

Mossbauer analysis of the f.c.c. Fe–Ni–C alloys structure after heat and ultrasonic treatments

V.M.Nadutov, D.V.Semenov, Ye.O.Svystunov, G.I.Kuzmich

G.Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine, 03680 Kyiv, Ukraine

Mossbauer spectroscopy has been used for atomic scale investigation of austenitic Fe–Ni–C alloys after ultrasonic and low-frequency impact surface treatments. The phase composition and hyperfine structure of the Fe–30.5 %Ni–1.5 %C and Fe–25.3 %Ni–0.78 %C alloys with the f.c.c. lattice after annealing at 1373 K and 773 K in vacuum and following ultrasonic surface treatment (UST, $f = 1\text{--}3$ kHz, the amplitude 20 μm , $t = 8\text{--}24$ s) have been studied. The results were analyzed in comparison with the low-frequency impact surface treatment (IST) of the alloys. The microhardness of the alloys after UST has been analyzed.

Мессбауэровская спектроскопия использована для исследования на атомном уровне аустенитных Fe–Ni–C сплавов после ультразвуковой и низкочастотной ударной поверхностной обработок. Изучен фазовый состав и сверхтонкая структура ГЦК сплавов Fe–30.5 %Ni–1.5 %C и Fe–25.3 %Ni–0.78 %C после нагрева до 1373 K и 773 K в вакууме и последующей ударной ультразвуковой обработки (УЗО), $f = 1\text{--}3$ кГц, амплитуда 20 мкм, $t = 8\text{--}24$ с. Результаты проанализированы в сравнении с влиянием низкочастотной ударной поверхностной обработки (УПО) сплавов. После УЗО проанализирована микротвердость сплавов.

The ultrasonic surface treatment (UST) is an effective method improving mechanical properties and performance characteristics of metal products. The hardening is associated with special defect structure formed under the UST resulting in anomalous diffusion of atoms and phase transformations [1]. A power ultrasonics produces defects of crystal structure with the density different from that after rolling or impact low-frequency treatment (IST). The electron microscopy of metal samples after UST has shown the increased (by 2–3 orders) density of dislocations and more homogeneous distribution of these defects in the surface layers [2]. Moreover, the high concentration of vacancies arising under the high-speed deformation is considered in [2] as a reason for the non-conservative movement of dislocations. The anomalous mass transfer is explained by high concentration of vacancies and interstitial atoms under the high-speed impact pulse loading of metal surface as compared to the low-speed deformation [3].

The UST effect on structure and properties of metal surface was studied in detail by structural methods and mechanical testing [1]. No detailed atomic scale study of the above-mentioned processes using Mossbauer spectroscopy was carried out. We assume that the anomalous mass transfer under the UST should follow redistribution of atoms in the crystal lattice that may be demonstrated in Mossbauer spectra. The main goal of this work was to reveal changes in phase composition and hyperfine structure of the austenitic Fe–Ni–C alloys after the UST by means of Mossbauer spectroscopy in comparison to the data relating to the samples after the IST. The f.c.c. Fe–Ni–C alloys under study are of industrial interest as the basis of Invar materials and their hardening is one of the main tasks.

The objects of this study were the f.c.c. Fe–Ni–C alloys of the chemical compositions listed in Table 1. The alloys were melted in the vacuum induction furnace under protective argon atmosphere. The carbon concen-

Table 1. The chemical composition of the alloys

| Alloy | Ni mass, % | C mass, % | Fe mass, % |
|---------------------|---------------|--------------|---------------|
| Fe-30.5 %Ni-1.5 %C | 30.5 | 1.5 | 68.0 |
| Fe-25.3 %Ni-0.78 %C | 25.3 | 0.78 | 73.92 |

tration was determined by chemical analysis and the Ni content was measured by X-ray fluorescence method. After surface cleaning, the ingots were aged at 1273 K in vacuum during 3 h. The 1 mm thick metal plates were mechanically polished on abrasive material and chemically thinned. The samples for Mossbauer spectroscopy were the 20–25 μm thick foils annealed at 1373 K during 30 min and quenched in oil. The Fe-25.3 %Ni-0.78 %C alloy after annealing at 1373 K was aged at 773 K in vacuum during 2 h. The phase composition was examined by X-ray diffraction. The alloys were in austenitic state after the heat treatment. The microhardness was measured on 2 mm thick plates of the alloys using standard equipment.

The mechanical surface treatment of the alloys was carried out using two methods: the power ultrasonics (UST and impact low-frequency treatment (IST). The frequency of ultrasonic generator was $f = 20$ kHz, the frequency of magnetostrictor was $f = 1\text{--}3$ kHz, the vibration amplitude was 20 μm . The foils were treated in vacuum chamber during 8 s. The Mossbauer spectra and microhardness were measured and then the samples were treated again for 8 s. The temperature was controlled during processing and found to remain unchanged for 8 s while its increase to 353 K was observed during the treatment for 1.5 min. In the IST, the frequency of impact was $f = 0.78$ Hz. The hammer mass was 78 g, the drop height 20 cm. The IST was carried out in air for 3.5 to 8 h. The difference between two treatment methods is associated with different power transmitted by metal cap to the sample surface, 24 J/s at UST 1–3 kHz and 0.15 J/s for IST.

The transmission Mossbauer spectra were measured on MS1101E spectrometer (Rostov na Donu) at room temperature. The ^{57}Co isotope in Cr matrix was used as gamma-radiation source. The spectra were stored in a multichannel scaler with 512 channels and fitted according to least square fit routine by Lorentz lines. The Window method was

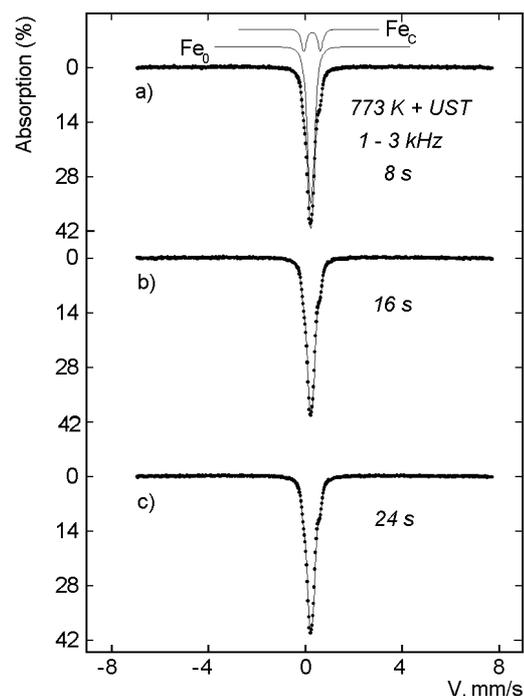


Fig. 1. Mossbauer spectra of the Fe-25.3 %Ni-0.78 %C alloy after ageing at 773 K and UST for 8 s (a), 16 s (b), 24 s (c).

applied to approximate smeared spectra with broadened lines [4]. The velocity calibration was performed at room temperature with a α -Fe foil. The accuracy of the velocity measurements was 0.008 mm/s.

Mossbauer spectra of the alloys after annealing and mechanical treatment are shown in Fig. 1, Fig. 2 and the hyperfine parameters are listed in Table 2. The spectrum of the Fe-25.3 %Ni-0.78 %C alloy in initial state is typical of such a composition and consists of broadened singlet and doublet. The broadened central line was fitted by sextet with low hyperfine magnetic field $H_0 = 0.6$ T (Table 2) following the approach considered in [5]. As determined in [5], the singlet 1 in Mossbauer spectra of the austenitic Fe-Ni-C alloys containing approximately 25 % Ni is attributed to Fe atoms with no carbon nearest neighbors (nn) (Fe_0) and the doublet 2 is related to Fe atoms with one or two carbon nn (Fe_C).

The spectra for samples annealed at 1373 K and aged at 773 K are similar in shape and a small decrease of intensity of the doublet 2 after ageing was observed. The decrease of the doublet intensity points to clustering of interstitial atoms in austenite. Note that new lines with quadrupole splitting lagged twice than for component 2 were not detected in the spectrum.

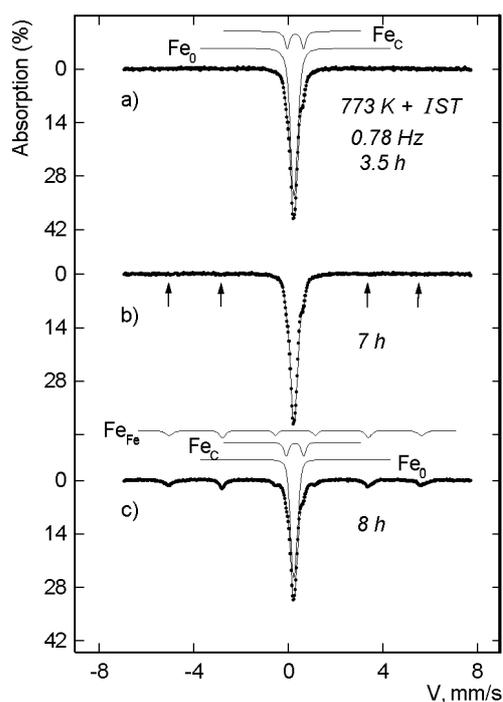


Fig. 2. Mossbauer spectra of the Fe-25.3 %Ni-0.78 %C alloy after ageing at 773 K and IST for 3.5 h (a), 7 h (b), 8 h (c).

This means that atomic ordering as Fe₃NiC in the alloy does not occur after aging. The structure of the Fe-25.3 %Ni-0.78 %C alloy spectra was not changed after UST during 8 s (Fig. 1, a), however, the doublet 2 intensity was decreased (Table 2). The increasing processing time to 16 s and 24 s resulted in the decrease of total area under the doublet by approximately 21 %. No other subspectra which could be attributed to structural transformations or atomic ordering were revealed.

The reduction of the doublet intensity in the spectrum after UST is associated with the decreased relative number of Fe atoms having one or two C nn and could be explained as follows. The generation of the crystal structure defects by power ultrasonics increases the mobility of interstitial atoms resulting in their clustering. The C-C pairs in the Fe-Ni-C austenite were revealed in [5] and explained by the soft C-C repulsion in the first and second coordination shells [6, 7]. In addition, the interaction of interstitial atoms with vacancies and dislocations produce segregations that may decrease the number of Fe_C atoms.

Table 2. The parameters of Mossbauer spectra*

| Alloy | Treatment | Subspectrum | δ_i , mm/s ± 0.008 | Δ_i , mm/s ± 0.008 | H_i , T ± 0.2 | $\Gamma_{i,6}$, mm/s ± 0.008 | $S_i/\sum S_i$, % ± 0.5 |
|---------------------|--------------------|-----------------|----------------------------------|----------------------------------|---------------------|--------------------------------------|------------------------------|
| Fe-25.3 %Ni-0.78 %C | Ageing, 773 K, 2 h | Fe ₀ | -0.038 | 0.00 | 0.60 | 0.252 | 81.10 |
| | | Fe _C | 0.004 | 0.660 | - | 0.232 | 18.90 |
| | UST, 8 s | Fe ₀ | -0.040 | 0.00 | 0.60 | 0.282 | 83.10 |
| | | Fe _C | 0.006 | 0.679 | - | 0.233 | 16.90 |
| | UST, 16 s | Fe ₀ | -0.036 | 0.00 | 0.60 | 0.282 | 84.80 |
| | | Fe _C | 0.007 | 0.683 | - | 0.232 | 15.20 |
| UST, 24 s | Fe ₀ | -0.038 | 0.00 | 0.60 | 0.282 | 85.12 | |
| | Fe _C | 0.004 | 0.689 | - | 0.233 | 14.88 | |
| Fe-25.3 %Ni-0.78 %C | IST, 3.5 h | Fe ₀ | -0.041 | 0.00 | 0.60 | 0.282 | 85.45 |
| | | Fe _C | 0.009 | 0.690 | - | 0.234 | 14.55 |
| | IST, 7 h | Fe ₀ | -0.038 | 0.00 | 0.60 | 0.282 | 85.73 |
| | | Fe _C | 0.013 | 0.693 | - | 0.234 | 14.27 |
| | IST, 8 h | Fe ₀ | -0.044 | 0.00 | 0.60 | 0.282 | 70.66 |
| | | Fe _C | -0.008 | 0.737 | - | 0.234 | 11.80 |
| Fe _{Fe} | | 0.018 | -0.001 | 33.5 | 0.368 | 17.54 | |

* H_i , is the hyperfine magnetic field; δ_i , the isomer shift with respect to α -Fe; Δ_i , the quadrupole splitting; $\Gamma_{i,6}$, the line width; $S_i/\sum S_i$, the relative integral intensity of i subspectrum.

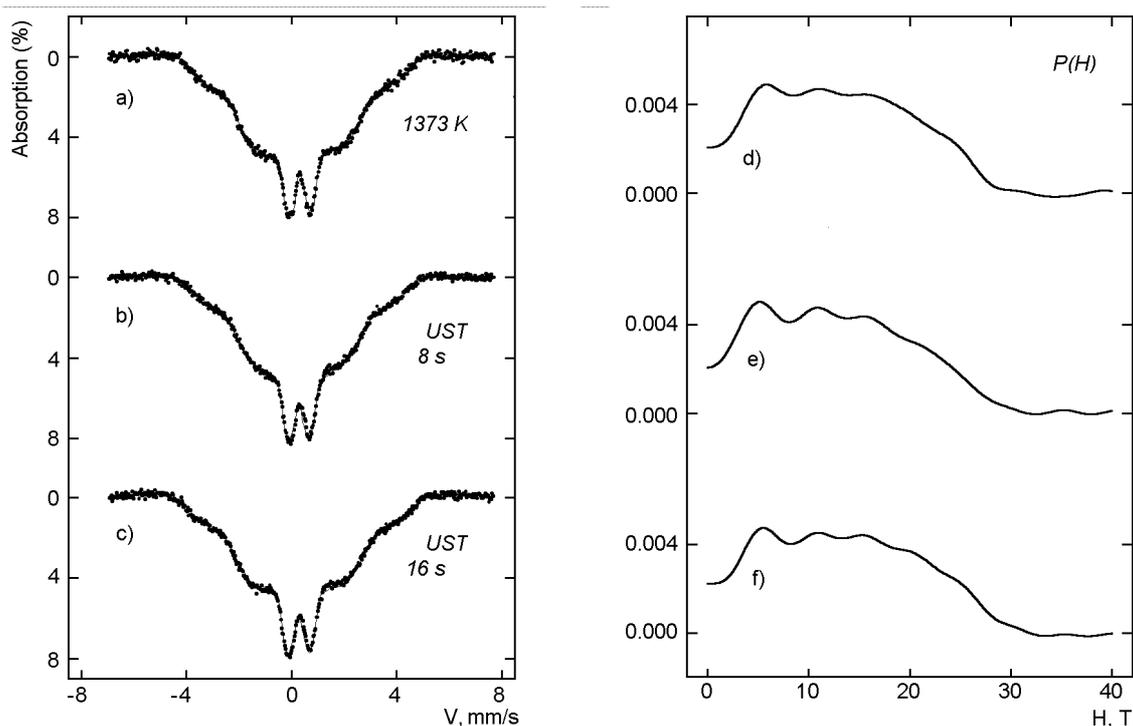


Fig. 3. Mossbauer spectra of the Fe-30.5 %Ni-1.5 %C alloy and the distribution of the hyperfine magnetic fields after ageing at 1373 K (a,d) and UST for 8 s (b,e), 16 s (c,f).

Another picture is observed under the treatment of the Fe-25.3 %Ni-0.78 %C alloy foil by low-frequency IST. The spectrum shape depends considerably on the IST duration (Fig. 2). The intensity of doublet decreased by 23 % after the 3.5 h of IST as compared to aged state and this effect is similar to the result derived from foil after UST (Table 2). Such a change results from formation of carbon segregations on dislocations arisen under the IST, which contributed into background and were not separated in the spectrum.

The IST during 7 h did not principally change the doublet intensity, however, the traces of the sextet lines are appeared that, in our opinion, corresponds to the martensitic phase (Fig. 2b). In fact, the IST for 8 h results in increased intensity of this sub-spectrum with the magnetic field of 33.5 T (Fig. 2c). This field corresponds to iron atoms in martensite [8, 9]. The amount of martensitic phase estimated from the sextet intensity was approximately 18 % (Table 2). Attempts to increase the IST duration over 8 hr results in damage of foil due to the heavy cold work and appearance of martensitic phase.

The estimations show that the total number of impacts is $N_{IST} = 22560$ for 8 h IST and $N_{UST} = 72000$ for 24 s UST. Thus, the

martensite transformation in the Fe-25.3 %Ni-0.78 %C alloy induced by IST occurs at room temperature, which is higher than martensitic point M_s . The effect of strain and stresses on martensitic transformation was considered in detail by G.B.Olson and M.J.Cohen [10] and described by G.V.Kurdyumov [11]. As it has been shown, the stresses favor the formation of martensite in micro-areas where the martensitic nuclei would be appeared spontaneously under cooling without stresses. The deformation creates new areas for appearance of the nuclei. The blocking of dislocations with carbon and martensitic phase hardens considerably the alloy resulting in localization of strain as the IST duration increases and finally damaging the alloy that was observed. Unlike the IST, the UST does not change the phase composition of the Fe-25.3 %Ni-0.78 %C alloy and does not damage the foil. We assume that this is caused by more homogeneous distribution of crystal structure defects after UST than after IST and the absence of the strain localization.

In order to check this assumption, we studied the UST and IST effect on the microhardness, phase composition, and hyperfine interactions in the Fe-30.5 %Ni-1.5 %C alloy with high C and Ni concentra-

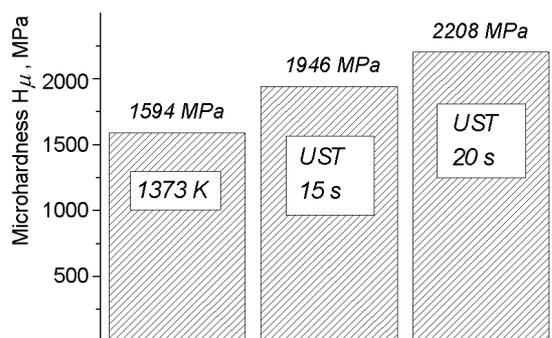


Fig. 4. Microhardness of the Fe-30.5 %Ni-1.5 %C alloy in initial state (1373 K) after UST for 15 s and 20 s.

tions. The choice of this composition is associated with the fact that the hyperfine magnetic structure is considerably developed in this alloy [12, 13] which could be changed under the UST and IST. Moreover, the martensitic point decreases below the liquid nitrogen temperature due to the high C and Ni concentration and the martensite transformation does not occur under cooling. Besides, the higher concentration of carbon should result in more effective strain hardening of the alloy.

The Mossbauer spectrum of the Fe-30.5 %Ni-1.5 %C alloy in initial state after annealing at 1373 K is presented in Fig. 3a. The spectrum shape differs from that relating to the Fe-25.3 %Ni-0.78 %C alloy by considerable developed magnetic structure evidencing magnetic ordering. This spectrum was analyzed by the Window

method [4]. This means that the Curie temperature lies above the room one. The magnetic measurements of the Fe-30.5 %Ni-1.5 %C alloy have shown that $T_c = 438$ K [14]. The magnetic ordering in the alloy occurs due to carbon dissolution and is characterized by existing of structural and magnetic inhomogeneities [15]. The distribution of the hyperfine magnetic fields is relatively wide and lies within the range of 2–32 T (Fig. 3d).

The microhardness measurements of the Fe-30.5 %Ni-1.5 %C alloy before and after UST has shown that H_{μ} increases from 1594 MPa (1373 K) to 1946 MPa (UST for 15 s) and to 2208 MPa (UST for 20 s) (Fig. 4). The data obtained point to a surface hardening that may be attributed to the strain hardening or to the martensitic component appearance.

As is shown, the UST during 8 s corresponding to the impact number 24000 and the next 8 s (total 16 s) did not considerably change the hyperfine magnetic structure of the spectra (Fig. 3b,c). This result means that the phase composition of the alloy is not changed. The distribution of the hyperfine magnetic fields was changed on the high-field side, which is shifted towards larger values (Fig. 3e,f). Since a correlation exists in Fe-Ni-C alloys between magnetic order and atomic distribution [12, 13], the observed change in $p(H)$ curve points to the more homogeneous atomic distribution in the solid solution induced by UST.

In contrast, the Mossbauer spectrum of the Fe-30.5 %Ni-1.5 %C alloy after IST is changed considerably as compared to its in-

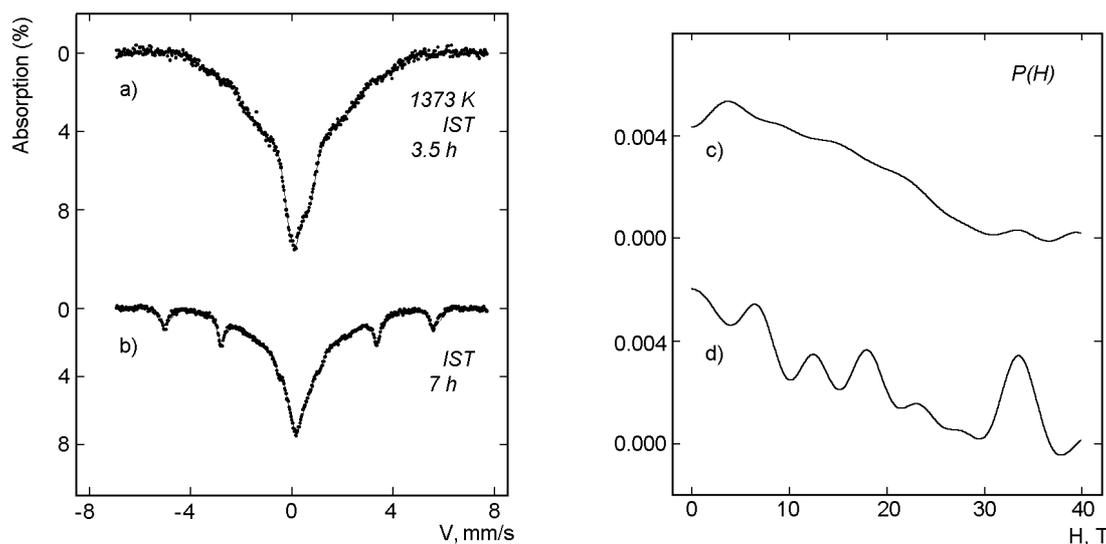


Fig. 5. Mossbauer spectra of the Fe-30.5 %Ni-1.5 %C alloy and the distribution of the hyperfine magnetic fields after IST for 3.5 h (a,c), 7 h (b,d).

initial state (Fig. 5a). The treatment results in the spectrum narrowing even for 3.5 h (Fig. 5a) and decreasing the mean magnetic field value (Fig. 5b). The reason is the redistribution of carbon atoms between induced defects and solid solution and the destroying the short-range atomic order. The new components was appeared in the spectrum after IST during 7 h (Fig. 5c) with the magnetic field $H = 133.5$ T (Table 2) of this subspectrum corresponds to martensitic phase. The additional intense high-field component corresponding to martensite, the decreasing middle-field contribution and increasing the low-field component relating to austenite are observed in the $p(H)$ function after such a treatment (Fig. 5d). The martensitic phase amount estimated from integral intensity in the $p(H)$ curve is 11 % that is less by the factor of two than for the Fe-25.3 %Ni-0.78 %C alloy after such a treatment (Table 2).

Thus, the surface low-frequency deformation of the alloy having the martensite point below the liquid nitrogen temperature results in martensitic transformation even at room temperature. We assume that the difference between UST and IST is associated with different defect structure and with the energy transferred to metal sample in these two cases. The estimations have shown that for 8 h of IST, the energy is 3175 J while being 56.8 J for 24 s of UST.

Thus, as is established by means of Mossbauer spectroscopy, the UST and IST change the hyperfine magnetic structure in f.c.c. Fe-Ni-C alloys resulting from redistribution of interstitial atoms due to interaction with the crystal structure defects. The UST in the considered mode does not change the phase composition of the alloys and increases the microhardness approximately by 40 % due to blocking of crystal structure defects with carbon atoms. The IST causes both atomic redistribution and martensitic transformation in both Fe-25.3 %Ni-0.78 %C and Fe-30.5 %Ni-1.5 %C alloys. The ultrasonic treatment is more effective method for strain hardening

of f.c.c. interstitial alloys than impact surface treatment; this results from more homogeneous distribution of crystal structure defects and their effective blocking with interstitials.

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References

1. A.V.Kulyomin, *Ultrasound and Diffusion in Metals*, Metallurgia, Moscow, (1978) [in Russian].
2. A.V.Kulyomin, V.V.Kononov, I.A.Stebelkov, *Problemy Prochnosti*, **1**, 70 (1981).
3. L.N.Larikov, in: *Metals, Electrons, Lattice*, Naukova Dumka, Kiev (1975), p.440 [in Russian].
4. B.Window, *J. Appl. Phys.*, **44**, 2853 (1973).
5. V.G.Gavriljuk, V.M.Nadutov, *Fiz. Metal. Metalloved.*, **55**, 520 (1983).
6. V.M.Nadutov, V.A.Tatarenko, K.L.Tsynman, in: *Proc. 3rd Int. Conf. on High Nitrogen Steels*, ed. by V.G.Gavriljuk and V.M.Nadutov, Kiev, Institute for Metal Physics (1993), p.106.
7. V.G.Balanyuk, V.N.Bugaev, V.M.Nadutov, A.L.Sozinov, *Phys. Stat. Sol.*, **207(b)**, 3 (1988).
8. K.Ullakko, V.M.Gavriljuk, V.M.Nadutov, *Acta. Met.*, **25A**, 889 (1994).
9. V.M.Nadutov, *Materialovedeniye*, **4**, 15 (2000).
10. G.B.Olson, M.J.Cohen, *Less Common Metals*, **28**, 107 (1972).
11. G.V.Kurdyumov, *Transformations in Iron and Steels*, Nauka, Moscow (1977) [in Russian].
12. V.M.Gavriljuk, V.M.Nadutov, *Fiz. Metal. Metalloved.*, **56**, 555 (1983).
13. V.M.Gavriljuk, V.M.Nadutov, *Cryogenics*, **34**, 485 (1994).
14. V.M.Nadutov, Ye.O.Svystunov, T.V.Efimova, A.V.Gorbatov, in: *Material Research in Atomic Scale by Mossbauer Spectroscopy*, ed. by M.Mashlan, M.Miglierini and P.Schaaf, NATO Sci. Series, vol.94, Kluwer Academic Publishers, Dordrecht (Boston-London), The Netherlands (2003), p.361 and V.M.Nadutov, V.A.Tatarenko, S.A.Pankratiev, *Metallofiz. Novejshie Tekhnol.*, **25**, 1633 (2003).
15. V.M.Nadutov, V.M.Garamus, R.Willumeit, Ye.O.Svystunov, *Metallofiz. Novejshie Tekhnol.*, **24**, 717 (2002).

Мессбауерівський аналіз структури Fe–Ni–C сплавів після термічної та ультразвукової обробок

В.М.Надуртов, Д.В.Семенов, Є.О.Свистунов, Г.І.Кузьмич

Мессбауерівську спектроскопію використано для дослідження на атомному рівні аустенітних Fe–Ni–C сплавів після ультразвукової та низькочастотної ударної поверхневої обробки. Вивчено фазовий склад і надтонку структуру ГЦК сплавів Fe–30.5 % Ni–1.5 % C та Fe–25.3 % Ni–0.78 % C після нагрівання до 1373 К і 773 К у вакуумі та наступної ударної ультразвукової обробки (УЗО) ($f = 1\text{--}3$ кГц, амплітуда 20 мкм, $t = 8\text{--}24$ с). Результати проаналізовано у порівнянні з впливом низькочастотної ударної поверхневої обробки (УПО) сплавів. Після УЗО проаналізована мікротвердість сплавів.