

Effect of Nitriding on Phase Transformations in the Fe-Mn Alloys

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Abstract

We present results concerning the nitriding effects on phase transformations in Fe – 40 at. % Mn and Fe – 50 at. % Mn alloys. These alloys were studied by means of X-ray diffraction and Mössbauer-effect spectroscopy methods at room temperature. Results indicate that, after nitriding, in the absorption spectra of these alloys appears lines with hyperfine field $H \sim 330$ kOe which corresponds to the field on the ^{57}Fe nuclei in the α -Fe. Annealing of the alloys at 650°C temperature (nitriding temperature) in argon atmosphere do not change the form of the Mössbauer absorption spectra. It appears that the nitriding process affect the microstructure of these alloys and leads to $\gamma \rightarrow \alpha$ phase transformations in the Fe-Mn alloys.

The distribution function of effective hyperfine magnetic field $P(H)$ on the ^{57}Fe nuclei in the Fe-40 at.% Mn alloy after hardening processes has one maximum with $H_{eff} \sim 37$ kOe, while nitriding processes leads to the appearance of two maxima with $H_{eff} \sim 6$ kOe and $H_{eff} \sim 27$ kOe in the $P(H)$ curve of this alloy. Analogical results were obtained after nitriding processes for Fe-50 % Mn alloy.

Key Words: Fe-Mn alloys; Nitriding; Fine atomic structure; Mössbauer-effect spectroscopy

1. Introduction

The influences of the interstitial element atoms on the ordering and decomposition processes in metallic alloys are still insufficiently studied. The Fe-Mn alloys are the bases for most construction materials. The Mössbauer absorption spectra of these alloys

represent non-splitting Zeeman sextets. The alloys of the Fe-Mn system are metastable in nature and have tendency towards decomposition with formation of atomic short-range order. The character of the alloy composition suggests the possibility of different types of martensite transformations ($\gamma \rightarrow \alpha$ and $\gamma \rightarrow \varepsilon$) in these alloys. It was shown that the phase transitions in iron-manganese alloys has a complex nature and the third component impurities can be radically change the nature of the martensite transformations in these alloys [1-8].

The purpose of this work is to investigate the fine atomic structure of the alloys of Fe-Mn system with 40 and 50 at. % of Mn before and after nitriding.

2. Experimental Procedure

The alloys were analysed by means of X-ray diffraction and Mössbauer-effect spectroscopy methods. X-ray diffraction measurements were carried out *in vacuo* with Fe- K_{α} radiation monochromatized by a flat single crystal of silicon (plane (111)) in a DRON-2 X-ray powder diffractometer. Mössbauer-effect measurements have been performed with an IGRS-4M constant-acceleration-driving unit in combination with a multichannel analyzer. The Mössbauer source was a 60 mCi of ^{57}Co isotope diffused in chromium.

Nitriding processes of Fe-Mn alloys have been provided in the special experimental set-up at temperature 650°C in the presence of NH_3 gas. Optimum nitriding time has been chosen as 30 min. After nitriding, the composition of N element measured in the γ -phase of Fe-Mn alloys was 3 to 3.2 at.% N.

3. Results and Discussion

The X-ray diffraction pattern of hardened Fe-Mn alloys revealed (111), (200) and (311) fundamental diffraction peaks. All peaks had a doublet structure that can be associated with the non-strictly monochromatic Fe- K_{α} radiation. For the nitrides samples of Fe-Mn alloys the fundamental diffraction peaks remained unchanged; however their maximums shifted to lower values of Bragg diffraction angles. Such a shifting of diffraction peaks maxima may be associated with the expansion of crystal lattice due to formation of Fe-Mn-N ternary interstitial solid solutions. Comparisons of the fundamental diffraction peaks for pure and nitrides Fe-Mn alloys show that nitriding processes leads also to the broadening of the diffraction peaks. The broadening of diffraction lines is due to nonuniform deformations and microstrains in the structure of Fe-Mn-N solid solutions. Phase analysis of the Fe-Mn-N solid solutions did not reveal the formation of any nitride phases.

To study the effect of nitrogen atoms on the fine atomic structure of Fe-Mn alloys Mössbauer-effect spectroscopy method has been used. The absorption spectra of Fe-40 at.% Mn alloys for hardened and nitriding states are shown in Fig. 1, which were taken at room temperature. These spectra look like non-splitting Zeeman's sextets. Due to very weak splitting of diffraction spectra, it is difficult to obtain any information concerning the distribution character of the constituent element atoms in the submicro

volumes of the alloys under investigation. Therefore, for this purpose it seems more reasonable to use the method based on the determination of the distribution function of effective hyperfine magnetic field $P(H)$ on the ^{57}Fe nuclei in the Fe-Mn alloys. For magnetically ordered systems the value of the effective magnetic field H_{eff} on the ^{57}Fe nuclei can be used for analysis of fine atomic structure [9,10]. In the approximation of quasicontinuous distribution of the H_{eff} on the nuclei of atoms one can characterise them by some probability function of $P(H)$. Then, Mössbauer absorption spectra represent the linear superposition of nondiscrete subspectra that differ from one another by the values of H_{eff} fields on the ^{57}Fe nuclei [9,10]. For the analysis of Mössbauer absorption spectra (Fig. 1), it was supposed that the lines of sextets have Lorentzian form with a width of 0.29 mm/s, the ratios of intensities are 3:2:1:1:2:3, isomer shifts are same for all lines and that the quadruple splitting are absente in the spectra.

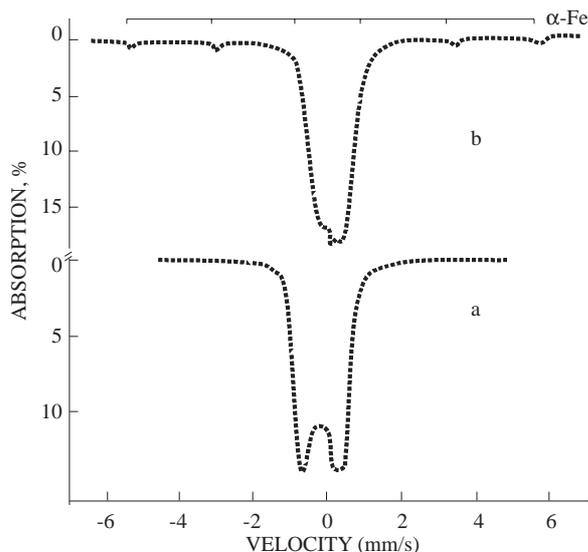


Figure 1. Mössbauer absorption spectra of hardened (a) and nitrided (b) Fe-40 at.% Mn alloys

As can be seen in Fig. 1, the nuclear gamma resonance (NGR) spectra of Fe- 40 at.% Mn alloys before and after nitriding are radically different. After nitriding, the new lines appears in the γ -resonance spectra of Fe-Mn alloys associated with α -Fe having effective magnetic field of 330 kOe on the ^{57}Fe nuclei. Appearance of these lines after nitriding processes were observed for all investigated alloys. It is worthwhile to note that annealing of samples at 700°C in the argon atmosphere and under high vacuum during 30 min. did not change the form of Mössbauer absorption spectra. This fact indicates that the $\gamma \rightarrow \alpha$ phase transformation in γ -Fe-Mn alloys take place as a result of the influence of nitrogen atoms only.

The density of effective hyperfine magnetic field distributions $P(H)$ on the ^{57}Fe nuclei in the Fe-40 at.% Mn alloy after hardening and nitriding for during 30 min. are shown

in Figure 2. The calculation of the $P(H)$ functions from the experimental NGR spectra have been carried out by using computer programs based on the Window method [9]. As expected, the $P(H)$ function after hardening has one maximum at $H_{eff} = 37$ kOe. This value of H_{eff} is corresponded to the antiferromagnetic state of Fe-Mn alloy. At the same time it is evident from Figure 1 that the elementary components of NGR spectra show negative isomer shifts relative to the α -Fe of -0.07 mm/s. This result can be explained by the decreasing of density of d-electrons on ^{57}Fe nuclei of Fe-Mn alloy.

The density distribution function $P(H)$ after nitriding (Fig. 2b) has two maxima at $H_{eff} = 6$ and $= 27$ kOe. It is known that the alloys of Fe-Mn system are metastable and have a tendency towards decomposition with the formation of the short-range atomic order [11]. Therefore, an appearance of two maxima on the $P(H)$ curve can be explained by the formation of concentration nonuniformities, i.e. by the nonuniform distribution of constituent element atoms within the submicro volumes of Fe-Mn alloys. It looks like that a peak on the $P(H)$ curve at $H_{eff} = 6$ kOe is associated with the formation of paramagnetic ε -phase and that the effective magnetic field on ^{57}Fe nuclei of $H_{eff} = 27$ kOe may be connected with Fe atoms in antiferromagnetic state, i.e. γ -phase of Fe-Mn alloys.

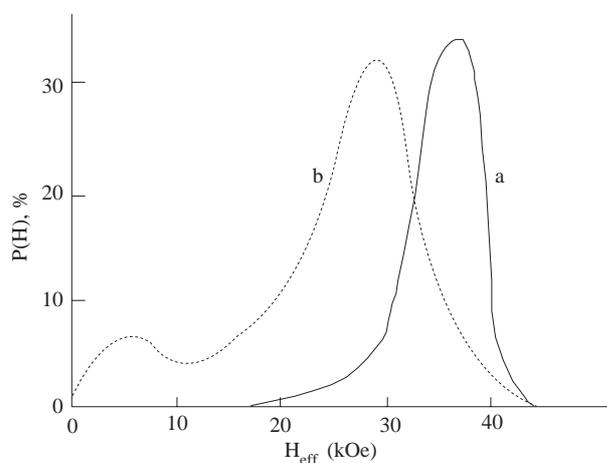


Figure 2. The effective hyperfine magnetic field distributions on the ^{57}Fe nuclei in the Fe-40 at.% Mn alloy after hardening (a) and nitriding during 30 min. (b) processes

It is known that a metastable ε -phase in the Fe-Mn alloys appears in the narrow concentration range of 10-30 at.% Mn and that at higher content of Mn (more than 30 at.%) element atoms the ε -phase disappears and alloy consist of only γ -phase [12]. Formation of ε -phase Fe-Mn alloys with HCP (hexagonal close-packed) structure can be explained by the compression deformations in the microplanes of iron element atoms, where due to the nonuniform distributions the concentration of Mn atoms are very low within such regions. At the same time, the formations of local regions with higher than

average composition of Mn element atoms in the alloy leads to the formation of γ -phase regions with high expansion deformations.

At low Mn content (less than 10 at.%) in the alloy, the regions enriched with Mn atoms with high interatomic spacings are formed, where there are no normal conditions for occurrence of all directional compressions in the intermediate layers. However, when each second or third Mn atoms (for alloys with >30 at.% Mn) take part in the interatomic interactions with Fe atoms, i.e. where specific volume are increased for each of unit cell and for all the crystal lattice, there will be non-expanded or stressed microregions within the Fe-Mn alloys.

The same type results have been obtained for Fe-50 at.% Mn alloys after nitriding processes. Fig. 3 represents $P(H)$ dependencies of H_{eff} hyperfine magnetic field on the ^{57}Fe nuclei for hardened and nitrides Fe-50 at. % Mn alloys. It is evident that after nitriding, the $P(H)$ curve has a two maxima, which can also be associated with the formation of ε -phase in Fe-50 at. % Mn alloy.

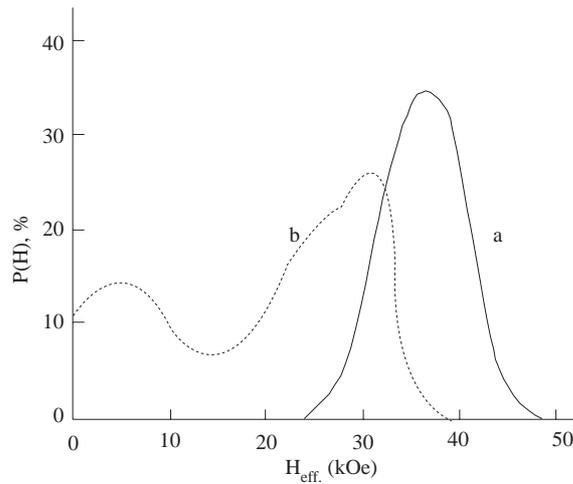


Figure 3. The effective hyperfine magnetic field distributions on the ^{57}Fe nuclei in the Fe-50 at.% Mn alloy after hardening (a) and nitriding during 30 min. (b) processes

4. Conclusions

The effect of nitriding processes on the fine atomic structure of Fe-Mn alloys with 40 and 50 at.% of Mn have been studied by X-ray diffraction and Mössbauer-effect spectroscopy methods. The results for on the N element effect on the phase characteristics of Fe-Mn alloys can be summarised as follows:

1. Nitrogen atoms form chemical bonds mainly with Mn atoms at the interstices of the unit cell of Fe-Mn alloys.

2. The distribution function of effective hyperfine magnetic field $P(H)$ on the ^{57}Fe nuclei in the Fe-40 at.% Mn alloy after hardening processes has one maximum with $H_{eff} \sim 37$ kOe, while nitriding processes leads to the appearance of two maxima with $H_{eff} \sim 6$ kOe and $H_{eff} \sim 27$ kOe in the $P(H)$ curve of this alloy. The peak on the $P(H)$ curve with $H_{eff} \sim 6$ kOe can be associated with the formation of paramagnetic ε -phase and peak with $H_{eff} \sim 27$ kOe with the formation of antiferromagnetic γ -phase.
3. The crystal structure of Fe-Mn alloys are affected by the presence of N element atoms in the alloy such that it leads to the formations of microstresses at the submicro volumes of alloys and to the $\gamma \rightarrow \varepsilon$ phase transformations in these alloys.
4. The appearance of α -phase in the microstructure of Fe-Mn alloys after thermomechanical processing can be explained by the full destruction of chemical bonds of Fe atoms with the Mn atoms as a result of formation of bonds between Mn and N atoms in these alloys.

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