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"Some Features of $\gamma-\varepsilon$ Martensitic Transformation and Shape Memory Effect in Fe-Mn-Si Based alloys"

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Abstract. In the present paper several important aspects concerning the shape memory behavior of the $\varepsilon$-martensite in the cost-saving Fe-Mn-Si-based alloys and its application are reported. Some kinetic features of the $\gamma-\varepsilon$ martensitic transformation are discussed. The effects of the composition, volume change induced by the transformation, strength of austenite, temperature of pre-strain on the shape memory effect have been investigated.

1. INTRODUCTION

A study of the shape memory effect (SME) in Fe-Mn-Si alloys has been the subject of a number of works [1-5]. It has been found that the good SME can occur in polycrystalline Fe-Mn-Si shape memory alloys (SMA) with 28-33% Mn and 4-6% Si [2-4]. These SMA can contain some additions of Cr, Ni, Co [4-5] too. In contrast to other SMA, such as Ni-Ti and Cu-Al-Ni, the $\gamma-\varepsilon$ martensitic transformation observed in Fe-Mn-Si alloys is not thermoelastic and the SME for these alloys results only from the reverse transformation of the stress-induced $\varepsilon$-martensite. It has been shown [1-5] that the SMA in these alloys is defined by several factors due to Si additions to binary Fe-Mn alloys. However some important features of the $\gamma-\varepsilon$ martensitic transformation and the SME in Fe-Mn-Si-based alloys are not well clarified. Among this features we distinguished and studied the following problems: a) the effect of the magnetic state of austenite on the $\gamma-\varepsilon$ martensitic transformation, b) the influence of the composition on the volume change associated with the $\gamma-\varepsilon$ transformation, change in length and recovered stress of the pre-straining specimens upon heating.

2. EXPERIMENTAL PROCEDURES

The alloys were melted in a vacuum induction furnace. The chemical compositions of alloys were in the range of 20 to 36% Mn, 0 to 6.5% Si, 0 to 8% Cr, 0 to 5% Ni, 0.02 to 0.3% C, 0 to 0.2% V, 0 to 0 to 0.2% N in weight percent. Ingots were annealed at 1273K, forged and rolled to sheets of 1-3 mm thickness. Specimens were solution treated at 1273K for 3.6 ks. and water quenched. Mechanical tests were carried out on an Instron type testing machine at various temperatures between 77K and 573K. The microstructure was investigated by light and electron microscopy. An X-ray diffractometer was used to determine the volume change due to the $\gamma-\varepsilon$ transformation $V_\gamma - V_\varepsilon$ / $V_\varepsilon$ = $\Delta V/V$ and the phase contents. The transformation temperatures, the Néel temperature ($T_N$) and the change in length of the pre-straining specimens upon heating were...
measured by a dilatometer. For measuring the degree of the shape recovery (the SME), sheet specimens with a thickness of 1 mm were bent at at 293K (the maximum strain of specimens was 5%) and heated up to 573K (above $A_f$). The SME was determined by measuring the change in the bend angle of the deformed specimens before and after heating.

3. RESULTS AND DISCUSSION

3.1. Some kinetic features of the $\gamma$- $\varepsilon$ martensitic transformation upon cooling in Fe-Mn and Fe-Mn-Si alloys.

According to the data of majority authors, the $M_s$ temperature of Fe-Mn alloys decreases with increasing Mn content and especially sharply below the room temperature (Fig.1a, dotted line).

![Fig.1. Effect of Mn(a) and Si(b) contents on the $M_s$ and $T_N$ temperatures in alloys: Fe-Mn (a, left), Fe-Mn-3Si (a, right), Fe-28Mn-Si (b, left), Fe-30Mn-Si (b, right).](image)

However, taking into consideration some data [6-8] and the dependence $T_N(\%Mn)$ for Fe-Mn alloys (Fig.1a), it is possible to suppose, that the $\gamma$- $\varepsilon$ martensitic transformation upon cooling occurs only in the paramagnetic austenite and the meeting point of the curves $M_s(\%Mn)$ and $T_N(\%Mn)$ is peculiar for Fe-Mn alloys (we marked it C*), as with $C_{Mn}>C^*$ the martensitic transformation upon cooling in the antiferromagnetic austenite does not occur. Therefore, in Fe-Mn alloys with $C_{Mn}>C^*$, the $M_s$ temperature does not drop sharply as was assumed earlier, but closes in a jump. The stabilization of austenite with $C_{Mn}>C^*$ can be explained by the following factors[8]. First, the Gibbs free energy of austenite decreases, but the stacking fault energy and strength of austenite increase due to the magnetic ordering. Second, there is an Invar effect in the antiferromagnetic austenite (Fig.2a), including the fact that at $T<T_N$ the linear expansion of specimens changes more slowly with decreasing temperature than in the paramagnetic state as the result of which the volume effect $(\Delta V/V)$ of the $\gamma$- $\varepsilon$ martensitic transformation increases. It should be noted that for the $\gamma$- $\alpha$ martensitic transformation in Fe-based SMA (Fe-Pt, Fe-Ni-Ti-Co, etc) the situation is contrary. As the volume change of the $\gamma$- $\alpha$ transformation has the another sign (positive), a position of the magnetic ordering temperature (the Curie temperature) must be some above the $M_s$ temperature for decreasing of the $\Delta V/V$. 
With additions of Si to Fe-Mn alloys there is practically no change in the $M_S$ temperature, but $T_N$ decreases (Fig.1a, right) and the meeting point $C'$ is shifted in the direction of lower temperature and higher Mn concentration. The influence of Mn and Si contents on the $M_S$ and $T_N$ temperatures in Fe-Mn-Si alloys is shown in Fig.1b.

![Diagram showing changes in $M_S$, $T_N$, and $C'$](image)

Fig.2. Volume changes due to the $\gamma$- $\varepsilon$ (a) and $\gamma$- $\alpha$ (b) martensitic transformation, schematic.

It should be noted, that apparently the additional barrier due to the magnetic ordering is insignificant and can be get over by a small deformation forming the stress-induced $\varepsilon$-martensite. It is important to note also that for Fe-Mn-Si alloys with the optimum Mn content (30%) and various Si contents, the thermal-induced $\varepsilon$-martensite which reduces the SME, either does not form at all ($T_N > M_S$) or forms below 293K. In this case the pre-strain usually applied at 293K leads to the formation only of the stress-induced $\varepsilon$-martensite.

3.2. Volume change due to the $\gamma$- $\varepsilon$ martensitic transformation

Fig.3 shows the composition dependence of the volume changes associated with the $\gamma$- $\varepsilon$ transformation. It is important to note that the additions of Si to Fe-Mn alloys lead to significant decreasing of $\Delta V/V$.

![Diagram showing the effect of Si content on $\Delta V/V$ and SME](image)

Fig.3. Effect of Si content on the $\gamma$- $\varepsilon$ transformation in Fe-30Mn-Si alloy.

Fig.4. Effect of the pre-straining temperature on the SME in Fe-30Mn alloy (dotted line) and Fe-20Mn-8Cr-5Ni-5.5Si (solid line). Arrows indicate positions of $M_S$.

The low value of $\Delta V/V$ is a typical feature of the SME as this leads to decreasing of the normal component of the shape strain and to increasing of a coherency of the $\gamma/\varepsilon$ interface and its mobility.
3.3 Effect of the pre-straining temperature on the SME.

The results of measurements of the SME of the specimens of the Fe-30Mn-5.5Si and Fe-20Ni-8Cr-5Ni-5.5Si alloys after pre-straining at temperatures between 77K and 393K are presented in Fig.4. The positions of the $M_s$ temperatures in this alloys are also shown. It can be seen that the curves have a maximum correlated with the position of $M_s$ for both alloys. The results shown in Fig.4 can be explained that the plastic deformation of these alloys near $M_s$ is affected exclusively on account of the formation of a single-variant of stress-induced $\varepsilon$-martensite (reversible type of deformation), that leads to the good SME. The TEM investigation confirmed this supposition and showed also that when the pre-straining temperature is lower than $M_s$, the decrease in the SME is determined by the formation of the many-variant $\varepsilon$-martensite formed upon cooling. When the pre-straining temperature is much higher than $M_s$, $\varepsilon$-martensite forms after the plastic deformation of austenite by slip and twinning (irreversible type of deformation) and the SMA decreases too.

3.4. Influence of alloying elements and testing temperature on mechanical properties.

The effect of Si and other elements on the mechanical properties of Fe-Mn alloys are shown in Tabl.1. The yield stress and tensile strength of the Fe-30Mn-5.5Si alloy after testing at 573K (above $M_d$ and $A_f$, when the stress and strain-induced martensites do not form) are higher then ones for the Fe-30Mn alloy. Strengthening of austenite in the Fe-30Mn-5.5Si alloys is assisted by the solid-solution hardening due to the small size of Si atoms and features of the interaction between Si, Mn and Fe atoms [3]. These influence of Si on the strength of austenite leads to the suppression of slip and twinning and make easier the formation of the stress-induced $\varepsilon$-martensite. The structural investigation showed that the Fe-50Mn alloy begins to deform by slip (at 573K and 293K) or by slip and twinning (at 77K), while the Fe-30Mn-5.5Si alloy begins to deform by slip and twinning at 573K and by stress-in-

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Deformation temperature,K</th>
<th>Yield stress,MPa</th>
<th>Tensile strength,MPa</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-30Mn</td>
<td>573 ($&gt;M_d$)</td>
<td>110</td>
<td>420</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>293 ($&gt;M_d$)</td>
<td>180</td>
<td>600</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td>77 ($&lt;M_d$)</td>
<td>400</td>
<td>800</td>
<td>25</td>
</tr>
<tr>
<td>Fe-30Mn-5.5Si</td>
<td>573 ($&gt;M_d$)</td>
<td>200</td>
<td>620</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>293 ($&lt;M_d$)</td>
<td>350</td>
<td>920</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>77 ($&lt;M_d$)</td>
<td>550</td>
<td>1250</td>
<td>25</td>
</tr>
<tr>
<td>Fe-20Mn-8Cr-5Ni-5Si</td>
<td>293 ($&lt;M_d$)</td>
<td>325</td>
<td>780</td>
<td>45</td>
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<tr>
<td></td>
<td>77 ($&lt;M_d$)</td>
<td>480</td>
<td>1170</td>
<td>42</td>
</tr>
<tr>
<td>Fe-28Mn-5.5Si-0.17V-0.11C</td>
<td>293 ($&lt;M_d$)</td>
<td>450</td>
<td>1050</td>
<td>35</td>
</tr>
</tbody>
</table>
duced γ-ε martensitic transformation at 293K and 77K. As shown in Table 1, effect of Ni and Cr contents on the mechanical properties is small, but V and C (or W) additions can increase the strength of austenite and improve the SME.

3.5 Effect of temperature and Si content on the change in length and recovered stress of pre-strain specimens.

Specimens of the Fe-30Mn and Fe-30Mn-Si alloys were pre-strained (compressed) by 3% at 293K. After that, several specimens were unloaded and heated in a dilatometer to 573K, and several specimens were heated to 573K in the fixed (loaded) state in a testing machine. The effect of the Si content and temperature on the change in length of unloaded specimens and on the recovered stress of fixed specimens are shown on Fig.5 and Fig.6. The curves on these figures have some similarities.

\[ \Delta L/L, 10^{-4} \]

\[ \sigma, \text{MPa} \]

Fig.5. Effect of Si content and temperature on the length change of specimens of Fe-30Mn-Si alloys deformed by 3% at 293K.

Fig.6. Effect of Si content and temperature on the recovered stress of specimens of Fe-30Mn-Si alloys deformed by 3% at 293K.

For the Fe-30Mn alloy the length change of the deformed specimen equal only its thermal expansion, but for the Fe-30Mn-Si alloys the length change of the deformed specimens equals their thermal expansion plus length change due to the reverse γ-ε transformation (this change is smaller than 40 \( 10^{-4} \)) plus change due to the shape recovery (the SME), which starts at \( A_S \) and increases with increasing Si content up to 6%Si. At more higher Si content the formation of silicides leads to the decrease in the SME. As shown in Fig.6, the recovered stress does not arise in the Fe-30Mn alloy, but arises in the Fe-30Mn-Si alloys at \( A_S \), increases with increasing Si content and some decreases upon cooling (relaxation of stress). It should be noted that the effect of Mn content on the change in length, recovered stress, strength of austenite and volume effect of the γ-ε transformation in the Fe-Mn-Si alloys is much smaller than the effect of Si content [3].

3.6. Application of Fe-Mn-Si SMA for practical engineering.

As the shape recovery in Fe-Mn-Si alloys is accompanied with the appearance of the recovered stress, it can be used for pipe couplings. The muffs of the Fe-30Mn-5.5Si alloy was machined from a hot-forging rod to have an inner diameter somewhat smaller than the diameter of the tubes to be joined, annealed at 1273K, quenched to 293K and mechanically expanded in the austenitic state by the piercer to an inner diameter somewhat larger than the diameter of the tubes. The expanded
muff was put on the ends of tubes and then was heated to 525K (above \(A_g\)). The coupling shrunk back to its original dimensions and a tight fit was established, as the stress-induced \(\varepsilon\)-martensite formed during expanding, reverted to the austenitic state. For example, in our experiments carried out with the Fe-30Mn-5.5Si alloy, the initial diameter \((D_0)\) of the muff was 14.0mm, the diameter of the piercer \((D_p)\) was 14.6mm, the diameter of the muff after expanding \((D_1)\) was 14.45mm, and the diameter of the muff after heating in the free state (without pipe connection) was \(D_2=14.1\)mm. We measured the total deformation \(E^t = D_p - D_0 / D_0\), elastic deformation \(E_e = D_p - D_1 / D_1\), recovered deformation \(E_r = D_1 - D_2 / D_2\) and remained deformation \(E_R = D_2 - D_0 / D_0\). For our experiment: \(E^t = 4.23\%\), \(E_r = 2.48\%\), \(E_R = 0.71\%\), \(E_e = 1.04\%\). It is possible to change \(E^t\) by means of changing \(D_p\). As shown in Fig.7, \(E_R\) and \(E_e\) increase with increasing \(E^t\), but \(E_r\) is changed with the curve having the maximum.

![Fig.7. Effect of the pre-strain (total) deformation of muffs of Fe-30Mn-5.5Si alloy on the elastic, recovered and remained deformation.](image)

This results can be explained by taking into consideration that the increase of \(E^t\) leads to increasing the irreversible part (slip, twinning) of the plastic deformation and to decreasing its reversible part (the stress induced \(\gamma\)-\(\varepsilon\) martensitic transformation) and as the result the SME decreases.

The pull-out strength of such connection at 300K equals 180MPa, and the temperature interval of the stability of this connection is 4-900K.

4. CONCLUSION.

This work emphasizes the importance of the kinetic of the \(\gamma\)-\(\varepsilon\) martensitic transformation, strength of austenite, temperature of pre-straining, volume effect of the \(\gamma\)-\(\varepsilon\) transformation on the SME in Fe-Mn-Si based alloys. The appearance of the recovered stress in Fe-Mn-Si alloys leads to the possibility to use their for pipe connection.

References