Martensitic transformations in Fe-Mn alloy with low stacking fault energy

S Parshorov\textsuperscript{1}, S Valkov\textsuperscript{2,*}, P Petrov\textsuperscript{2}

\textsuperscript{1} IMSETHC of Bulgarian Academy of Sciences, 67 Shipchenski prohod Blvd, Sofia 1574, Bulgaria

\textsuperscript{2} Emil Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee blvd., 1784 Sofia, Bulgaria

Abstract. Object of investigation is highly alloyed binary Fe-Mn alloys which in austenitic state are characterized with different stacking fault energy (SFE). Experimental results using the internal friction and X-Ray methods are obtained for the martensitic non isothermal transformation upon cooling and heating. It was determined that mainly the structural characteristics of the alloys define the type of the possible transformation mechanisms and the products of the martensitic reaction. The role of the SFE for the mechanisms of formation and growth of the martensite phase and the relation between the micro-structural parameters of the solid solution and the mechanism of non isothermal martensitic transformations is shown. On the basis of the existing models of dynamic relaxation associated with phase transformations, here are pivotal conclusions about the characteristics of the non-diffusion mechanism of transformation into a low SFE.

1. Introduction

Manganese is an austentabilizable element, it does not form carbides and nitrides in the steel and thus affects the properties of the iron solid solution. According to the state diagram, the phase composition of the dual alloy Fe-Mn depends on the manganese concentration and the alloy temperature as shown in Fig. 1. Conversions may be diffusion, straight and reverse reactions - $\gamma$-austenite $\leftrightarrow\alpha$-ferrite and may have a nondiffusional martensite character - $\gamma$-austenite $\leftrightarrow\varepsilon$- or $\alpha$-martensite [1-10].
The reason for this “unusual” character of these type transformations lies in the specific dislocation structure of the initial austenite phase, characterized with high density of the low energy “surface” type of defects known as “stacking fault energy” (SFE) [3-10]. The defect lies right between the Shockley’s partial dislocations- part of the main dislocations and is characteristic for the close- packed crystal structures (hexagonal an face-centered cubic) [11-14]. As measure for the SFE the elastic energy for a given area is adopted in the following form- erg/cm². The complete energy is a sum of the elastic energy of the partial dislocations and the SFE locked between them. As the SFE is decreasing the concentration and the size of the defects for a given volume are increasing. As long as SFE is connected to the atomic forces in the crystal lattice it is mainly determined by the type and the concentration of the alloying elements in the solid solution, the morphology of the high temperature phase, such as structural defects, size of the initial austenitic grain and temperature [11].

The general pattern of SFE dependence on manganese and carbon concentration, austenitic grain size and temperature are shown in Fig. 2 (a) - (d). Observed carbon and manganese concentration limits are in the range determined by the maximum solubility of each element in the defects in the arrangement, called the Suzuki-atmospheres. Another feature of the SFE is its strong temperature dependence. With decreasing of the temperature the SFE decreases, with the dependence being leapy - Fig.2 d). Plastic deformation increases the concentration and the width of stacking faults, thus causing phase transformation. This effect is typical for low SFE alloys and is known in the literature as TRIP - Transformation Induced Plasticity/. These effect which is not subject of the current research but on its basis alloys with low SFE are found [5, 11,13].

The aim of the present work is to investigate the features of the martensitic phase transitions in the Fe-Mn double alloys related to their structural features by means of structure-sensitive methods.
2. Materials and methods

Object of investigation are alloys Fe-4% [wt] Mn, Fe-8% [wt] Mn and Fe-12% [wt] Mn, produced in the Institute of Metal Science. The specimens for investigation are manufactured by the following flow diagram: Casting of plates by vacuum furnace; Hot plastic deformation; The degree of the finally deformation was in range of 40%. Some of the plates were reduced to size of 5,5 mm and 1.2 mm. In order to reduce the internal stresses and remove the inherited structure obtained during the plastic deformation another set of samples were annealed for 10 hours at temperature of 700 °C. In order of not changing the microstructure and the phase composition the cutting was made under water with electro-sparking machine. The specimens are heat treated for finer structure - high temperature treatment - quenching from 1150 °C after 10 min of holding in water. The present investigations are led using three structural-sensitive methods- X-ray diffraction-(specimens 15x15x5 mm), dilatometric-(specimens 5x50 mm) and the internal friction (specimens 50x1x1.2 mm) methods. In order of not changing the microstructure and the phase composition the cutting was made under water with electro-sparking machine. The X-ray structure analysis is performed by standard apparatus “Philips”using Co-Kα (λ=1,7880.10⁻⁸ cm) emission. The speed and the step of the goniometer are as follows-0,02°/min and 20 sec/step. On the base of standard calculations including the average value of the wave length for Co-radiation the unit cell parameter ‘a’ was determined from the considered profile line (211)₀.

Figure 2. Dependence of SFE on: a) manganese concentration in austenite; (b) carbon concentration in austenite; (c) the size of the austenitic grain; d) temperature; [11]
The common integral profile line can be separated to its structural components ($2.\alpha_1$ and $2.\alpha_2$-doublet) using the Gauss function for two maxima, by the programme „Origin“. During the approximation, the values for the areas of the two maxima are considered to be constant in ratio of 2:1. Standard method for phase analysis based on the diffraction line (110)$_{\alpha}$ of the martensite is used. The microstructure parameters of the martensite solid solutions – the domain size - $D$ and the micro strains of the crystal lattice - $\varepsilon$, are studied by the so called “single line analysis” shown in details in [15-17]. This method allows calculating the microstructure parameters of austenite and martensite on the basis of one diffraction line, for each of the phases. For reference sample of “armco” iron is used after full annealing. The dilatometric tests were carried out with standard equipment "NETZSCH- Geratebau GmbH". Linear expansion values of standard samples in micrometers are recorded as a function of temperature and time. The tests were conducted in the temperature range 20-1200°C with heating and cooling. Dilatation data is processed with the Origin program. The apparatus for the internal friction measurements is built on the principle of the reverse balanced pendulum also known as Ke’s pendulum. The operational frequency is in the range 1-1.3 Hz. The relaxation spectra of the specimens are recorded for the temperature range of 50-800K during heating and cooling in vacuum at rates of 20 oC/min. The degree of the relative deformation during the measurements is $5.10^{-5}$-$5.10^{-6}$.

3. Results and discussion

According to the published data, during cooling from the austenite region diffusion reactions of $\gamma\rightarrow\alpha$ ferrite phase (Fe-4% [wt] Mn, Fe-8[w] %Mn) or diffusion-free reactions of $\gamma\rightarrow\alpha$ - or $\gamma\rightarrow\varepsilon\rightarrow\alpha$ - martensite (Fe-12% [wt] Mn) type occur in Fe-Mn alloys in dependence of the manganese concentrations. Fig. 3 presents the X-ray structure spectra of the studied alloys for manganese alloys, respectively in the range of doubled reflection angles from 40 to 140o for Fe-8% [wt] Mn. and Fe-12% [wt] Mn after quenching. The result for Fe-4% [wt] Mn is analogous.

![Figure 3. X-ray diffraction pattern of manganese alloys](image-url)
The results show that the resulting spectrum corresponds to that of $\alpha$-iron, irrespective of the concentration of manganese. Other authors find experimental presence of minimal quantities of $\varepsilon$-martensite that are not observed in our results [5]. This is probably due to the presence of $\varepsilon$-phase quantities in alloys, which are difficult to detect by the X-Ray method. The results obtained show (Fig. 3), that no alloys on Fe-Mn base form residual austenite. It is well known that the presence of residual austenite is caused by high internal stresses to which the austenite is subjected by the growth of the martensite lamellae and acicular. The absence of residual austenite shows that the formation of ferrite or $\varepsilon$-martensite is connected with the occurrence of active relaxation processes resulting in decrease of the internal stress value. Verification of that is also the experimentally obtained by us very low value of the martensite lattice micro strains. Fig. 4 presents the microstructure parameters of the solid solutions of the martensite – size of the domains - $D$ and the micro strains of the crystal lattice - $\varepsilon$. The results obtained show: (i) the concentration limit of the transition of the austenitic phase to ferrite or martensite is lower than that published in the literature. Martensitic phases are still formed at the manganese at 8% by weight; (ii) in the manganese alloys, the formation of epsilon-martensite in manganese concentrations of 8% [wt] reduces the microdeformations of the lattice.

![Figure 4. Dependence of domain size and micro strains on the manganese contents](image)

The presence of two types of martensite transformations in the considered alloys is defined in the most general aspect by the thermo dynamical, crystallographic and other specific features of alloys. Determining parameter for that is mainly the energy of the austenite stacking faults from which the respective martensite phase has transformed. The published investigations [11] for the phase compositions and transformations in Fe-Mn alloys mainly show that Fe-12%Mn alloy is characterized by a very low energy of stacking faults, of the order of 18 erg/cm$^2$, which suggests a formation of $\varepsilon$-martensite.

In order to determine the influence of manganese concentration, hot plastic deformation and annealing on the structural state of austenite, the parameter of its crystal lattice was investigated according to the methodology shown above. After casting some of the samples were hot rolled to plates with thickness of 0.8 mm under the following conditions: preliminarily heating of the ingots to temperature of...
1050°C; repeated hot rolling in the temperature interval of 1050-980 °C; cooling down on air. The degree of the finally deformation was in range of 41-43%. Some of the plates were reduced to size of 15x15x0.8 mm suitable for the further XRD measurements. In order to reduce the internal stresses and remove the inherited structure obtained during the plastic deformation another set of samples were annealed for 10 hours at temperature of 700°C. Fig. 5 shows the corresponding values for the unit cell parameter ‘a’ of the lattice, calculated for the investigated alloys after hot rolling and annealing.

Fig. 6 a) shows the dilatation curves of Fe-12% [wt] Mn steel obtained under heating and cooling. Fig.6 b) shows enlarged cooling curve marked in a). According to the state diagram of alloy Fe-12% [wt] Mn, some published researches and our dillatometric investigations, the phase composition at room temperature is martensite [1]. On heating above 700 K the martensite transforms into austenite i.e. the reaction α→γ takes place. On cooling below 400 K the austenite turns into ε-martensite, passing through the so-called, ε-martensite with hexagonal lattice. During cyclic heating and cooling below 700 K, the straight and the reverse martensite reactions of the type γ→ε and γ→α take place - Fig.6 a) and b). The results showed that the γ→ε phase transformation is associated with minor dilatation changes in the alloy volume. That's why the internal friction method was used in our research, connected with the dynamic relaxation of the solid solution Fig. 7 presents the relaxation spectra of the Fe-Mn alloys at heating and cooling. It is characteristic that at room temperature they are martensitic [1] and on cooling, in compliance with the constitution diagrams, the martensite in them transforms into austenite. In case of cyclic heating and cooling in the alloy Fe-12%Mn runs the direct and reverse reaction of the martensite transformation of the type α→γ and ε→γ. These phase reactions are reflected as maxima on the temperature dependence of the internal friction. Fig. 8 shows the same are presented separately from the internal friction background after numerical integration and normalization. In practice, the numerical integration and normalization of the experimentally obtained maxiums, shown in Fig. 8, represents the kinetics of the martensite reaction in non-isothermal conditions. The results show that the direct reactions of α→γ and ε→γ transformations run close or in the high temperature background of the internal friction where the mobility of the dislocation structure is the highest, and the reverse α→γ and ε→γ in the temperature interval before the high temperature background where the “pure”, conservative dislocation creep/glide in an atomic plane is basic.
Figure 6. Dilatation curves at heating and cooling; b) The same enlarged heating curve marked in a) between 550 and 900 K.

Figure 7. Relaxation spectra of alloy Fe-12% [wt] Mn (EN X0Mn12) at heating and cooling below 700 K.

Figure 8. Numerical integration and normalization of experimentally obtained maxima after subtraction against the backdrop of internal friction: a) cooling; b) heating.
According to published data, the alloy Fe-12% [wt] Mn characterizes by SFE which presumes formation of ε-martensite. In that sense, the dislocation structure of the manganese alloys is easily mobile and consists of widely sheared partial dislocations surrounding large areas of stacking faults. In the publications there are several models that describe the connection between the internal friction value and the phase transformation parameters that refer to the fact that: (i) the height of the internal friction maximum is proportional to the phase transformation rate and the heating rate; (ii) the height of the internal friction maximum is inversely proportional to the frequency of the measurement. In the base of these models [19] is the fluctuation mechanism of nucleation related to the process of nuclei thermal activation. It is assumed that the activation energy of nucleation is decreased by the presence of internal stresses which perform work in the nucleation process itself. It is proportional to the lattice non-elastic deformation, in this case the life time of the nucleus being much greater than the time of the process relaxation.

The dependence deduced by the authors allows by means of the area of the internal friction maximum to calculate the activation volume of the phase transformation. The values obtained by them are in good agreement with the number of atoms that normally enter in one critical nucleus during martensite transformations in some alloys, e.g. Co-Ni. We have made an attempt to calculate the nucleus critical size of the two alloys studied in the same way it is made by the above said authors. Unfortunately, our calculations in compliance with this theory do not give real values for the nuclei critical size; they are smaller than the volume of an elementary cell. In spite of all, V. Belko’s theory shows that the presence of stresses in the lattice affects the size of the nuclei capable to grow. In respect of the boundary mobility in the model there are four possibilities according to the model of Dejonghe – Fig.9 [19].

![Figure 9](image_url)

**Figure 9.** Scheme of addictions of the type of relaxation maximum of the temperature associated with movement of the boundaries of phase transformations

In respect of the boundary mobility in the model there are four possibilities: (i) absence of relaxation maximum when the applied stress is comparatively low and below the critical stress; (ii) presence of symmetrical relaxation maximum that shows that under the action of the applied stress the boundary between the new phase and martensite shifts; (iii) presence of symmetrical relaxation maximum that shows that under the action of the applied stress besides the boundary new phase/martensite the phase boundary martensite/martensite also shifts; (iv) occurrence of a step in the temperature dependence of internal friction - then the mobility of the boundary martensite/martensite is greater than the boundary new phase/martensite. It is obvious that for the studied by us α→γ and ε→γ transformations the second case is relevant, i.e. the available relaxation maximum is caused by the motion of the phase boundary - new phase/martensite in both alloys studied by us. It is seen that there is a significant difference in the activation energies of the direct and reverse reactions of martensite type. The low values of the kinetic parameters of the austenite-martensite transformations in cooling show relieved mechanism of nucleation and growth of the martensite aciculae related with the low value of the SFE.
It is assumed that as martensite nuclei serve wide areas of the stacking faults surrounded by partial dislocations [11-13] which in crystallographic respect represent α-phase ready nuclei. The crossing of two packs of ε-phase results in α-phase nuclei that are ready nuclei for the heterogeneous mechanism of γ→α transformation. Up to now in the publications this mechanism is assumed to be the most probable and experimentally proved one. In our judgment basic moment in the nucleation mechanism is the temperature dependence of the austenite SFE. It is well known that it depends strongly on the temperature and changes at leaps by it. The temperature range of SFE change at leaps is below room temperature of the order of 280-230 K. The sharp SFE increase with the temperature increase results in high values of the activation energies of martensite phases transformation in austenite and in this connection a shift of the processes towards high temperatures, i.e. there is a strong temperature hysteresis of the direct and reverse martensite reactions that is observed also in our experimental results.

4. Conclusion

The results show that the complete X-ray structure spectrum of manganese alloys corespondes to that of α-iron irrespective of the concentration of manganese. No experimental presence of ε-martensite was observed. The X-ray diffraction measurements of Fe-Mn alloys showed different value for the unit cell parameter ‘a’ of the crystal lattice depending on the concentration of the alloying element and the presence of plastic deformation. Probably these facts are due to a difference in the stacking fault energies of the two alloys. The concentration limit of the transition of the austenitic phase to ferrite or martensite is lower than that published in the literature. Martensitic phases are still formed at the manganese at 8% by weight. In the manganese alloys, the formation of epsilon-martensite in manganese concentrations of 8% reduces the microdeformations of the lattice. The temperature range of conversion of austenite to martensite is below room temperature in the range of 280-230 K, meaning that there is a process of leaping the EDP. The symmetry of the obtained maximums and the absence of a step of the internal friction temperature dependence show that the relaxation processes in these alloys are defined by the motion of the phase boundary new phase/martensite. Presence of symmetrical relaxation maximum that shows that under the action of the applied stress besides the boundary new phase/martensite the phase boundary martensite/martensite also shifts. The results show that the direct reactions of α→γ and ε→γ transformations run close or in the high temperature background of the internal friction where the mobility of the dislocation structure is the highest, and the reverse α→γ and ε→γ - in the temperature interval before the high temperature background where the “pure”, conservative dislocation creep/glide in an atomic plane is basic.

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