

https://doi.org/10.15407/ufm.19.01.070 PACS numbers: 64.60.Bd, 64.70.kd, 66.10.cd, 66.30.Lw, 81.16.Hc, 81.30.Kf

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# EFFECT OF CYCLIC MARTENSITIC $\gamma - \epsilon - \gamma$ TRANSFORMATIONS ON DIFFUSION CHARACTERISTICS OF CARBON IN AN IRON-MANGANESE ALLOY

Carbon-diffusion characteristics in metastable  $\Gamma 18C2$  iron-manganese alloy after the cyclic  $\gamma - \epsilon - \gamma$  (f.c.c.-h.c.p.-f.c.c.) martensitic transitions were investigated using the radioactive-isotope method. As shown, the process of carbon transport acceleration in the alloy phase-hardened by means of the  $\gamma - \varepsilon - \gamma$  transformations was caused by two independent mechanisms. They are as follow: athermal one realized via the stress field occurrence under the cyclic martensitic transitions and thermoactivated one realized during subsequent diffusion annealing due to low-angle subboundaries as well as the one-dimensional and two-dimensional crystal structure defects in f.c.c. austenite and h.c.p.  $\varepsilon$ -martensite generated during these transitions. After the cyclic  $\gamma - \epsilon - \gamma$  martensitic transformations, the diffusion coefficient of carbon at low temperatures (100-350 °C) increased by more than three orders of magnitude. In this case, the diffusion coefficient at 325 °C corresponds to the stationary diffusion coefficient at 900 °C. Maximum carbon-diffusion coefficient rising was observed when number of thermal cycles was increased up to 100 and maximum structure defects density increasing was fixed. Phase composition variation was as an additional cause of carbon-diffusion characteristics changing during the  $\gamma - \epsilon - \gamma$  cycling and subsequent diffusion annealing.

**Keywords:** diffusion, martensite, austenite, radioisotope, dislocation, stacking fault defect.

### Introduction

Different phase transformations can efficiently affect the diffusive mobility of substitutional and interstitial atoms in metastable alloys. The degree and quality of such an influence depend on the structural state of the alloys that formed due to the phase transformations [1-3]. A significant acceleration of diffusion is found in nanocrystalline materials with a structure splintered due to severe plastic deformation [4-8].

Phase and structural transformations occurring in metals and alloys with a bulk effect and therefore forming a certain system of defects in the crystalline structure cause an amplification of diffusion processes and stimulate the mass transport of atoms on macroscopic distances. Martensitic transformations that can be realized *via* the shear diffusionless mechanism significantly accelerate diffusion of substitutional and interstitial atoms in the reversible parent phase [9–14]. Diffusive mobility of alloying atoms substantially depends on cooling and heating regimes necessary for realization of direct and reversible martensitic transformation. A considerable change in the diffusion coefficient in iron and thallium was observed only when a certain critical thermal cycling rate was reached [2, 3].

Due to the atomic  $\gamma$ - $\alpha$  (f.c.c.-b.c.c.) restructuring of original crystal lattice into the martensitic one in alloy with an explosive transformation kinetics without additional annealing the atomic mass transport on a large distance (up to 60–100 µm) was observed [12, 13]. Behaviour of concentration dependence of diffusing atoms on a penetration depth indicates about the bulk character of diffusion at the cryogenic temperatures.

Because of  $\gamma - \alpha - \gamma$  (f.c.c.-b.c.c.-f.c.c.) martensitic transformations in austenite phase of iron-nickel alloys, the dislocation density was increased by more three orders of magnitude [14, 15], which resulted to enhanced diffusion of substitutional atoms as well as carbon atoms at low temperatures [16, 17]. Particularly, diffusion coefficients of Fe and Ni atoms at 400 °C corresponded to coefficients of stationary diffusion at 900 °C [17]. The enhanced diffusion was affected by two factors: high dislocation density and additional low-angle subboundaries of disorientated nanofragments together with subboundaries of deformation twins formed due to the  $\gamma - \alpha - \gamma$  cycles. The low-temperature diffusion anomaly in iron-nickel alloys after the cyclic  $\gamma - \alpha - \gamma$  transformations is similar to that described in the literature diffusion anomaly in nanocrystal materials obtained by the gas-condensate, electrodeposition, and severe plastic deformation methods [4]. Due to the  $\gamma - \alpha - \gamma$  transformations, the diffusive mobility of carbon atoms was also appreciably enhanced.

The  $\gamma - \varepsilon - \gamma$  martensitic transformations in iron-manganese alloys result to one order increasing of dislocation density in reversible austenite phase [18]. The difference in increase of dislocation density in comparison with  $\gamma - \alpha - \gamma$  transformations is caused by different degree of the volume effect  $\gamma - \alpha$  and  $\gamma - \varepsilon$  transformations (3% and 1.75%, respectively). The  $\gamma - \varepsilon - \gamma$  transformations in iron-manganese reversible austenite with low stacking fault energy cause accumulation of random stack-

ing faults, but do not result to significant structural fragmentation and formation of additional subboundaries. A considerable difference of the structural state and imperfection degree in the crystal lattice of phase components, generated due to the  $\gamma-\alpha-\gamma$  and  $\gamma-\epsilon-\gamma$  transformations, stimulate further investigations of effect of martensitic  $\gamma-\epsilon-\gamma$  transformations on diffusion characteristics in alloys with a low stacking fault energy. Authors of Ref. [10] studied an effect of  $\gamma-\epsilon-\gamma$  transformations in cobalt and iron-manganese alloys on diffusion characteristics of substitutional (Fe and Co) atoms and revealed a significant enhancement of their diffusive mobility.

Experimental studies of effect of  $\gamma - \varepsilon - \gamma$  martensitic transformations on diffusion characteristics of interstitial atoms still were not carried out. That is why the purpose of this work is to investigate the effect of the cyclic  $\gamma - \varepsilon - \gamma$  martensitic transformations on the diffusion characteristics of carbon in the iron-manganese alloys using the method of radioactive isotopes.

### **Materials and Experimental Technique**

The studies were performed for a metastable  $\Gamma$ 18C2 alloy (18.3 mas.% Mn; 2.1 mas.% Si), where a large amount of martensitic  $\varepsilon$ -phase was generated due to the thermal cycling and  $\gamma - \varepsilon - \gamma$  transformations. This allowed to reach a high degree of the phase hardening from the  $\gamma - \varepsilon - \gamma$ transformations. Cyclic  $\gamma$ - $\varepsilon$  straight lines and reversible  $\gamma$ - $\varepsilon$  transformations were sequentially realized in alloys during cooling in the liquid nitrogen and subsequent heating in the salt bath at a temperature of 800 °C. In this case, the cooling rate within the range of direct transformations and the heating rate in the range of reversible transformation were reached: 20 °C/s and 80 °C/s, respectively. Such a thermal cycling regime resulted to deceleration of relaxation processes and provided an effective accumulation of structural defects (due to both direct and reversible transformations) that can strongly affect diffusion processes in the phase-hardened alloys. Indeed, a considerable increasing of diffusion coefficients in Ni and Tl were observed as long ago as 1962 [19] only when a certain critical thermal cycling rate was reached. After the  $\gamma - \varepsilon - \gamma$  transformations, a diffusion annealing (homogenization) of the phase hardened alloys was carried out at the temperatures of 100 °C and 200 °C.

X-ray studies were performed using the automated diffractometer DRON-3 in the radiation of iron anode monochromatized with a lithium fluoride. The amount of  $\varepsilon$ -phase was measured *via* the ratio of integral intensity of  $(111)_{\gamma}$  and  $(002)_{\varepsilon}$  diffraction reflexes [18]:

$$M_{\scriptscriptstyle{
m c}} = rac{100\%}{1+0.27rac{I_{(111)\gamma}}{I_{_{(002)
m c}}}}\,.$$

Using of these reflexes from the austenite and  $\varepsilon$ -martensite crystallographic planes, which were parallel in accordance with orientation relations between f.c.c. and h.c.p. lattices, enabled to calculate an amount of  $\varepsilon$ -phase without decrease in accuracy of the measurement in case of the appearance of texture during the thermal cycling process.

In order to characterize structural state of the phase-hardened alloy and crystal lattice defectiveness degree of the phase components, the maximal angle disorientation  $\psi$  of austenite lattice and  $\varepsilon$ -martensite as well as concentration of random stacking faults were measured. The  $\psi$ value, which characterizes formation possibility for low-angle dislocation subboundaries, was measured by the value of azimuth smearing of (200) $\gamma$  and (101) $\varepsilon$  reflexes at the diffraction pattern from the single crystal samples [15].

The concentration ( $\alpha$ ) of random stacking faults in f.c.c. lattice was measured *via* the change of Bragg angles of certain diffraction reflexes [18, 20-23] or *via* the value of their physical broadening [24]. According to Refs. [20, 21], for f.c.c. structure that contains stacking faults in {111} planes, the Bragg angle remains invariable for that reflexes, the Miller indexes for which satisfy the conditions (in cubic coordinates):

$$(h + k + 1) = 3N, (2h - k - 1) = 6N',$$

where N and N' are integers.

The value of  $\alpha$  for austenite of  $\Gamma$ 18C2 alloy was determined by the mutual shift of Bragg angles of (200), and (111), reflexes,

$$\Delta(2\theta_{200} - 2\theta_{111}) = -\frac{45\alpha_{\Sigma}\sqrt{3}(2tg\theta_{200} - tg\theta_{111})}{2\pi^2}, \qquad (1)$$

where  $\theta$  is a Bragg angle, and  $\alpha_{\Sigma}$  denotes concentration of random stacking faults.

The value of  $\alpha_{\Sigma}$  was determined using the reflex half-width [18]:

$$B = \frac{3\sqrt{1 - [(1 - 3\alpha_{\Sigma}(1 - \alpha_{\Sigma})]})}{\sqrt{1 + [(1 - 3\alpha_{\Sigma}(1 - \alpha_{\Sigma})]})}},$$
 (2)

where B denotes a half-width of the reflex in radians.

The value of  $\alpha_{\Sigma}$  for h.c.p. lattice can be determined *via* the physical broadening of the reflexes that meet conditions  $H - K = 3N \pm 1$  and  $L \neq 0$  (*N*—integers) [22, 23, 25, 26]. In this case, we have to take into account that random stacking faults do not cause broadening of (*hk*0) reflexes.

Concentration of random stacking faults within the  $\{001\}_{\epsilon}$  crystallographic planes was calculated using the formula [20]

$$B = \frac{\sqrt{1 - [(1 - 3\alpha_{\Sigma}(1 - \alpha_{\Sigma})]]}}{\sqrt{1 + [(1 - 3\alpha_{\Sigma}(1 - \alpha_{\Sigma})]]}};$$
(3)

here, *B* denotes a half-width of (*hkl*) reflex. The value of  $\alpha_{\Sigma}$  in this expression denotes concentration of random stacking faults without their separation into deformed and twinned.

Diffusion characteristics of carbon were determined by the radioactive isotope method. Radioactive isotope of carbon <sup>14</sup>C was deposited on the alloy surface of  $10 \times 10 \times 5$  mm<sup>3</sup> in size during the cementation process at a temperature of 800 °C using the carburizer containing impurities of BaCO<sub>3</sub> compound with a radioactive isotope of carbon <sup>14</sup>C. During the cementation of the samples for X-ray investigation, the carburizer BaCO<sub>3</sub> was used without <sup>14</sup>C isotope. Thereby, the radiation safety during the X-ray diffraction procedure was attained.

The depth distribution of carbon atoms was determined *via* the layer skimming with a measurement of  $\beta$ -activity radioisotope <sup>14</sup>C. Diffusion coefficient of carbon (*D*) was calculated as

$$D = -\frac{1}{4\tau t g \alpha}, \qquad (4)$$

where  $\tau$  is a diffusion annealing time,  $\alpha$  is a slope angle of a straight line to the abscissa axis at the graphs of dependences of  $\ln I$  on  $x^2$ , where I is a specific  $\beta$ -activity of a sample residue after skimming of a layer of x in depth.

### Effect of the Cyclic $\gamma$ - $\epsilon$ - $\gamma$ Martensitic Transformations and Cementation of Alloy Surface on its Phase Composition

The alloy of  $\Gamma$ 18C2 grade had a temperature of direct martensitic  $\gamma$ - $\epsilon$  transformation higher than a room temperature, therefore the alloy contained a considerable amount of martensite  $\epsilon$ -phase in an initial state. An amount of  $\epsilon$ -martensite did not decrease after the reversible  $\epsilon$ - $\gamma$  transitions and subsequent cooling in a liquid nitrogen. The phase-hardened alloy contained more than 90% of  $\epsilon$ -martensite after the hundredth  $\gamma$ - $\epsilon$ - $\gamma$  cycle. The microstructure of the alloy phase-hardened during 100  $\gamma$ - $\epsilon$ - $\gamma$  transformations is represented in a metallographic image in Fig. 1. The microstructure resembles Widmanstätten patterns (also known as Thomson structures) which are typical for alloy with a large amount of  $\epsilon$ -phase.

One can see in Fig. 1 that  $\varepsilon$ -martensite occupy practically all field of image. Observed (*via* an optical microscope) straight lines on the Widmanstätten pattern of iron-manganese alloys sometimes are considered in the literature [27-30] as the boundaries that separate austenite and  $\varepsilon$ -martensite. The content of  $\varepsilon$ -phase reached under 100%, which indicated that the mentioned straight lines were not boundaries between



Fig. 1. Microstructure of the alloy after 100  $\gamma$ - $\epsilon$ - $\gamma$  cycles

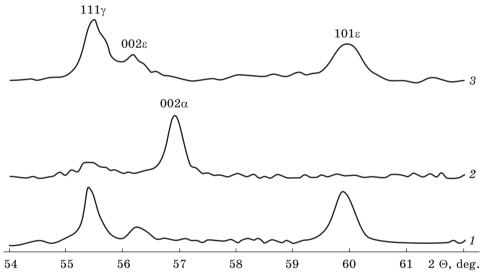
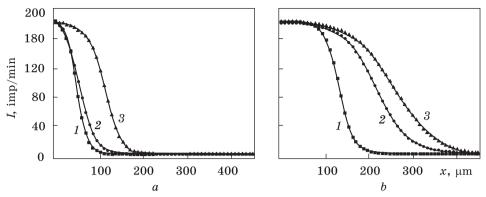


Fig. 2. The diffraction patterns of the alloy in the initial state (1), after cementation (2) and at a depth of 0.05 mm from the cemented surface (3)

the  $\gamma$ - and  $\varepsilon$ -phase. They should be considered as effect of crystallographic orientation shift during the  $\gamma$ - $\varepsilon$  reconstruction.

Thus, there were no a stabilization of reversible austenite due to the increase in degree of phase hardening as it has place for some other iron-manganese alloys [26, 29]. The established fact of increase in  $\varepsilon$ -martensite content as a result of sequential  $\gamma - \varepsilon - \gamma$  transformations indicated a considerable decrease in the stacking fault energy during an increase in a degree of phase hardening of the reversible austenite.



*Fig. 3.* Concentration distribution of radioisotope <sup>14</sup>C by the depth after one (1), 10 (2), and 200 (3)  $\gamma - \varepsilon - \gamma$  cycles (*a*) and 10 (1), 100 (2), and 500 (3)  $\gamma - \varepsilon - \gamma$  cycles and additional diffusion annealing at 200°C during 2500 hours (*b*)

Cementation of the alloy led to the carbon saturation of near-surface layer and resulting change in the phase composition. In an initial state, the alloy contained the  $\varepsilon$ -martensite and residual austenite (Fig. 2, curve 1), whereas after the cementation the diffraction pattern of near-surface carburized layer contained reflexes of the residual austenite and intense reflexes of  $\alpha$ -martensite (Fig. 2, curve 2). There were already no reflexes of  $\varepsilon$ -martensite fixed for the alloy in an initial state. From the value of the parameter  $a_{y}$  for austenite, it was calculated that 0.38 mass percent of carbon dissolved in the  $\gamma$ -phase of near-surface layer. The  $\varepsilon$ -martensite was observed at a depth of 0.05 mm and more (Fig. 2, curve 3). The content of  $\varepsilon$ -martensite increased along the depth from 0.05 to 0.5 mm. The penetration of carbon atoms into the  $\varepsilon$ -solid solution along the sample depth in a process of diffusion annealing occurred from the residual austenite and  $\alpha$ -martensite of near surface carburized layer via through the  $\gamma-\varepsilon$  and  $\alpha-\varepsilon$  interphase boundaries. Such boundaries can serve as diffusion barrier for the movement of carbon atoms. Evidently that the effectiveness of barriers differed for boundaries between different phases, since in one case carbon atoms are transported into the lattice with a more close-packed structure ( $\alpha$ - $\varepsilon$  barrier), whereas, in another case, into the lesser close-packed lattice ( $\gamma$ - $\varepsilon$  barrier). The analysis of diffusion transport of carbon atoms from the  $\alpha$ -phase into the  $\varepsilon$ -one became more complicated because  $\alpha$ -solid solution decomposed and depleted with a carbon to the state of equilibrium solubility in the  $\alpha$ -phase at the diffusion annealing temperatures (100–200 °C). In this case, when carbon leaves the  $\alpha$ -solid solution, it can occupy crystal-lattice defects (dislocations, stacking faults), enter into the carbide content or form graphite globules. The diffusion path of carbon into the sample depth can significantly differ and differently affect the integral diffusion characteristics of carbon in phase-hardened alloys. A role of interphase boundaries in the change of diffusion characteristics of carbon in iron-manganese alloys with  $\gamma-\epsilon$  transformation deserves additional investigations.

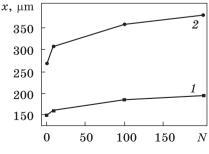
# Effect of Cyclic $\gamma$ - $\epsilon$ - $\gamma$ Martensitic Transformations on the Diffusion Characteristics of Carbon

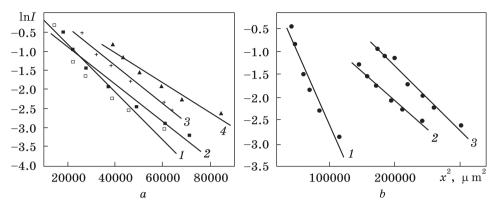
Measurements of diffusion profiles for carbon in alloys, phase-hardened with the  $\gamma - \varepsilon - \gamma$  transformations, were carried out for two cases: after the cementation and transformation cycles, and after subsequent additional diffusion annealing at 100 °C and 200 °C. It turned out that transport of carbon, as a result of  $\gamma - \varepsilon - \gamma$  cycles, occurred on the macroscopic depth without additional diffusion annealing. After the first transformation cycle, the penetration depth (x) of carbon (without diffusion annealing), amounted 127  $\mu$ m. As the cycle number increased up to 100, the depth increased up to 200 µm. Figure 3 represents typical distributions of  $\beta$ -activity of radioisotope <sup>14</sup>C along the depth in the alloys with different phase hardening degree. Subsequent diffusion annealing has led to a significant increase in the x-value (Fig. 3, b). The difference in the increase in the depth of total carbon penetration via two different diffusion mechanisms increased significantly with increasing number of cycles as Fig. 4 shows. For instance, after 10 cycles, the mentioned difference was 97  $\mu$ m, whereas, after 100 cycles, it reached 204  $\mu$ m. In addition to experimental results in Fig. 4, we carried out 500  $\gamma$ - $\epsilon$ - $\gamma$  cycles and corresponding diffusion annealing. We revealed that an increment of the penetration depth (due to such a treatment as compared to the treatment with 200  $\gamma$ - $\epsilon$ - $\gamma$  cycles) was 27  $\mu$ m, *i.e.*, 6%. A small increase in depth for a significant number of thermocycles showed that the active penetration of carbon atoms occur during the first  $100-200 \gamma - \epsilon - \gamma$  transformations, whereas the penetration process gradually attenuate during the next cycling.

The dependence  $\ln I(x^2)$  for all cycling regimes was found to be close to the linear one as Fig. 5 demonstrates. This indicates about predominately bulk character of diffusion.

Calculation of carbon diffusivity from the corresponding curves in

Fig. 4. Penetration depth vs. number of  $\gamma - \varepsilon - \gamma$  cycles for <sup>14</sup>C atoms without annealing (1) and after additional diffusion annealing at 200 °C during 2500 hours (2)





*Fig. 5.* The estimated dependence of  $\ln I x^2$ ) for two cases: (*a*) after one (1), 10 (2), 100 (3), and 200 (4)  $\gamma - \varepsilon - \gamma$  cycles; (*b*) after 10 (1), 100 (2), and 500 (3)  $\gamma - \varepsilon - \gamma$  cycles and additional diffusion annealing at 200 °C during 2500 hours

Fig. 3, a is impossible due to impossibility of correct determination of diffusion process time, which evidently is commensurable with time of martensitic transformation elapse. Actually, transport mechanism for carbon atoms is connected with the structural f.c.c.-h.c.p. reconstruction and accompanying resulting propagation of the stress force field as a result of the transformation-induced change in crystal volume and shape. Apparently, movement over the interstitial sites is the most probable diffusion mechanism for carbon atoms in the field of stresses. The increase of the penetration depth in case of the cycle repetition (Fig. 3, a) is indicative of possibility to accumulate internal stresses that sequentially stimulate an additional carbon transport. Apparently, this carbon transport mechanism should be athermal. It was shown earlier that an athermal mechanism of mass transport of substitutional and interstitial atoms was realized under the explosive kinetics of the martensitic f.c.c.-b.c.c. transformation in the iron-nickel alloys [12, 13].

During the  $\gamma - \varepsilon - \gamma$  transformations in the local regions of the alloy, internal structural tensile and compressive stresses appeared in accordance with a sign of the bulk effect of direct  $\gamma - \varepsilon$  (increase in specific volume) and reverse  $\varepsilon - \gamma$  (decrease in specific volume) transformations. Stretched regions appeared due to direct  $\gamma - \varepsilon$  transformation at low temperatures when relaxation processes were decelerated and internal stresses were conserved. This created conditions for the movement of carbon atoms in such areas. We can assume that the inverse  $\varepsilon - \gamma$  transformation contributed lesser to conditions for the migration of carbon atoms *via* the athermal mechanism.

The penetration depth for carbon atoms in alloy phase-hardened at  $100 \,^{\circ}$ C and  $200 \,^{\circ}$ C significantly increased as the number of previous

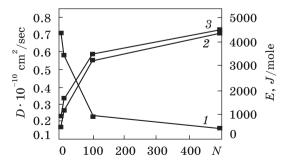
transformation cycles increased (Fig. 3, *b*). Thermoactivated character of transport process enabled calculation of carbon diffusion characteristics. After the first  $\gamma \leftrightarrow \varepsilon$  transformations, calculated carbon diffusion coefficient was equal to  $1.7 \cdot 10^{-11}$  i  $2.3 \cdot 10^{-11}$  cm<sup>2</sup>/sec for 100 °C and 200 °C, respectively. Increase in number of  $\gamma - \varepsilon - \gamma$  cycles up to 100, caused increase in diffusivity by 2.5 and 3.2 times. Further increase in number of cycles induced an additional, lesser significant, increase in *D* value and deviation of D(N) dependence from the linear one. After 500  $\gamma - \varepsilon - \gamma$  cycles, diffusion coefficient (*D*) increased by 3.2 and 4.2 times at 100 °C and 200 °C, respectively (Fig. 6, curves 1 and 2).

Difference between the diffusivity D at 100 °C and 200 °C was sufficient for determination of diffusion activation energy E. The value of E decreased monotonically as the number of  $\gamma - \varepsilon - \gamma$  transformations increased (Fig. 6, curve 3). The main change of E (by 4 times approximately) occurred when number of cycles was increased up to 100.

For comparison, it should be noted that, for titanium, the increase in the self-diffusion coefficient D in both the low-temperature  $\alpha$ -modification and high-temperature  $\beta$ -modification approximately linearly depends on the number of cycles during martensitic transformations [2, 3]. Note that we observed deviation from the linearity for  $\Delta D(N)$  dependence at high number (more than 100) of cycles. The above-mentioned difference in  $\Delta D$  value for  $\gamma \leftrightarrow \varepsilon$  and  $\alpha \leftrightarrow \beta$  transformations in ironnickel alloys and titanium, respectively, is attributed to different nature of structural defects generated by different types of martensite transformations.

The revealed experimental dependence of the phase composition of the alloy at hand on number of  $\gamma - \varepsilon - \gamma$  cycles, *i.e.*, on phase hardening degree, allowed to separate carbon diffusion coefficients in austenite and martensite. After 100  $\gamma - \varepsilon - \gamma$  cycles in the reversible austenite, the sufficiently active direct  $\gamma - \varepsilon$  transformation took place. Further thermal cycling resulted to observation of the traces of austenite only on the diffraction pattern. It means that, starting from 100 cycles, the value of *D* should be referred to  $\varepsilon$ -martensite. From the dependence of carbon concentration on the penetration depth (Fig. 4, curves 1 and 2), we cal-

*Fig. 6.* The dependences of the diffusion coefficient of carbon *D* at the diffusion annealing temperatures of 100 °C (1) and 200 °C (2) and diffusion activation energy *E* (3) on the number of  $\gamma$ - $\epsilon$ - $\gamma$  cycles



culated coefficients D for 100 °C and 200 °C (Fig. 6, curves 1 and 2) and diffusion activation energy (Fig. 6, curve 3). The value of D was found to be higher for  $\varepsilon$ -martensite in comparison with austenite.

Thus, the intensification of the transport of carbon by the  $\gamma - \varepsilon - \gamma$  transformations occurred *via* the two independent mechanisms: athermal one, which was realized in the process of martensitic transformation, and thermoactivated one, which was realized in the process of the subsequent diffusion annealing.

In connection with this, the conditions for the formation and accumulation of certain structural defective elements of the phase-hardened alloy, which can accelerate the diffusion processes *via* the thermoactivated mechanism, were investigated.

### Characteristics of Disorientation Accumulation in the Crystal Lattices of Austenite and $\epsilon$ -martensite Due to the Phase Hardening

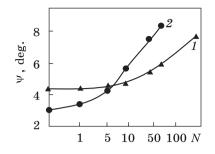
As a result of reverse  $\varepsilon - \gamma$  transformation in the iron-manganese alloys, the dislocation density in reversible austenite increased approximately by one order of magnitude [18, 26]. Electron microscopic investigations showed that further enhancement of the number of  $\gamma - \varepsilon - \gamma$  transformations up to hundreds does not induce an appreciable increase in dislocation density [14]. It means that intensification of the carbon diffusion after the first circle of  $\gamma - \varepsilon - \gamma$  transformations in  $\Gamma 18C2$  alloy is mainly attributed to the enhancement of dislocation density in the reversible  $\gamma$ -phase and  $\varepsilon$ -martensite. Dislocation contribution to the further increase of D value due to many thermal cycles was already insignificant in accordance with an insignificant growth of the dislocation density.

For the iron-manganese alloys, there were no observed formations of large-angle boundaries of austenite grains analogously to iron-nickel alloys [18]. However, due to the many  $\gamma - \varepsilon - \gamma$  transformations in this alloy, the small-angle dislocation subboundaries, which can be characterized by the angle  $\psi$  denoting maximal disorientation of the crystal lattice, appeared.

The  $\psi$  angle increased monotonically with increase in the number of  $\gamma - \varepsilon - \gamma$  transformations and reached value of 6.4° and 8.7° for  $\varepsilon$ - and  $\gamma$ -phase, respectively, as a result of 70 thermal cycles (Fig. 7, curves 1 and 2). After the first 5  $\gamma - \varepsilon - \gamma$  cycles, the  $\psi$  angle for martensite was found to be higher as compared with it was found for austenite. In this range of the cycling, there were no appreciable disorientation accumulation for f.c.c. and h.c.p. lattices because of high crystallographic reversibility of direct  $\gamma - \varepsilon$  and reverse  $\varepsilon - \gamma$  transformations. However, after the tenth transformation cycle, the ability to accumulate disorientation in the lattice of austenite, as well as in the lattice of martensite, began to

Fig. 7. The maximum orientation angle  $\psi$  of the crystalline lattice of  $\varepsilon$ -martensite (1) and austenite (2) vs. the number of  $\gamma$ - $\varepsilon$ - $\gamma$  cycles

manifest itself. In this case, the possibility to compare  $\psi$  angle for  $\gamma$ - and  $\varepsilon$ -phase in the cycling range up to 100 cycles appeared. As the number of cycles increased up to 100, we fixed by means of diffrac-



tion only  $\varepsilon$ -phase, since during the cooling from the end of reverse  $\varepsilon - \gamma$  transformation to the room temperature, direct  $\gamma - \varepsilon$  transformation in the phase-hardened alloy occurred practically completely. Due to this circumstance, already there were no a possibility to measure  $\psi$  angle for the  $\gamma$ -phase lattice at room temperature after 100 cycles (Fig. 7, curve 2). The disorientation accumulation for  $\varepsilon$ -martensite lattice, continued develop continuously with increase of the  $\gamma - \varepsilon - \gamma$  cycles up to 500 (Fig. 7, curve 1). In this case, the growth of diffusion coefficient was also observed.

Above-mentioned regularity of disorientation accumulation for  $\varepsilon$ -martensite lattice indicated on a substantial difference between dependence of degree of the phase hardening and strengthening reached *via* the  $\gamma-\alpha-\gamma$  transition recycles in one case and  $\gamma-\varepsilon-\gamma$  recycles in another one. Authors of Ref. [14] found that strengthening of the metastable iron-nickel alloys can grow only when an additional volume fraction of austenite will take part in each subsequent circle of  $\gamma-\alpha-\gamma$  transformations. For a studied iron-manganese alloy, the phase hardening degree continued to grow after 100 of  $\gamma-\varepsilon-\gamma$  transformations, when austenite phase with a practically 100% volume fraction contributed. This was seen from a considerable increase in the  $\psi$  angle value for  $\varepsilon$ -phase lattice at an increase in number of  $\gamma-\varepsilon-\gamma$  cycles up to 500, whereas the diffraction pattern of the phase-hardened alloy at a room temperature already did not contain reflexes of the  $\gamma$ -phase.

Disorientation of the austenite lattice after the first 5–7 cycles exceeded disorientation of the  $\varepsilon$ -martensite lattice. Larger  $\psi$  angle of austenite lattice indicated about deceleration of  $\gamma$ – $\varepsilon$  martensitic transformation in the maximally disoriented fragments of the reversible austenite. It is known that barrier action of subboundaries of fragmented structure for growth of martensitic crystal is always lesser than action of grain boundaries and is determined, except the fragment sizes, by the angle of the mutual disorientation of adjacent fragments [29]. It was shown earlier by the electron microscopic studies that  $\alpha$ -martensite crystals passed through several weakly disoriented subboundaries of the fragments and stopped by meeting with subboundaries overcritical deformation [29]. Subboundaries of overcritical disorientation affected

the martensitic crystal growth already as grain boundaries. Barrier effect of disorientated subboundaries for  $\alpha$ -martensite crystals [18] was stronger as compared with action for  $\epsilon$ -martensite crystals. Really, after  $3-5 \gamma - \alpha - \gamma$  cycles, the difference of the lattice disorientation for  $\gamma$ - and  $\alpha$ -phase reached 3° [18], whereas after 100  $\gamma - \epsilon - \gamma$  cycles, the difference of the lattice disorientation for  $\gamma$ - and  $\epsilon$ -phase was 6° only. This difference defined also difference in dislocation structure of low-angle subboundaries generated by the cyclic  $\gamma - \alpha - \gamma$  and  $\gamma - \epsilon - \gamma$  martensitic transformations. This, in turn, can determine the different impact degree of such subboundaries on the diffusion characteristics in phase-hardened alloys.

As a result of multiple cycles, the magnitude of the angle was significantly lower than that achieved as a result of cycles in iron-nickel alloys [15, 16]. This is caused by much more higher structural reversibility of direct  $\gamma$ - $\varepsilon$  and reverse  $\varepsilon$ - $\gamma$  transitions. Note that  $\psi$  angle even for intensive  $\gamma$ - $\varepsilon$ - $\gamma$  cycling (1000 cycles) did not exceed value of 9° for austenite, though large-angle grain boundaries possess a disorientation angel of 14–15°. It means that cyclic  $\gamma$ - $\varepsilon$ - $\gamma$  transformations can generate only low-angle subboundaries of the fragments and it is impossible to form new grains of reversible austenite, which would differ from the initial grain orientation, due to the accumulation of the lattice disorientations, as was the case for iron-nickel alloys due to the multiple martensitic transformations.

The subfragments with accumulated disorientation should be considered as a factor in the intensification of the diffusion mobility of carbon. Indeed, it was established earlier that the intensity of diffusion processes significantly increased with increasing angle of disorientation of grain fragments [28]. For example, in the study of the grain boundary diffusion, it was revealed that the self-diffusion coefficient of the silver increased by 500 times with changing  $\psi$  from 9° to 28°. Such dependence can be attributed to the dependence of surface energy of grain boundaries on the disorientation angle. Experimental findings showed that surface energy of grain boundaries for germanium grew sharply for small values of  $\psi$  (up to 14–16°), whereas the surface energy of grain boundaries remained constant in case of large  $\psi$  values [28]. The  $\psi$ -dependences of surface energy of grain boundaries and diffusion coefficient agree with dislocation model for low-angle grain subboundaries.

# Characteristics of the Formation of Random Stacking Faults in the Phase-Hardened Austenite and $\epsilon$ -martensite

As a result of cyclic  $\gamma - \varepsilon - \gamma$  transformations in a reversible austenite and  $\varepsilon$ -martensite of the iron-manganese alloys with a low stacking fault energy, the random stacking faults along the {001}<sub> $\varepsilon$ </sub> crystallographic

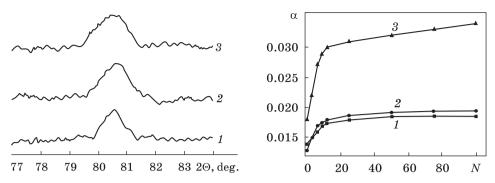
plane were found to be generated. The random stacking faults in f.c.c. and h.c.p. structures showed ability to the accumulation [18, 22, 26]. Therefore, we studied the regularities of the formation and accumulation of the random stacking faults in the austenite and  $\varepsilon$ -martensite of  $\Gamma$ 18C2 alloy due to  $\gamma-\varepsilon-\gamma$  cycles.

It was revealed that the Bragg angle difference  $\Delta \theta = \theta_{(200)\nu} - \theta_{(111)\nu}$  of austenite reflexes decreased due to their mutual shift, whereas the halfdepth of  $\beta$  reflex (200), increased with increasing number of the  $\gamma - \varepsilon - \gamma$ cycles. According to the Paterson theory [20, 22, 23], it indicated about enhancement of the random stacking fault concentration. The value of  $\beta$  grew appreciably for the (102), reflex (Fig. 8), physical broadening of which (in accordance with a theory in Ref. [25]) was the most sensitive to the presence of the twin stacking faults. For the  $(101)_{c}$  reflex, which is sensitive to the presence of deformation stacking faults, the value of  $\beta$  varied much more slightly. To calculate physical broadening of the  $\varepsilon$ -martensite reflexes, as a standard, we used the (100), reflex, the halfwidth of which was practically independent on the random stacking faults. Some changes in the diffusion pattern characteristics of the phase-hardened  $\Gamma$ 18C2 alloy indicated on accumulation during thermal cycling of the random stacking faults in the  $(111)_{y}$  and  $(001)_{z}$  planes of austenite and  $\varepsilon$ -martensite, respectively.

Using values of  $\Delta\theta$  and  $\beta$ , we calculated concentration of the stacking fault defects in austenite and  $\varepsilon$ -martensite. After the first cycle of  $\gamma-\varepsilon-\gamma$  transformations, concentration of the random stacking faults in austenite was circa 0.015. The value of  $\alpha$  grew with increasing N up to 10. After 50 such cycles, the value of  $\alpha$  reached value of 0.02, and due to the further increasing N up to 100, grew in insignificantly (Fig. 9). There was obtained quantitatively the same  $\alpha(N)$  dependence for calculation via the value of  $\Delta\theta$  (curve 1) and value of  $\beta$  (curve 2).

Concentration of the random stacking faults in  $\varepsilon$ -martensite also grew as the N increased (Fig. 9, curve 3). Total concentration of the random stacking faults (without their separation on the twin and deformation ones) calculated via Eq. (3) reached a significant value of 0.033 (curve 3).

The presence of random stacking faults in austenite and martensite phases enabled to assume [18] that because of the rapid cooling and subsequent rapid heating cycles, thermal-stress-induced disordered (randomly located) stacking faults were generated and accumulated in austenite f.c.c. lattice. They tended to ordering in some regions of the f.c.c. structure (as in Refs. [31–33]), where critical concentration of the random stacking faults was reached. In this case, austenite region transformed into  $\varepsilon$ -martensite one. Electron-microscopic studies [26] showed that austenite matrix between the  $\varepsilon$ -martensite wafers is filled with stacking faults in [111], planes, which contributed to the mutual orien-



*Fig. 8.* The change of the diffraction reflex  $(102)_{\epsilon}$  depending on the number of  $\gamma - \epsilon - \gamma$  cycles: *1*—the initial state, *2* and *3*—after 5 and 100 cycles

*Fig. 9.* Concentration of the random stacking faults in austenite, calculated *via* the  $\Delta\theta$  (1) i  $\beta$  (2) values, and in  $\varepsilon$ -martensite (3), where 1, 2, and 3 are deformation  $\alpha$ , twin  $\beta$ , and total  $\alpha_{\Sigma}$  random stacking faults, respectively

tation of the stacking faults and hexagonal phase wafers, and made easier reconstruction of f.c.c. structure, which contained accumulated random stacking faults, into h.c.p. structure.

Authors of Ref. [26] pointed out that concentration of stacking faults in the residual austenite increased as the temperature or stresses varied. Thus, characteristics and regularities of generation of the random stacking faults revealed in this work and electron-microscopic observations in Ref. [26] made possible to explain activation of direct  $\gamma-\varepsilon$  transformation effect due to  $\gamma-\varepsilon-\gamma$  cycles by a decrease in the stacking fault energy.

### Correlation of the Change in the Structural Defect Concentration and Carbon Diffusion Characteristics in a Phase-Hardened Alloy

The change in concentration of the random stacking faults correlates with the growth of the carbon diffusion coefficient (Fig. 6). Increase in the random stacking faults' concentration up to 0.033 (Fig. 9) accompanied with accumulation of other defects (dislocations, low-angle grain subboundaries) resulted to increase in the carbon diffusion coefficient by 3.3 times at 100 °C.

In order to analyse effect of random stacking faults on the diffusion characteristics, we have to take into account local structure within the stacking fault regions. This is due to the prevailing ideas about the splitting of complete dislocations into the partial ones with the formation of the stacking faults. For the close-packed metals, the ability to split dislocations and the formation of the stacking faults [22] lies in the possibility of slipping along the planes of the slightest displacement. There are different dislocation reactions proposed for the formation of the stacking faults in the f.c.c. and h.c.p. [18, 22, 34] as well as b.c.c. [35] structures. In accordance with this scheme, it was experimentally observed that the formation of a hexagonal structure in the  $\Gamma 20$  alloy cooled from 400  $^{\circ}$ C occurred with the formation of the stacking faults bounded by partial dislocations. For the austenite  $\Gamma$ 19M6 alloy quenched in water 1100 °C there were observed initial splitting stages for dislocations and wide stacking faults bounded by partial dislocations [26]. Authors of Ref. [34] showed that depending on the energy of the stacking faults, the degree of dislocations' splitting can vary, and therefore their ability to multiplication can vary as well. Taking into account local structural reconstruction related with generation of random stacking faults, they can be considered as the complexes of 'stacking faultspartial dislocations'. Both partial dislocations and actually stacking faults can contribute to the acceleration of diffusion processes. The component of the diffusion intensification due to the random stacking faults in the f.c.c. and h.c.p. structures was implemented during the thermal cycling regime, when maximum number of random stacking faults accumulated, *i.e.*, during the first  $30-40 \ \gamma-\epsilon-\gamma$  cycles.

At the temperatures lower than half of the melting point, diffusion occurs mainly in dislocations, grain boundaries, fragment subboundaries, and other crystal structure defects [1–3]. Results of the present work show that the phase hardening from the  $\gamma - \varepsilon - \gamma$  transformations in the  $\Gamma 18C2$  alloy appreciably accelerate diffusion of carbon atoms due to effect of dislocations, random stacking faults, and subboundaries of disoriented fragments of austenite and  $\varepsilon$ -martensite crystal lattices.

To separate the contribution of various defects into the change of diffusion characteristics, it does not seem to be feasible based on the obtained results. However, one can conclude qualitatively about ranges of  $\gamma - \varepsilon - \gamma$  cycling with the maximal contribution of different defects into the diffusion intensification during subsequent diffusion annealing. Analysis of the characteristics of accumulation of each type of structural defects (Fig. 9) showed thermal hardening ranges with predominant contribution of certain defect type. Effect of dislocations generated via reverse  $\varepsilon - \gamma$  transformation was observed after the first transformation cycle. Such dislocations can be randomly distributed in lattice of each of the phase components. Their spatial distribution may have the character of a dislocation network. Dislocation distribution depends on the degree of intensification of diffusion processes. In the case of the dislocation network formation, carbon atoms diffuse predominantly along dislocation tubes, which compose a continuous diffusion pathway, and there is no C diffusion in dislocation-free bulk regions. In this case, the diffusivity significantly exceeds diffusion coefficient at a random distribution of dislocations. Electron microscopic studies of the disloca-

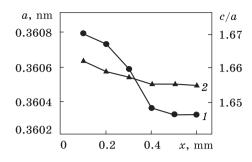


Fig. 10. The dependence of crystalline lattice parameter for austenite (1) and the c/a ratio for  $\varepsilon$ -martensite (2) on the penetration depth x after 500  $\gamma$ - $\varepsilon$ - $\gamma$  cycles and subsequent annealing at 200 °C during 1000 hours

tion distributions in austenitic and martensitic lattices of the phasehardened alloy can resolve this problem. The exponential dependence of the carbon concentration on the squared penetration depth indicates about the bulk character of diffusion. Due to bulk diffusion (over the crystal lattice), the parameters of the crystal lattice of austenite and martensite became higher (Fig. 10). Using these parameters, we can calculate the depth distribution of carbon in austenitic and martensitic phases. The carbon dissolution in  $\gamma$ - and  $\varepsilon$ -solid solution of the phasehardened alloy indicated that the dislocations and the low-angle fragment subboundaries, generated by the  $\gamma - \varepsilon - \gamma$  transformations, did not form a continuous dislocation network capable to create continuous dislocation tubes along which the carbon atoms could diffuse.

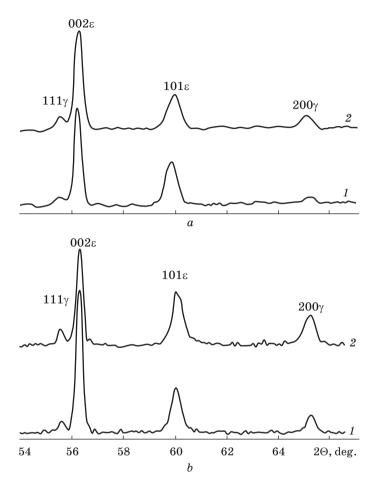
An increase in the contribution of the random stacking faults took place during the first 30-40 cycles. This fact concerns the contribution of the random stacking faults in both austenite and martensite. Disoriented low-angle subboundaries, which began to accumulate after the first 5-7 cycles, acted during all term of the thermal cycling interval.

Analysing the formation of a concentration profile, it is necessary to take into account the segregation effects of dissolved carbon atoms on subboundaries, dislocations and stacking faults, and, consequently, to estimate the corresponding contribution to the diffusivity value. Indeed, as far back as 1963 [28], it was reported that the equilibrium concentration of dissolved metal atoms at the boundaries depends on the disorientation angle; at the same time, the degree of atomic segregation increased rapidly after 16°. For some diffusers, a nonmonotonic dependence of the diffusion coefficient along subboundaries on the disorientation angle was observed [1, 28]. Due to high diffusion mobility of carbon atoms, they formed saturated atmospheres at the dislocations in the b.c.c. martensite of the quenched steel. Approximately 0.2 wt.% C was required for atmospheric saturation [36]. The nature of the segregation effects in the phase-hardened  $\Gamma$ 18C2 alloy may be different. Diffusion annealing created favourable conditions for atomic chains of C to be generated along an extra plane of the edge dislocations (Cottrell atmosphere) and for diffusion in the stacking fault regions (Suzuki atmosphere). Carbon atoms segregated on the structural defects did not give a contribution into the diffusion path value and consequently into the diffusion coefficient.

Except the described structural defective elements, an important factor for changing diffusion characteristics is also a change of the phase composition of the phase-hardened allow during the thermal cycling process and subsequent diffusion annealing. The increase in the of  $\varepsilon$ -martensite content as a result of  $\gamma - \varepsilon - \gamma$  cycling can be considered as a factor that increases the diffusion mobility of the substitution and interstitial atoms, since diffusion processes in the bulk of martensite possessing h.c.p. crystalline lattice are more intensive as compared with austenite that has an f.c.c. lattice with a closer atomic packing. As a result, the contribution of carbon diffusion over the residual austenite f.c.c. lattice to the integral diffusion flux decreased as the number of cycles increased, which corresponded to decreasing its volume fraction. For comparison, let us note that for some iron-manganese alloys, behaviour of N-dependent  $\varepsilon$ -martensite content differed. With increasing of N, there was observed a stabilization of austenite with respect to the subsequent  $\gamma - \varepsilon$  transformation, and, accordingly, the  $\varepsilon$ -martensite content decreased due to the multiple transformation cycles [18, 26]. In such alloys, the contribution of carbon bulk diffusion over the residual austenite reduced the integral diffusion flow.

As the number of transformation cycles increased, the contribution of the *D* coefficients in austenite and martensite to the magnitude of the effective coefficient *D* for the two-phase  $\gamma + \varepsilon$  alloy (Fig. 6) continuously changed in accordance with the change in phase composition. After the first cycle, the contribution of the coefficients for austenite and martensite to the value of *D* was commensurate. As for 100 cycles, the *D* coefficient at 100 °C, equal to  $5.5 \cdot 10^{-11}$  cm<sup>2</sup>/s, can be practically related to the  $\varepsilon$ -martensite. Due to the further cycling up to  $500 \ \gamma - \varepsilon - \gamma$  transformations, the *D* coefficient in  $\varepsilon$ -martensite grew up to  $6.85 \cdot 10^{-11}$  m<sup>2</sup>/s, *i.e.*, circa by 25%. The above-mentioned increase in the value of *D*, in case of a diffusion annealing within the range of the existence of martensite, prior to the inverse  $\varepsilon - \gamma$  transformation, should be attributed only to the effect of the dislocations that formed the polygonal walls of the low-angle subboundaries in the f.c.c.  $\varepsilon$ -phase lattice (Fig. 7).

It is known that random stacking faults in austenite were generated simultaneous with formation of  $\varepsilon$ -martensite. They disappeared (were 'healed') at a temperature slightly higher than the temperature of reverse  $\varepsilon-\gamma$  transformation [27]. Therefore, we can believe that the random stacking faults in the austenite, formed due to the  $\gamma \leftrightarrow \varepsilon$ -martensitic transformations, are more thermally stable in case of annealing than the  $\varepsilon$ -martensite. That is why, after the completion of the  $\varepsilon-\gamma$  transfor-



*Fig. 11.* The diffraction pattern changing of the phase-hardened alloy after its diffusion annealing at 200 °C during 430 (1) and 1000 (2) hours after 10 (a) and 50 (b)  $\gamma - \epsilon - \gamma$  cycles

mation, the diffusion of atoms in the reversible austenite was lesser accelerated than it was in the  $\varepsilon$ -martensite containing a certain content of random stacking faults. Therefore, in order to determine the diffusion characteristics of carbon, the diffusion annealing of the alloy was carried out within the temperature range of the  $\varepsilon$ -phase existence: 100–200 °C. Being subjected to such annealing conditions, the random stacking faults contributed as much as possible into the changing the diffusion characteristics.

During the annealing of a phase-hardened alloy, a partial isothermal inverse  $\varepsilon - \gamma$  transformation may occur in the  $\varepsilon$ -phase existence range (Fig. 11). Such a transformation occurred more intensively when a degree of phase hardening grew; this is evident from the increase in the

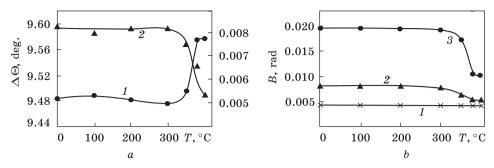


Fig. 12. Change in the difference of the Bragg angles of the  $(111)\gamma$  and  $(200)\gamma$  reflexes (1) as well as the half-width of the  $(200)\gamma$  reflex (2) for austenite (a), and the half-width of the  $(100)_{\epsilon}$  (1),  $(101)_{\epsilon}$  (2), and  $(102)_{\epsilon}$  (3) reflexes for  $\epsilon$ -martensite (b) depending on the temperature of annealing during 30 min  $(150 \ \gamma - \epsilon - \gamma \text{ cycles})$ 

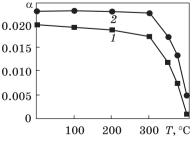
intensity of the reflexes of reversible austenite during annealing for the alloy, in which 50 cycles of  $\gamma - \varepsilon - \gamma$  transformation were implemented, as compared with alloy after 10  $\gamma - \varepsilon - \gamma$  transformations. Indeed, as a result of annealing during 1000 hours, the content of  $\varepsilon$ -martensite decreased by 18% for alloy after 50 cycles, whereas it decreased only by 5% for alloy after 10 cycles.

Within the range of reverse  $\varepsilon - \gamma$  transformation, simultaneously with decrease in the content of  $\varepsilon$ -martensite, there was observed a decrease in concentration of the random stacking faults in the austenite and martensite phases. In order to establish regularities in the changing concentration of the random stacking faults during the annealing of the phase-hardened alloy, we chose an alloy, where there were accumulated a considerable (up to 0.025) content of the random stacking faults due to  $150 \gamma - \varepsilon - \gamma$  transformations. The change in the Bragg angles of austenite reflexes and the half-widths of austenite and martensite reflexes indicated a change in the concentration of random stacking faults (Fig. 12). Heating of such an alloy up to the temperatures lower the temperature of onset of the  $\varepsilon - \gamma$  transformation, did not result to decrease in the concentration of the random stacking faults significantly decreased and reached the level in the initial state of the alloys after the first cooling

in the liquid nitrogen. Such a heating withdrew phase hardening from  $\gamma - \varepsilon - \gamma$ transformations concerning accumulation of the random stacking faults. Results of these experiments showed that

Fig. 13. Concentration of the random stacking faults vs. the temperature of annealing during 30 min for austenite (1) and  $\varepsilon$ -martensite (2)





maximal amplification of diffusion processes takes place when annealing of the  $\varepsilon$ -martensite occurs in the range of its existence.

Contribution of the random stacking faults to the change of diffusion characteristics during a reverse transformation dropped due to decreasing amount of  $\varepsilon$ -martensite and thus concentration of the random stacking faults. Annealing at the higher temperatures, resulted to the 'healing' (disappearance) of the random stacking faults in the austenite (Fig. 13) and elimination of effect of the random stacking faults on diffusion characteristics of carbon.

### Conclusions

Significant acceleration of carbon transport due to the cyclic  $\gamma - \varepsilon - \gamma$  martensitic transformations in the iron-manganese  $\Gamma 18C2$  alloy was determined *via* two independent mechanisms: athermal one, which was realized in the process of martensitic transformations, and thermoactivated one, which was realized during the subsequent diffusion annealing. The difference in the increase in the penetration depth of carbon *via* two different diffusion mechanisms increased with an increase in the phase hardening degree of the alloy, *i.e.*, with an accumulation of the structural defects in the austenite and  $\varepsilon$ -martensite.

Transport of carbon atoms to macroscopic distances by the athermal mechanism occurred in the field of stresses, which appeared and were accumulated during  $\gamma - \varepsilon - \gamma$  retransformations, apparently, *via* the interstitial diffusion mechanism. Appearance of extended regions as a result of direct  $\gamma - \varepsilon$  transformation at low temperatures, when relaxation processes were decelerated, whereas internal stresses were conserved, created conditions for transport of carbon atoms to such regions without thermal activation.

As a result of the annealing, subsequent after cycle transformations, diffusion mobility of carbon atoms additionally increased due to the effect of the one-dimensional and two-dimensional defects of the crystal structure of the residual austenite and  $\varepsilon$ -martensite being forming during these transformations (dislocations, low-angle dislocation fragment subboundaries, random stacking faults). The maximal enhancement of carbon diffusion coefficient was found as a thermal cycle number increased up to one hundred, when the main increase in the defect density was observed in the f.c.c. and h.c.p. crystal structures.

After the first  $\gamma - \varepsilon - \gamma$  transformation cycle, the diffusion coefficient of carbon was found to be equal to  $1.7 \cdot 10^{-11}$  and  $2.3 \cdot 10^{-11}$  cm<sup>2</sup>/s at the temperatures of 100 °C and 200 °C, respectively. Further increase in number of  $\gamma - \varepsilon - \gamma$  cycles up to 500 induced additional enhancement of diffusion coefficient by 3.2 and 4.2 times, respectively.

Contribution of different defects into the diffusion intensification-

during the diffusion annealing manifests itself within the different ranges of  $\gamma - \varepsilon - \gamma$  cycling. Analysing characteristics and regularities in a process of accumulation of different types of structural defects enabled to determine a certain succession of their effect on diffusion:

(i) dislocation effect was observed after the first  $\gamma - \epsilon - \gamma$  transition cycle;

(ii) enhancement of contribution of the random stacking faults occurred during the first 30-40 cycles;

(iii) disoriented low-angle subboundaries did not strongly affect the diffusion after the first 5-7 cycles, however, they were found to be continuously accumulated and effectively influenced on the diffusion processes already in a whole thermal cycling range.

An increase of the value of *D* after 100 cycles of transitions during the diffusion annealing in the range of existence of  $\varepsilon$ -martensite, up to the onset of the reverse  $\varepsilon - \gamma$  transformation, should be attributed only to the effect of dislocations, which formed polygonal networks of the lowangle subboundaries in the h.c.p. lattice of the  $\varepsilon$ -phase.

An additional factor in changing the diffusion characteristics of carbon in a phase-hardened alloy is the change in the phase composition, in one case, in the process of thermal cycling and, in another case, due to the subsequent diffusion annealing. The annealing of the phase-hardened alloy in the temperature range of existence of  $\varepsilon$ -martensite induced a partial reverse  $\varepsilon - \gamma$  transformation. When a degree of the phase hardening increased, the reverse  $\varepsilon - \gamma$  transformation occurred more actively. Because of decreasing amount of  $\varepsilon$ -martensite and accordant content of the random stacking faults during the partial  $\varepsilon - \gamma$  transformation, the effect of amplification of diffusion processes became weaker. That is why, in order to increase impact of defects on the diffusion processes, the alloy should be annealed at the temperatures when  $\varepsilon$ -martensite exists (onset of the reverse  $\varepsilon - \gamma$  transformation). In case of the annealing temperatures higher the temperature of the completion of  $\varepsilon - \gamma$  transformation, the random stacking faults do not contribute to the amplification of diffusion processes.

An exponential dependence of the content of carbon on the squared penetration depth indicated about the bulk character of carbon diffusion at the low temperatures. Effect of the bulk diffusion resulted to the enhanced crystal lattice parameters for austenite and  $\varepsilon$ -martensite; using these parameters, we can calculate the depth distribution of dissolved carbon atoms in both austenite and martensite phases. The dissolution of carbon in  $\gamma$ - and  $\varepsilon$ -phases of the phase-hardened alloy indicated that randomly distributed dislocations and low-angle dislocation subboundaries of the fragments, generated by the  $\gamma - \varepsilon - \gamma$  transformations, did not form continuous dislocation network capable to create continuous dislocation tubes for a diffusion of carbon atoms along them.

The revealed fundamental regularity for acceleration of carbon diffusion *via* the cyclic  $\gamma - \varepsilon - \gamma$  martensitic transformations has a practical importance. It is expedient to use it to intensify the technological processes of cementation of metastable iron-manganese alloys, as well as to accelerate the processes of decomposition of carbon-based solid solutions and dispersion hardening in martensite-aging alloys. Accelerated diffusion of carbon and, apparently, nitrogen will allow realization of the processes of cementation and nitriding at the temperatures that are hundreds of degrees lower as compared with those used in the practice of surface chemical and thermal treatments of metal devices.

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Received February 2, 2018; in final version, March 30, 2018

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#### ВПЛИВ ЦИКЛІЧНИХ МАРТЕНСИТНИХ ПЕРЕТВОРЕНЬ 7–ε–7 НА ДИФУЗІЙНІ ХАРАКТЕРИСТИКИ КАРБОНУ В ЗАЛІЗОМАНІ́АНОВОМУ СТОПІ

Методою радіоактивних ізотопів досліджено дифузійні характеристики Карбону у метастабільному залізоманґановому стопі Г18С2, наклепаному циклічними мартенситними перетвореннями  $\gamma$ – $\varepsilon$ – $\gamma$  (ГЦК–ГЩП–ГЦК). Показано, що інтенсифікація процесу транспорту Карбону у стопі, фазонаклепаному  $\gamma$ – $\varepsilon$ – $\gamma$ -перетвореннями, визначалася двома незалежними механізмами: атермічним, який реалізовувався за рахунок ґенерації поля напружень у процесі мартенситних перетворень, і термоактивованим, який реалізовувався в процесі наступного дифузійного відпалення за рахунок дії малокутових субмеж та одновимірних і

двовимірних дефектів кристалічної будови ГЦК-аустеніту і ГЩП-є-мартенситу, що формувалися в результаті цих перетворень. Після багаторазових циклів  $\gamma$ - $\epsilon$ - $\gamma$ -перетворень коефіцієнт дифузії Карбону за низьких температур (100– 350 °C) підвищувався на понад три порядки. При цьому коефіцієнт за температури у 325 °C відповідав коефіцієнту стаціонарної дифузії при 900 °C. Максимальний приріст коефіцієнта дифузії Карбону спостерігали при збільшенні кількости термоциклів до ста, коли фіксували основний приріст густини дефектів будови. Додатковим чинником зміни дифузійних характеристик Карбону у фазонаклепаному стопі є зміна фазового складу як у результаті  $\gamma$ - $\epsilon$ - $\gamma$ -циклування, так і в процесі наступного дифузійного відпалення.

Ключові слова: дифузія, мартенсит, аустеніт, радіоізотоп, дислокація, дефект пакування.

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### ВЛИЯНИЕ ЦИКЛИЧЕСКИХ МАРТЕНСИТНЫХ ПРЕВРАЩЕНИЙ ү–є–ү НА ДИФУЗИОННЫЕ ХАРАКТЕРИСТИКИ УГЛЕРОДА В ЖЕЛЕЗОМАРГАНЦЕВОМ СПЛАВЕ

Методом радиоактивных изотопов исследованы диффузионные характеристики углерода в метастабильном железомарганцевом сплаве Г18С2, наклёпанном циклическими мартенситными превращениями у-є-у (ГЦК-ГПУ-ГЦК). Показано, что интенсификация процесса транспорта углерода в сплаве, фазонаклёпанном  $\gamma - \epsilon - \gamma$ -превращениями, определялась двумя независимыми механизмами: атермическим, который реализовывался за счёт генерирования поля напряжений в процессе мартенситных превращений, и термоактивированным, который реализовывался в процессе последующего диффузионного отжига за счёт действия малоугловых субграниц, а также одномерных и двухмерных дефектов кристаллического строения ГЦК-аустенита и ГПУ-є-мартенсита, сформированных в процессе этих превращений. После многократных циклов у-є-у-превращений коэффициент диффузии углерода при низких температурах (100-350 °C) повышался более чем на три порядка. При этом коэффициент диффузии при температуре 325 °С соответствовал коэффициенту стационарной диффузии при температуре 900 °С. Максимальный прирост коэффициента диффузии углерода наблюдали при увеличении количества термоциклов до ста, когда фиксировали основной прирост плотности дефектов строения. Дополнительным фактором изменения диффузионных характеристик углерода в фазонаклёпанном сплаве было изменение фазового состава как в процессе у-є-у-циклирования, так и последующего диффузионного отжига.

Ключевые слова: диффузия, аустенит, мартенсит, радиоизотоп, дислокация, дефект упаковки.