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# Hydrogen induced martensite in a Fe–17Mn–1.9Al–0.1C steel

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**Abstract**

As found earlier, cold work can induce the formation of $\alpha'$ and $\varepsilon$ martensites in Fe–17Mn–1.9Al–0.1C (wt.%) alloy. In the present work the martensitic transformations as induced by hydrogen electrolytic charging were investigated by X-ray diffraction in the same alloy. The results show that only $\varepsilon$ martensite is formed by cathodic hydrogenation. The stability of this martensite was studied with time and temperature and compared to that resulting from cold working. The results are discussed taking into account previous analysis of hydrogen induced martensitic transformations in austenitic stainless steels.


*Keywords:* Metals; X-ray diffraction

## 1. Introduction

Fe–Mn–Al alloys have been extensively studied due to their interesting mechanical and corrosion resistance properties. Martensitic transformations $\gamma \rightarrow \alpha'$ and $\gamma \rightarrow \varepsilon$ induced by cold deformation are observed in many austenitic alloys [1–4]. The martensite $\alpha'$ is body centred cubic and ferromagnetic while the martensite $\varepsilon$ is hexagonal close packed and paramagnetic. In a previous work [5], we have observed the formation of these two types of martensite in the Fe–17Mn–1.9Al–0.1C austenitic alloy during cold deformation. The reversion reactions $\alpha' \rightarrow \gamma$ and $\varepsilon \rightarrow \gamma$ were also investigated during heating. The $\varepsilon$ martensite as produced by deformation was found to start to revert into austenite at about 300 °C and it was completely eliminated between 400 and 450 °C. The reversion of the martensite $\alpha'$ could only be investigated in continuous heating by thermomagnetic analysis, and it was found to start at 390 °C ($A_s$) and to finish at 540 °C ($A_f$). When the alloy was heat treated in the 450–750 °C temperature range the ferrite phase was found to precipitate via a diffusion mechanism.

Martensitic transformations can also be induced in common stainless steels by hydrogen charging [6–9]. Accordingly to Mathias et al. [6] hydrogen insertion by electrolytic charging of the 304L and 316L steels promotes the formation of martensite $\varepsilon$ followed a few hours after hydrogenation by a partial transformation to martensite $\alpha'$. On the other hand, Zakroczymski et al. [7] have observed the increase of a ferromagnetic phase, defined as $\alpha'$ martensite, during the electrolytic hydrogenation when catalysed by addition of small amounts of $As_2O_3$ in the solution. With stable austenitic stainless steels (e.g. AISI 310 and Cr18Ni16Mn10) only the $\varepsilon$ martensite is produced by hydrogenation and its disappearance during room temperature ageing is not accompanied by the formation of $\alpha'$ martensite [6,8].

In the present work we investigate the martensitic transformation induced by hydrogen charging of the Fe–17Mn–1.9Al–0.1C austenitic steel. The phase stability was also investigated during subsequent room temperature ageing and heat treatments in the 200–450 °C range. The results are discussed and compared with those of previous works on hydrogen induced martensitic transformations in austenitic steels [6–9].

## 2. Experimental

The Fe–17.13Mn–1.89Al–0.10C (wt.%) alloy was melted in an arc furnace from elements of 3N to 3N5 grade of purity. The chemical composition was checked by plasma spectroscopy. The ingot was hot forged at 1000–

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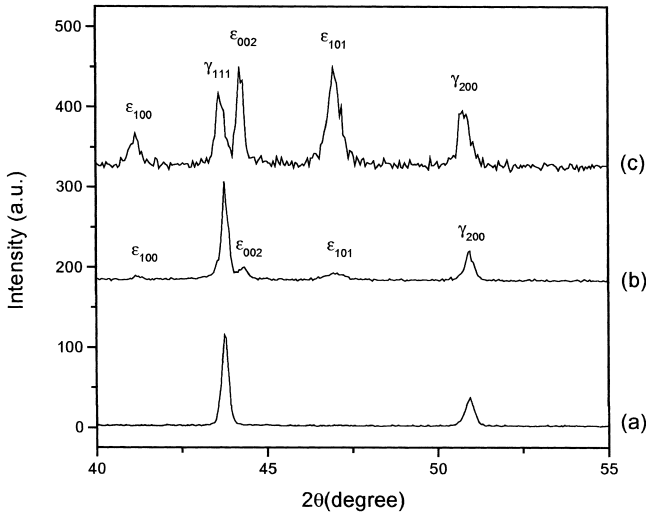


Fig. 1. X-ray diffractograms of the material solution treated (ST), after cathodic hydrogenation with and without $As_2O_3$.

900 °C with a high-speed hammer. It was then solution treated at 1050 °C and water cooled. The material was cold rolled to 0.25 mm thickness and solution treated once again. After that, X-ray diffraction analysis confirmed that the structure was 100% austenitic after this treatment. The hydrogenation procedure was carried out in a 1N $H_2SO_4$ solution, with and without $As_2O_3$ addition as catalyst. The hydrogenated samples were analyzed by X-ray diffraction after charging, after room ageing and after heat treatments in the 100–450 °C range for 1 h.

The X-ray diffraction was carried out using a Phillips® diffractometer with Cu Kα radiation. The samples were rotated to minimize texture effects.

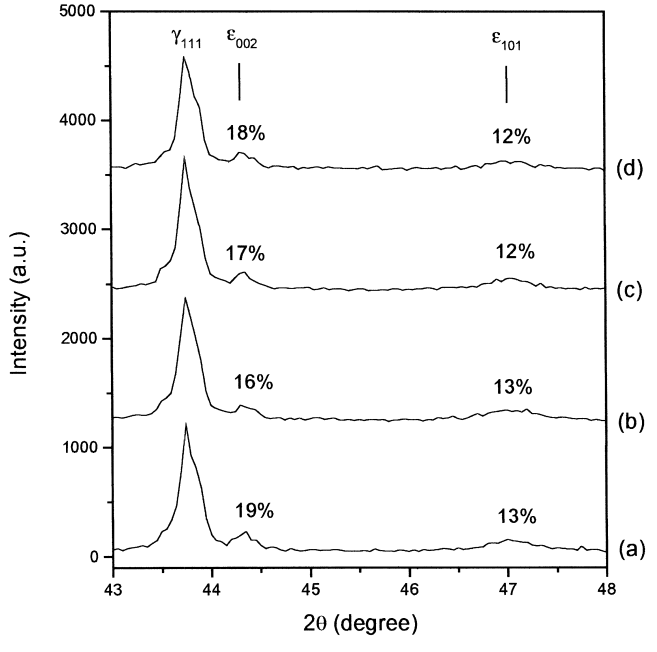


Fig. 2. X-ray diffractogram of hydrogenated samples: (a) just after hydrogenation; (b) 20 h later; (c) 46 h later and (d) 92 h later.

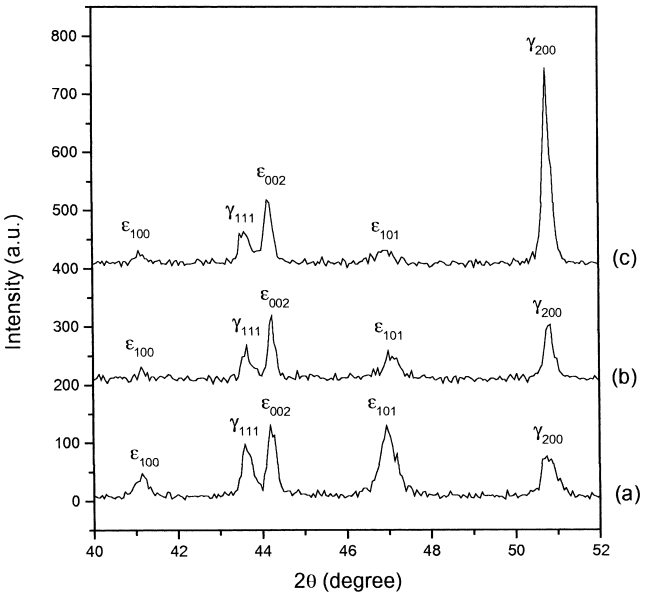


Fig. 3. X-ray diffractogram of hydrogenated and heat-treated samples: (a) as hydrogenated; (b) as heat-treated at 200 °C; and (c) as heat-treated at 250 °C.

## 3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of the samples solution treated (a), hydrogenated with (c) and without (b) $As_2O_3$ addition to the $H_2SO_4$ solution. The

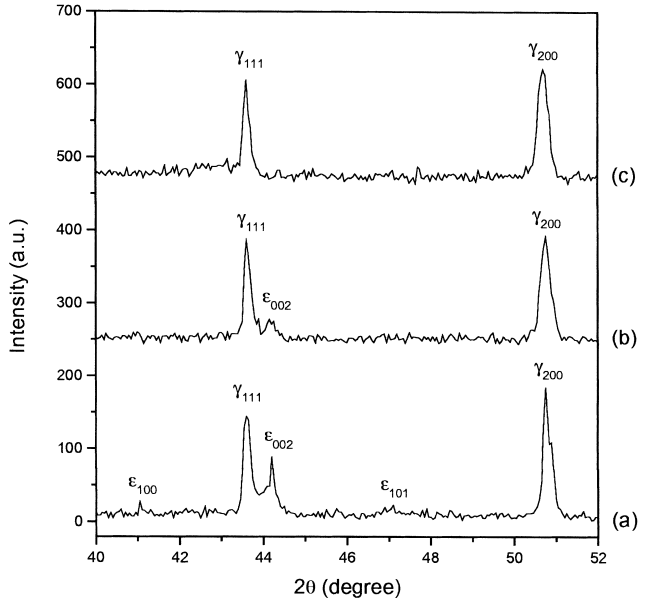


Fig. 4. X-ray diffractograms of hydrogenated and heat treated samples at: (a) 300 °C; (b) 350 °C; and (c) 400 °C.

Table 1
Main features of the martensitic transformations in austenitic stainless steels and in the Fe–17Mn–1.9Al–0.1C alloy

| Material | Deformation | Hydrogenation | | |
|---|---|---|---|---|
| | | As hydrogenated | RT ageing | Heat treatment |
| Metastable steels (304, 304L, 316, 316L) | $\varepsilon$ (small deformations) and $\alpha'$ | $\varepsilon$ [6,9] or $\alpha'+\varepsilon$ [7] | $\varepsilon \downarrow$ $\alpha' \uparrow$ | – |
| Stable steels (310, 310S) | $\varepsilon$ (only if severe deformation is applied) | $\varepsilon$ | $\varepsilon \downarrow$ | – |
| Fe–17Mn–1.9Al–0.1C alloy | $\alpha'$ and $\varepsilon$ [5] | $\varepsilon$ | $\varepsilon \rightarrow$ | $A_s \approx 200$–$250\,^{\circ}C$ $A_f \approx 350$–$400\,^{\circ}C$ |

electrolytic hydrogenation promotes the formation of martensite $\varepsilon$, which can be strongly enhanced by the $As_2O_3$ addition. No trace of martensite $\alpha'$ was found. Hydrogenation also promotes a broadening of the peaks of the austenite phase and a parallel small expansion of the lattice parameter.

The martensite $\varepsilon$ produced by electrolytic hydrogenation was found to be very stable during room temperature ageing. Fig. 2 shows the X-ray diffraction pattern of the samples hydrogenated and aged at room temperature. The peaks of the martensite $\varepsilon$ are always present and their relative intensities were found to be almost constant. No trace of the martensite $\alpha'$ was found in the samples aged for up to 92 h.

The thermal stability of the martensite $\varepsilon$ was investigated in the samples hydrogenated with $As_2O_3$ addition. Fig. 3 compares the X-ray diffraction patterns of the samples as hydrogenated and hydrogenated and treated at 200 and then at 250 °C. An important decrease of the relative intensities of the peaks of the martensite $\varepsilon$ was observed between 200 and 250 °C, which indicates that the starting temperature for the $\varepsilon \rightarrow \gamma$ transformation belongs to this range. Fig. 4 shows the diffraction patterns of samples treated at 300, 350 and 400 °C. As can be seen, the final temperature for the $\varepsilon \rightarrow \gamma$ transformation lies between 350 and 400 °C. Comparing these results with those on the same alloy cold deformed [5], the reversion of the hydrogen induced martensite $\varepsilon$ into austenite occurs at temperatures of 50–100 °C lower then when the martensite is deformation induced.

Table 1 summarizes the main features of martensitic transformations found in the metastable and stable stainless steels (AISI 304 and 310, respectively) compared to the Fe–17Mn–1.9Al–0.1C alloy. Although this latter alloy is susceptible to martensites $\alpha'$ and $\varepsilon$ formation during cold work [5], only the $\gamma \rightarrow \varepsilon$ transformation was found to occur during the cathodic hydrogenation. This $\varepsilon$ phase is found to be even more stable than in stable steels (e.g. AISI 310), and it does not transform into $\alpha'$ during room temperature ageing, as observed in the metastable steels (AISI 304, 304L, 316, etc.) [6,8,9].

## 4. Conclusions

The alloy Fe–17Mn–1.9Al–0.1C is susceptible to exhibiting martensitic transformation during cathodic hydrogenation. Only the martensite $\varepsilon$ (hcp) is formed by this process. This phase was very stable to room temperature ageing. By using X-ray diffraction we observed that the temperatures $A_s$ and $A_f$ for the $\varepsilon \rightarrow \gamma$ reaction occur in the 200–250 and 350–450 °C ranges, respectively.

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