_s$, ensuring that the deformation is carried out in the paramagnetic condition. If some of the samples here were deformed below their Neél temperature, in the antiferromagnetic condition, then their shape recoveries could be lowered as a result. The only alloy that was deformed below its Neél temperature was 5Mn. If this had a detrimental effect on the shape recovery of this sample, then the measured SME would be anomalously low. However, this sample did in fact have the highest SME of all the samples tested. It is not inferred that testing below the Neél temperature has a positive effect on SME, but that the magnetic transition probably exerts only a small effect on the SME. Research into the effect of $T_N$ on martensite formation is usually based on thermally induced $\varepsilon$.\textsuperscript{5,6} Although it has been shown that the antiferromagnetic transition can significantly inhibit the formation of thermal martensite, Yang et al.\textsuperscript{22} have clearly shown that it does not significantly inhibit stress-induced martensite formation. For this reason, it is concluded that the differences in Neél temperature between the samples is not responsible for their different shape recoveries, nor is it likely to significantly mask any other relationship such as the effect of SFP or composition on SME examined in this work.

5. Conclusions

A range of Fe–Mn–Si-based alloys has been examined to investigate the effects of stacking fault probability and composition on shape memory. The conclusions are as follows.

1. Substitution of Ni and Cr for Mn increased the stacking fault probability (decreased the stacking fault energy), but was associated with a decrease in the shape memory in samples quenched from 1 000°C.

2. No correlation was found between shape memory and stacking fault probability in either the austenitized condition or in the hot-rolled and recovery annealed condition.

3. The SME decreased with increasing C and/or N content after solution treatment.

4. For those alloys that could be tested for shape memory in the hot rolled and recovery annealed condition, there was only a marginal difference between the SMEs of the different alloys. This was with the exception of one alloy, alloy C3, which showed much reduced SME compared to the others. Samples containing high C (0.5 wt%) and Cr be-
came too brittle to test for shape memory after hot rolling and recovery annealing.

(5) It is concluded that SFE and $T_N$ have only marginal effects on shape memory in this alloy system.

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