Metallic materials for the hydrogen energy industry and main gas pipelines: complex physical problems of aging, embrittlement, and failure

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Abstract. The possibilities of effective solutions of relevant technological problems are considered based on the analysis of fundamental physical aspects, elucidation of the micromechanisms and interrelations of aging and hydrogen embrittlement of materials in the hydrogen industry and gas-main industries. The adverse effects these mechanisms and processes have on the service properties and technological lifetime of materials are analyzed. The concomitant fundamental process of formation of carbohydride-like and other nanosegregation structures at dislocations (with the segregation capacity 1 to 1.5 orders of magnitude greater than in the widely used Cottrell 'atmosphere' model) and grain boundaries is discussed, as is the way in which these structures affect technological processes (aging, hydrogen embrittlement, stress corrosion damage, and failure) and the physicomechanical properties of the metallic materials (including the technological lifetimes of pipeline steels).

1. Introduction

The study of the physical mechanisms of hydrogen embrittlement and degradation of the physicomechanical properties of metallic materials is a fundamental scientific problem that has been intensively studied around the world for the last several decades. In this connection, several important issues pertaining to science and technology remain unanswered:

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Received 4 February 2008, revised 6 March 2008 Uspekhi Fizicheskikh Nauk **178** (7) 709–726 (2008) DOI: 10.3367/UFNr.0178.200807b.0709 Translated by E Yankovsky; edited by A M Semikhatov (a) metal-science aspects of the hydrogen energy industry, such as the processing compatibility of metallic materials and hydrogen (arising from hydrogen embrittlement and degradation of the physicomechanical properties of such materials); and

(b) physical aspects, micromechanisms, and the interrelation between technological aging processes and hydrogen embrittlement of metallic materials; and the role of these processes in the degradation of the service properties and service life of pipeline steels and hydrogen infrastructure, including products of the motor transport, aviation, and space industries.

Within the scope of this problem, the specific goal of the present analytical review is to develop the necessary physical aspects called for by technology and to display the micromechanisms of and interrelation between the technological processes of aging and hydrogen embrittlement of metallic materials used in the hydrogen energy industry and gas pipelines. Another important aspect is the analysis of these processes and degradation of the service properties and service life of materials and structures.

2. The current state of research

As formulated in the Proceedings of the Basic Energy Sciences Workshop on Hydrogen Production, Storage and Use (in the chapter devoted to safety in the hydrogen economy), hosted in 2003 by the U.S. Department of Energy [1], corrosion and hydrogen embrittlement of metallic materials are closely related to certain elements of their microstructure and, in particular, to segregation and diffusion processes running on the inner structural phase interfaces (grain boundaries and the like) and associated defects of the dislocation type; it is noted that the micromechanisms of these process have been examined insufficiently. In the chapter of Ref. [1] devoted to potential interactions, it is also pointed out that fundamental knowledge about the nature of hydrogen embrittlement of



Figure 1. Disastrous rupture (in 1983) of a steel vessel used to transport gaseous hydrogen under high pressure. Hydrogen cracking initiated by pitting is shown in the figure [2].

metals and welded joints (structures) is needed to standardize the materials used in building a hydrogen infrastructure. In the chapter in Ref. [1] devoted to the principal research problems in accumulating (storing) hydrogen, it is noted that fundamental research on the mechanisms of hydrogen degradation and destruction of metals and alloys is needed in order to improve the structural materials used in building reservoirs, containers, and vessels for storing hydrogen (Figs 1-3).

In this connection, the U.S. Department of Energy formulated and recommended [1] the main areas of fundamental research into the physical micromechanisms of the process of mass transfer of hydrogen in metals and the hydrogen-initiated processes of degradation of properties and disintegration of metallic materials.

At this point, it is only proper to mention the mass production by the leading automobile companies of the U.S., Japan, Germany, and China of hydrogen-driven automobiles and buses with fuel cells in which hydrogen is stored mainly in high-pressure vessels (pressures up to 80 MPa) and in which there is an intricate infrastructure of steel pipes for transporting hydrogen under high pressure.



Figure 2. Explosion type of a disastrous rupture of a cylindrical steel vessel containing hydrogen. In particular, clearly visible is intergranular (hydrogen) cracking of the material [2].



Figure 3. Disastrous rupture of the explosion type of a steel reservoir for storing hydrogen under high pressure [2].

Therefore, the technological compatibility of metallic materials and hydrogen is becoming a pressing problem. For instance, it was discussed at the 2nd International Conference on Hydrogen Safety (Spain, September 11–13, 2007) and in the key report [2] delivered at the 16th World Hydrogen Energy Conference: Expanding Hydrogen. This report contained the results of a probability-and-effect analysis of industrial (technological) data on emergency situations (Figs 1–3) involving metallic materials and structures of the hydrogen energy industry.

In reports [3, 4], effective ways of solving this problem were examined based on the systematization and cause-andeffect analysis of the respective experimental, theoretical, and technological data, i.e., on expanding the micromechanisms of the processes, to which much of the present report is devoted.

There are reasons to believe (see Refs [1-34]) that the micromechanisms of the processes of hydrogen embrittlement, plasticizing, the degradation of properties, and the technological processes of hydrogen treatment of metallic materials have been studied insufficiently. This situation manifests itself most vividly in relation to the important scientific and technological problems of aging, hydrogen embrittlement, stress corrosion, and failure of pipeline steels (Figs 4–12) in which the pressure of natural gas (methane) may be as high as 8 MPa [13–27].

For instance, it was noted in [13] that analysis of disastrous failures of gas mains has shown that in addition to many factors, such as corrosion and gas temperature and pressure pulsations, a decisive factor is hydrogen saturation of the pipes. According to the data in [13], the hydrogen content in the walls of the failed pipes along the ruptured section amounted to $9-12 \text{ cm}^3$ per 100 g of steel (0.045–0.06 at.%), which is several times higher than the initial hydrogen content [up to 3 cm³ per 100 g of steel (0.015 at.%)] and the hydrogen content in stored pipes, which were never used in service mains. On the inner surface



Figure 4. Emergencies [22] involving avalanche brittle and extended viscous ruptures of sections of gas mains several kilometers long that became operational in the 1960s.



Figure 5. Relative accident rate of gas mains from different causes. Gazprom data for the period from 1991 to 2005 (according to Ref. [21]).



Figure 6. 'Age' distribution of SCD for gas pipelines of different diameters [20].



Figure 7. Dynamics of variation of failed gas pipelines (20 ± 10 years) with SCD in the period from 1991 to 2005 [21].

of the pipe walls, the authors of [13] observed precipitations of soot (carbon) and sulfide precipitations up to 1 mm thick. The above factors point to the possibility of dissociative dissolution of hydrogen in the steel from methane and the hydrogen sulfur in natural gas. The content of hydrogen sulfur in natural gas may be as high as 0.0047 g m⁻³ [13]. We note that at lower values of hydrogen content (0.032 at.%) in heavily corroded walls of gas-main pipes after 24-30 years in service were obtained in [27], whereas the hydrogen content in spare pipes that were never in service did not exceed 0.014 at.%, and in new pipelines it was no higher than



Figure 8. Dependence of SCD of gas pipelines on the length of time in service; the incubation period of the formation of a large number of SCD defects is about 13 years [23].



Figure 9. The effect of the number of years in service of gas pipelines on the temperature of transition to the brittle state (T_{50}) for pipes made of 17GS steel. The arrows pointing upward indicate cases where such a transition occurring at temperatures higher than 20 °C is also observed [27].



Figure 10. The effect of the number of years in service of gas pipelines on the characteristic time before destruction in a delayed fracture test of the metal in pipes made of 17GS steel [27].

0.013 at.%. The data gathered in [13] and [27] definitely prove the presence of hydrogen saturation of steels used in gas mains that have been in service for a long time, which obviously results in gas pipeline failure; in many cases, this involves stress corrosion of the pipeline metal (see Figs 4-12).

It is stated in report [14] that the mechanism of stress corrosion of pipeline steel is still a topic of discussion: the two basic models of cracking are the anodic dissolution of the metal at the vertex of the crack, and local hydrogen embrittlement.



Figure 11. Stress corrosion of a fracture nucleus of a failed main gas pipeline 1420 mm in diameter (Kh90 steel, 11 years in service) [25].

Reports presented at the workshop "Problems of Aging of Gas Pipeline Steels" (Nizhnii Novgorod, 23-25 January 2006), which was organized by the Research Physicotechnical Institute of the Lobachevsky Nizhnii Novgorod State University and the MELAKS Federal Financial and Industrial Company, can be found in Refs [15-27]. The participants acknowledged (probably, for the first time) the importance of the problem of aging of pipeline steels; in view of the highly significant problem of increasing the serviceability and safety of gas mains, the participants found it necessary to announce their decision while having the attention of the administration of Gazprom and the Ministry of Industry and Energy of the Russian Federation.

At the same time, it must be noted that in keeping with the name of the workshop, the reports in Refs [15-27](Figs 4–16) formulate more problems than answers. In particular, as noted in Ref. [15], there is ambiguity and a large range of opinions concerning the nature (the micromechanisms) and the role of the aging process and its effect on the properties of pipeline steels. According to the authors of the reports in Refs [15-27], this is exclusively due to the complexity of the problem and the imperfection of traditional methods of analysis.

3. Analysis of the main empirical facts, models, and problems

In view of what has been said above, we believe (see Ref. 4) that it is advisable to more closely examine some of the experimental facts discussed in Refs [15-27] (see Figs 4–13 and 16), the proposed concepts and models (see Figs 14 and 15), and the emerging questions:

(1) To what extent can the models of pipeline steel aging proposed in Ref. [16] be used to interpret the reasons for stress-corrosion attack and to estimate the service life of the steels?

(2) Why is there no SCD of similar steels in oil-trunk pipelines as they age [16, 20, 26]? Is this related to the absence and/or other conditions of their saturation with hydrogen during service? Is hydrogen saturation a necessary but not sufficient condition for stress-corrosion attack on steels?

(3) Can pipeline steels become saturated with hydrogen without aging? And isn't aging, i.e., in a certain sense (according to Ref. [16]), the carburization of the regions



Figure 12. Movement of SCD cracks along the boundaries of grains in 17G1S and Kh70 steels [16].



Figure 13. Carbide precipitations (SCC stands for structural component of cementite Fe_3C) on the boundaries of ferritic grains in the course of aging of gas-main pipes [16].

with boundaries of ferritic grains to carbide concentrations via diffusive redistribution of excess carbon from the grain bulk to these boundaries (see Fig. 16), the limiting and necessary stage in hydrogen saturation (in accordance with the data in Ref. [24] and Fig. 16)? Is there preferential local hydrogen saturation of the carburized boundaries of ferritic grains up to carbohydride concentrations [3, 4]? Does this lead to hydrogen (carbohydride) embrittlement of the



Figure 14. Types of local corrosion attackss on steels due to microgalvanic-cells [16]. Selective corrosion: 1 and 2, different phases; 3, principal metal; and 4, precipitations on grain boundaries.

boundaries of ferritic grains [3, 4] and to their structural phase heterogeneity, including the electrochemical properties (Refs [16, 25] and Fig. 14), which is necessary for stress-corrosion damage of the material (Refs [16, 24] and Figs 11 and 12)?

(4) Does a 'grid' of cementite precipitation form (in most cases) along the boundaries of ferritic grains and is this a necessary condition for the development of a stress-corrosion attack on pipeline steels (Ref. [16] and Figs 13-15)? Formation of such a grid requires a high degree of ferrite oversaturation with carbon, a situation called into doubt by some researchers (see Refs [20, 25]).

(5) What is the lowest possible degree of ferritic-grain oversaturation with carbon that is sufficient for the carburization of their boundaries (about 1 nm thick) to carbide concentrations, i.e., for the formation of a grid of carbide-like nanosegregations on grain boundaries [3, 4]? Is there enough hydrogen arriving at the material in service [13, 27] for the grain-boundary grid of carbide-like nanosegregations to transform into a grain-boundary grid of carbohydride-like nanosegregations [3, 4]?

In discussing these questions, we believe it would be productive to use new, effective approaches and methods of analysis [35, 36]. The results of numerous studies (see Refs [3, 4, 35, 37-57]) demonstrate the possibility of special phase transitions [57] occurring in segregation nanoregions on dislocations and grain boundaries in metals; in particular, into hydride-like, carbide-like, or carbohydride-like nanostructures [44, 46, 56].



Figure 15. Evolution of the structure of pipeline steels of gas mains in service [16]. (\perp) Dislocations, (\rightarrow) diffusing carbon atoms, (\bullet) carbide particles in the lattice, and (-) carbide plates at grain boundaries.



Figure 16. Structure of steel Kh16N15M3T1: (a) after quenching and aging, and (b) after saturation with tritium. Tritium is distributed among dislocation subboundaries, around inclusions, and around grain-boundary precipitations (Ni₃Ti).

3.1 The insufficiency of the proposed model of aging of pipeline steels for interpreting the reasons

for stress-corrosion attack and estimating their lifetimes As stated in [15] and [16], the aging of pipeline steels amounts to the excess carbon that builds up in the course of service in ferrite diffusing toward the ferritic grain boundaries. In [16], this was assumed to lead to a carbide grid being formed at the intergrain boundaries (see Figs 13-16) and, finally, to degradation of the service properties of pipeline steels. According to the concept in [16], such aging promotes the stress-corrosion cracking of steels, which in many cases is the main reason of the failure of main gas pipelines (Ref. [21] and Fig. 5).

In accordance with this concept, the characteristic time of the diffusion mass transfer of the larger fraction (approximately 63%) of the excess carbon atoms from the grain bulk to the boundaries largely characterizes the service life of pipeline steels. According to the estimates in [16], the time of diffusion mass transfer varies from 24 years (with grain sizes about 10 µm, a value typical of controlled-rolling steels) to

54 and 96 years (with grain sizes about 15 and 20 μ m, values respectively typical of normalized and hot-rolled steels). The first value (24 years) is close, in the order of magnitude, to failure (caused by SCD) 'ages' of gas mains examined in [20] and [21] (see Figs 6 and 7). The second value (54 years) and, to a lesser extent, the third value (96 years) are close, in the order of magnitude, to the results of an empirical estimate of the total service life reported in [22].

However, as noted in [18], there are reasons to believe that the estimates of the characteristic time relevant of the diffusion process in [16] may be understated by a factor of 10 to 100, and hence there may be no satisfactory correspondence to the recorded failure ages [20-22].

Using our results (see Refs [43, 44, 46, 52]), we can show [4, 38] that the understating in the estimates of the characteristic time of the given diffusion process in [16] is no less than one order of magnitude; the main reason is that the effect of dislocations on diffusion and segregation absorption of carbon atoms by the dislocations was not properly taken into account in [16]. The estimates in [16] were based on the widely used Cottrell atmosphere model, but the data in Refs [43, 44, 46, 52] on the formation of carbide-like nanosegregations of carbon on dislocations in iron (steel) were ignored. Such nanosegregations have the segregation capacity that is one to one-and-a-half orders of magnitude greater than those of Cottrell atmospheres and, in any case (in contrast to Cottrell atmospheres), do not accelerate the volume diffusion of carbon toward the grain boundaries in iron (steel).

We also note (see Refs [4, 38]) that in Ref. [28], referred to in [16], there is special mention of the experimental fact that in the process of strain aging of steel, up to 90 carbon and nitrogen atoms may segregate per atomic plane intersecting a dislocation (per dislocation of atomic length; the dislocation segregation capacity is $n_{C\perp}$); this is one to one-and-a-half orders of magnitude greater than the limit impurity content in Cottrell atmospheres [32, 33].

As noted in Ref. [32], which is also referred to in [16], measurements have shown that dislocation in iron crystals at low temperatures may attract a substantial number of impurity atoms (C, N), more than 40 atoms per dislocation of atomic length, according to Pietsch's data.

It was stressed in [34] that there are many indications of the fact that at low temperatures, the dislocation lines in metals similar to iron gather a large number of interstitial atoms per atomic plane intersecting the dislocation.

The question of whether Cottrell's formula can be used to correctly estimate the temperature of condensation of hydrogen atmospheres in iron, as well as the energy of interaction of hydrogen and dislocations, was posed in [30]. The inconsistency of the segregation capacity of hydrogen on dislocations in palladium (at 300-360 K) obtained by analyzing the well-known experimental data and the capacity calculated by the Cottrell model was discussed in [58].

As shown in Ref. [48], the experimental data in [59] confirm that in martensitic steels, about 0.2 mass% of carbon (or $C_{\rm C} \approx 0.92$ at.%) is bound by dislocations. This allows estimating the segregation capacity of dislocations at $n_{\rm C\perp} \approx C_{\rm C}(100b^2\rho_{\perp})$, with *b* being the shortest Burgers vector in the material, the same value as in Refs [28, 32] ($n_{\rm C\perp} \approx 90-45$ carbon atoms per dislocation of atomic length) for the dislocation number density $\rho_{\perp} \approx (2-4) \times 10^{11}$ cm⁻², which is a typical value for such steels. Mössbauer spectroscopy data and other data [60–62] on cold-rolled steels produce close values of $n_{\rm C\perp}$ (see Ref. [43]).

In [62], experimental indications were obtained of a decrease by a factor of 10 to 100 in the value of the diffusion coefficient for carbon in α -iron strained by 75% by cold rolling, i.e., in ferrite with the high dislocation number density $\sim 4 \times 10^9$ cm⁻², compared to annealed metal with the low dislocation number density $\sim 10^8$ cm⁻². The results of processing and interpreting these and other similar data, including the resulting high values of $n_{C\perp}$, can be found in Ref. [43].

All these data and many other experimental results have been verified both thermodynamically and crystal-chemically and have been interpreted in Refs [43, 46, 52, 56] as effects caused by carbide-like, carbonitride-like, and other nanosegregations on dislocations and grain boundaries in ferrites. In the same works, it was experimentally proved and theoretically justified that such nanosegregations (dislocation traps) may slow down the diffusion of carbon and nitrogen in ferrite. Such an effect occurs only if there is no saturation of traps that is close to the occupancy limit. When the diffusant occupancy of the dislocation traps is high, their effect on the diffusion of carbon atoms toward the ferritic gain boundaries becomes negligible [35], which may be the case in the aging of pipeline steels.

Using the data in Refs [28, 32, 43, 46, 52], we can estimate (see Ref. [38]) the content of the carbon absorbed by carbidelike nanosegregations on the dislocations in ferrite at room temperature. At the dislocation number density $\sim 1 \times 10^{10}$ cm⁻², which is characteristic of controlled-rolling pipeline steels [16], we obtain $\sim 1 \times 10^{-2}$ mass% (~ 0.05 at.%) for the value of the limit occupancy of dislocation traps, which is comparable to the presumed concentration of excess carbon atoms in the ferrite lattice ($\sim 3 \times 10^{-2}$ mass%) [16]. Some researchers believe that this value is overestimated by a factor of about ten and that further analysis is needed.

If we wish to remain within the extended concept of aging (see Ref. [38]), we must note that according to the data of electron microscope observations [19] of low-temperature aging of low-carbon iron with a relatively low dislocation number density (compared to that of pipeline steels), a metastable zone (cluster) structure forms inside the ferritic grains. This, however, does not contradict the process discussed earlier of the aging of pipeline steels with a relatively high dislocation number density, and can be described by the model of clusterization of the excess carbon in the ferrite lattice (e.g., see Refs [43, 51]). Using the data in [19], we can find the characteristic length of the diffusion path $(L \sim 0.1 \ \mu m)$ for the mass transfer of carbon atoms in ferrite to the closest cluster formations (zones), corresponding to such aging of the material at 295 K in the course of t = 672 h. This yields the volume diffusion coefficient of carbon in ferrite $D_{\rm V} \approx L^2/t \approx 4 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$, which is close to the value $D_{\rm V} = 5.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ given in Ref. [16]. Accordingly, at 373 K and t = 100 h, the characteristic diffusion length $L \sim 1 \ \mu\text{m}$, and $D_V \approx 3 \times 10^{-14} \ \text{cm}^2 \ \text{c}^{-1}$. From the values of $D_{\rm V}$ thus obtained at two temperatures, we can estimate the diffusion activation energy $Q_V \approx 80 \text{ kJ mol}^{-1}$ and the preexponential factor of the diffusion coefficient $D_{\rm V0} \approx$ $6 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$, which turn out to be close to the values $Q_{\rm V} = 82.7 \text{ mol}^{-1}$ and $D_{\rm V0} \approx 10^{-2} \text{ cm}^2 \text{ s}^{-1}$ given in Ref. [16].

Using the experimental data in Ref. [52] on the characteristic time and the mechanism of strain aging (volume diffusion of carbon and nitrogen atoms to the dislocation in the nearsurface strained ferrite layer with the activation energy $Q_V \approx 80 \text{ kJ mol}^{-1}$) of low-alloyed steel, we can estimate (see Ref. [38]) the coefficient of volume diffusion of carbon and nitrogen atoms in ferrite ($D_V \approx 8 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$). From this, for grain sizes $d_g \approx 10$, 15, and 20 µm, we find the characteristic times of volume diffusion of nitrogen and carbon atoms to the ferritic grain boundaries at room temperature are $\tau_b \approx d_g^2/4D_V \approx 100$, 220, and 400 years, respectively.

This is much longer than the respective times 24, 54, and 96 years given in [16], obtained using the model of the acceleration effect of Cottrell atmospheres and grain boundaries in ferrite. But if we justifiably ignore this effect of Cottrell atmospheres (and grain boundaries, according to [18]) and use the volume diffusion coefficient of carbon atoms in the ferrite lattice at room temperature given in [16], $D_V = 5.5 \times 10^{-17}$ cm² s⁻¹, we obtain (see Ref. [38]) values of the characteristic diffusion times (aging times) amounting to 140, 310, and 560 years, which are close to the extrapolated empirical values obtained from the data in Ref. [52].

Within the model in [16], an estimate of the characteristic aging period (and the lifetime) of controlled-rolling pipeline steels, which is the characteristic time of diffusion of carbon atoms from the volume of ferritic grains to their boundaries (τ_b), was made using the formulas

$$\tau_{\rm b} \approx \frac{L^2}{D_{\Sigma}^*} \,, \tag{1}$$

$$D_{\Sigma}^* \approx D_{\rm V} + \eta_{\perp}^* D_{\perp}^* + \eta_{\rm b} D_{\rm b} \,, \qquad (2)$$

$$\eta_{\perp}^{*} \approx \alpha_{\perp}^{*} \rho_{\perp} \,, \tag{3}$$

$$\eta_{\rm b} \approx \frac{\delta_{\rm b}}{d_{\rm g}} \,. \tag{4}$$

Here, D_{\perp}^* is the effective diffusion coefficient for carbon atoms in the material, $L \approx d_g/2$ is the characteristic diffusion length, approximately one-half of the grain size ($d_g \approx 10 \ \mu$ m), $D_V = 5.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ and $D_{\Sigma}^* \approx D_b \approx 2.5 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ are the respective coefficients of diffusion of carbon atoms in ferrite along the dislocations (obviously, along Cottrell atmospheres) and along grain boundaries, η_{\perp}^* is the volume (atomic) fraction of dislocations in ferrite, $\rho_{\perp} \approx 10^{10} \text{ cm}^{-2}$ is the dislocation number density in ferrite, $\alpha_{\perp}^* \approx 6 \times 10^{-15} \text{ cm}^2$ is the effective cross-sectional area of a dislocation, η_b is the volume (atomic) fraction of the grain boundaries in ferrite, and $\delta_b \approx 5 \times 10^{-8}$ cm is the grain-boundary width.

Thus, for controlled-rolling pipeline steels, we have $\tau_b \approx 24$ years [16], with the two main accelerating contributions to D_{Σ}^* from the second and third terms in the right-hand side of Eqn (2).

However, as was rightly noted in [18], the third term in the right-hand side of Eqn (2) associated with the accelerated diffusion along the grain boundaries should be discarded, because it is the diffusion mass transfer from the volume of each grain to the respective boundary that is examined. Dropping the third term in (2) gives a larger value, $\tau_b \approx 55$ years. And if we justifiably (see Ref. [38]) eliminate the second term in Eqn (2), which is responsible for accelerated diffusion, we obtain a still greater value, $\tau_b \approx 140$ years.

According to the results reported in Refs [29, 35, 38, 43, 49, 50], fuller (and more meaningful) expressions for the effective impurity-diffusion coefficient D_{Σ} and for the effective impurity solubility C_{Σ} in a metal with dislocations can be written in the local equilibrium approximation as

$$D_{\Sigma} = \frac{D_{\mathrm{V}}(1-\eta_{\perp}) + D_{\perp}\eta_{\perp}(\partial C_{\perp}/\partial C)}{1-\eta_{\perp} + \eta_{\perp}(\partial C_{\perp}/\partial C)}, \qquad (5)$$

$$\eta_{\perp} \approx d_{\perp}^2 \rho_{\perp} \,, \tag{6}$$

$$C_{\Sigma} = C(1 - \eta_{\perp}) + \eta_{\perp}C_{\perp} , \qquad (7)$$

where D_V is the volume diffusion coefficient for the impurity in the metal with a negligible number of dislocations, η_{\perp} is the volume (atomic) fraction of the regions of nanosegregations on dislocations with the number density ρ_{\perp} , with d_{\perp} being the averaged cross-sectional diameter of such regions, and C_{\perp} is the local averaged impurity concentration in the regions of nanosegregations on dislocations, which is also characterized by the averaged impurity-diffusion coefficient D_{\perp} . In many cases, including the one with carbon in a metal, D_{\perp} can be much smaller than D_V . Equations (5) and (6) are valid for Cottrell atmospheres (at $d_{\perp}^2 \approx \alpha_{\perp}^*$ and $D_{\perp} \approx D_{\perp}^* \gg D_V$) and for the above-mentioned carbide-like nanosegregations on dislocations (at $d_{\perp} \leq 3$ nm and $C_{\perp} \approx 10^{-1}$ [43, 46, 52]). In the case where the system is very close to the highest possible saturation of the regions of nanosegregations on dislocations by impurities, $\partial C_{\perp}/\partial C$ becomes almost zero and $D_{\Sigma} \approx D_V$, i.e., dislocations that are filled with an impurity to the highest possible degree cease to have an effect on the impurity mobility in the metal grains. Obviously, this is exactly the situation with controlled-rolling pipeline steels discussed in Ref. [16], because the time it takes the dislocations to become saturated with the impurity (carbon) ($\tau_{\perp} \approx (\rho_{\perp} D_V)^{-1} \approx$ 20 days for $\rho_{\perp} \approx 10^{10}$ cm⁻² and $D_V = 5.5 \times 10^{-17}$ cm² s⁻¹) is many orders of magnitude shorter than the material aging time τ_b .

Of course, the above questions concerning the nature and capacity of carbon nanosegregations on intragrain dislocations and on the ferritic grain boundaries remain open. Moreover, researchers must study the degree of ferriticgrain oversaturation with carbon atoms that is necessary and sufficient for the highest possible filling of segregation nanoregions on intragrain dislocations and ferritic-grain boundaries to carbide-like levels, as well as for further possible formation of carbide precipitation on the intergrain regions (see Fig. 13).

We note that Eqns (1)–(4), which correspond to the Cottrell model, cannot be used to interpret a large amount of experimental data (for instance, the data in Refs [43, 63]) of the substantial decrease, up to several orders of magnitude, in the effective diffusion coefficient and increase in the effective solubility of carbon and nitrogen in strained iron (steel). At the same time, these data are described fairly well by Eqns (5)–(7), which allow determining the diffusion, thermodynamic, capacitive, and dimensional (d_{\perp}) characteristics of carbide-like nanosegregations on dislocations in ferrite [43, 52].

For the length of the characteristic diffusion path of carbon atoms to the grain boundaries in ferrite, using the volume diffusion coefficient $D_V = 5.5 \times 10^{-17} \text{ cm}^2 \text{ s}^{-1}$ in Ref. [16] and the aging time about 10-20 years, we obtain a value about 1 µm, which is much smaller than the grain size in pipeline steels (10-20 µm). These values of τ_b agree with the most often accounted-for accident ages for gas-main pipelines caused by stress corrosion (Refs [20, 21] and Figs 6 and 7) and with the incubation period of the formation of stress corrosion about 13 years (Ref. [23] and Fig. 8).

It can be shown (see Refs [4, 38]) that such a local mass transfer of carbon from near-surface micrometer regions of ferritic grains (with the concentration of excess carbon atoms in the ferrite lattices about $\sim 3 \times 10^{-2}$ mass% [16]) is quite sufficient for the formation of a continuous grid of carbide-like nanosegregations approximately 1 nm thick [43, 52] at grain boundaries of the pipeline steels under investigation.

On the other hand, it can be shown (see Refs [4, 38]) that the lowest degree of oversaturation of 10 µm ferritic grains with carbon that is necessary and sufficient for the carbonization of grain boundaries, which are roughly 1 nm thick, to carbide-like concentrations (i.e., for the formation on ferriticgrain boundaries of a continuous grid of carbide-like nanosegregations [43, 52] as a result of diffusion mass transfer of all carbon from the volume of the grains) corresponds to the excess concentration $\sim 3 \times 10^{-3}$ mass% ($\sim 1.4 \times 10^{-2}$ at.%), which is ten times lower than suggested in [16]. However, in this case, we are forced to return to a Bearing in mind the results in [17] concerning the possibility of substantial ferrite oversaturation with carbon in the pearlitic regions of the material and Mössbauer and other data [43, 60-62] on the cementite decomposition in cold-rolled (90%) steels and the transition of the carbon released in this process from the lamellar-pearlite regions into carbide-like segregation nanoregions on dislocations, we can examine the possibility of local diffusion mass transfer of carbon from the pearlitic regions of pipeline steels to the grain boundaries in the neighboring ferrite regions. In the course of the 10-20 years that it takes the pipelines to age, this mass transfer occurs over distances of the order of several micrometers. Obviously, the model considered here allows reconciling the experimental and theoretical data of the service life of pipeline steels.

At this point, we briefly discuss the possibility, mentioned in [16], of accelerating the diffusion process of pipeline aging caused by the high degree of oversaturation ($\Delta C/C$) of the ferrite lattice with carbon and the need to introduce this quantity into Eqn (2) in order to be able to estimate τ_b [see Eqn (1)].

Usually, this factor is taken into account (e.g., in Ref. [64]) within the concept of diffusion mobility of the impurity atoms combined with the linear (Onsager) approximation of the thermodynamics of irreversible processes used to describe the driving force of the process. We note that in Ref. [64], in particular, we examined the effect of liquid-metal wetting or amorphization of intergrain nanoregions in metals (Bokshtein mentioned this effect in connection with intergrain embrittlement and crack formation). In this approximation, for gas pipelines that have been in extended service, we have

$$\tau_{\rm b} \approx \frac{L^2}{D_{\Sigma}(\Delta C/C)} \approx \frac{L^2}{D_{\rm V}(\Delta C/C)} \,, \tag{8}$$

which is similar to Eqn (3.2) in Ref. [64]. Here, $\Delta C \approx C_g - C_b$ is the difference between carbon concentrations at the grain center (C_g) and near the grain boundary (C_b is the equilibrium value), and $C \approx (C_g + C_b)/2$ is the mean carbon concentration in ferrite at the characteristic diffusion distance $L \approx d_g/2$. Assuming, according to Ref. [16], that $C_g \gg C_b$, we obtain the values $\Delta C/C \approx 2$, i.e., taking this factor into account does not lead to sufficient acceleration of the process (in accordance with the remarks in [18]).

As rightly stressed in [18], the model in [16] and the corresponding results of the estimate of a possible decrease by a factor of 2 to 3 of the characteristic time τ_b of the diffusion aging process due to active external stresses in gas pipeline steels cannot be considered fully justified.

We note (see Ref. [38]) that in [16] and [18], only the Cottrell model of carbon segregations on dislocations in ferrite is discussed; this model does describe the numerous experimental data mentioned earlier. At the same, in recent works (e.g., see Refs [63, 65]), unique Mössbauer and diffusion data were obtained that point to the formation of FeAl₆-like, i.e., intermetallic-compound-like, nanosegregations at grain boundaries in highly diluted solution of iron and aluminum. A detailed analysis of these and other data can be found in Ref. [50], which is devoted to a thermodynamic and crystal-

chemical study of intermetallic-compound-like (including $Fe\Box_{1.5}Al_6$ - and $Fe\Box_{1.3}Al_3$ -like, where \Box is the structural vacancy symbol) nanosegregations on dislocations [39-43] and grain boundaries [65, 66] in aluminum, as well as their effect on the effective characteristics of the diffusion and solubility of transition-metal impurities. The data used in this analysis (see Ref. [50]) embraced Mössbauer, diffusion, resistometric, and electron microscopic data [39-43, 65, 66], including the data in [39] obtained by 2.5-dimensional electron microscopy.

All this points to the need to do more studies [4, 38], including a certain refinement and development of the model of aging and the concept in [16] of the effect of aging on stress-corrosion damage and service life of the material.

3.2 Local hydrogen saturation of gas-main steels during their aging

Analytical review [16] and reports [17-19] devoted to discussing the theoretical bases of the aging process and problem-posing report [23] devoted to various aspects of aging and stress-corrosion damage of gas pipelines lack an analysis of the possible effects of the aging process and its relation to processes of local hydrogen saturation and hydrogen embrittlement discussed in Refs [13, 14, 24, 25, 27].

At the same time, the fact of hydrogen saturation of pipeline steels [13, 27] is directly related to the problem discussed in [20] and [26] that remaining within Bokshtein's theory of aging [16], it is difficult to explain why stresscorrosion damage is seldom encountered in oil mains despite the proximity of steel brands and service conditions. Obviously, hydrogen saturation is either very weak or absent altogether (in contrast to the case of gas-main steels), which apparently is why stress-corrosion damage manifests itself quite weakly in oil pipelines [4, 38].

We also note (see Ref. [38]) that according to the data of electron microscopic autoradiography [24] (see Fig. 16), large-angle grain boundaries remain almost totally free from hydrogen isotopes in the process of metal aging, up to the point where precipitations of the second phase (carbides, intermetallic compounds, etc.) begin to appear on them. Before this happens, tritium gathers (as the metal is aging) in dislocation traps inside grains, and only when second-phase precipitations begin to appear on grain boundaries is intensive saturation of the boundaries by hydrogen observed. It was noted in [24] that the local hydrogen saturation of the regions of second-phase precipitation on grain-boundary regions, which manifests itself in the course of prolonged steel aging, is conducive to the intergrain brittle fracture of these steels in SCD.

We emphasize (see Ref. [4]) that in Refs [13–27], as in most papers on hydrogen embrittlement of materials, no account is taken of the fundamental process [3, 4, 37, 38, 43, 44, 46, 55, 56] of the formation of carbonitridehydride-like (Fe₂(C, N)H_{0.6–2}, etc.) and intermetallic-compound-like (Ni₃TiH_{1±δ}, etc.) nanosegregations on dislocations and grain boundaries in metallic materials (steels). The process of formation of nanosegregations (thermodynamically stable nuclei of second-phase precipitations) is related to the process of aging of materials [52] and affects their physicomechanical properties [35, 48, 54, 55].

Therefore, we believe it is advisable (see Refs [4, 38]) to do more thermodynamic, crystal-chemical, and other experimental research concerning carbohydride-like nanosegregations on dislocations and grain boundaries in ferrite. According to the authors of Refs [5, 40–43, 53], such nanosegregations can be characterized as a special adsorbed (using the terminology in [40]) 'quasihydride' nanophase in nonhydride-forming metals (α -Fe). This phase cannot be isolated and identified in the form of a specific phase, but, just as in the case of carbide-like nanosegregations, it can serve as a preferable place (stable available nuclei) for the precipitation of the 3D second phase.

The thermodynamic stability of such an adsorbed [40] one-dimensional (on dislocations) or two-dimensional (on grain boundaries) segregation nanophase of a cluster nature is, in particular, due to the low value of interphase tension at the nanophase – metal interface [40–43, 53], which, obviously, is achieved through nanophase amorphization [43, 53]. This is quite possible for carbide-like and nitride-like nanophases, which are close in structure to Fe₃C, Fe₂C (Fe₂₀C₉), Fe₃N, Fe₄N, or Fe₈ and contain a number of vacant trigonal dipyramids of the Bernal type [43, 53] sufficient for nanophase amorphization [67, 68].

In contrast to ordinary three-dimensional phases, the adsorbed one- or two-dimensional segregation nanophases are unable to coagulate because they cannot exist (are not stable enough thermodynamically) separately from dislocations or grain boundaries [40-43, 53]. Hence, it is precisely the adsorbed segregation two-dimensional nanophases that can form a continuous grid over the grain boundaries in the metal, a grid that to a certain extent corresponds to the model in [16] (see Figs 14 and 15). Chuvil'deev noted that "the very presence of a carbide grid (irrespective of its thickness) is a sufficient factor for the development of stress corrosion." At the same time, the segregation nanophases adsorbed by grain boundaries are in a certain sense available nuclei of precipitations of the three-dimensional second phase, capable of coagulation in the prolonged service of pipeline steels; this fact is not taken into account by the model of quasicontinuous grid of plates of grain-boundary carbides [16] (see Fig. 15).

The essence of the model of a continuous grid of carbohydride grain-boundary nanosegregations in [4, 38], which is a further development of the model in [16] (see Figs14 and 15) and is based on the results discussed in Refs [35-37], consists in the following:

(i) The ferrite lattice carries (in the form of a solution) only an exceptionally small fraction of hydrogen (~ 0.03 at.% [27]) contained in pipeline steels that have been in service for a long time and aged in the process. Most of the hydrogen is in carbohydride-like nanosegregations (of the Fe₂CH_{0.6-2} type [43, 44, 46, 55, 56]) on dislocations and grain boundaries in ferrite. Therefore, the one- and two-dimensional segregation nanoregions of hydrogen localization (adsorbed nanophases) occupy a very small fraction of the material volume (several hundredths of one percent); an adequate amount of excess carbon is also localized in these nanoregions. A substantial amount of hydrogen may occupy regions of nonmetallic, e.g., sulfide, inclusions and pores [13], which are not considered in the present model.

(ii) Local 'carbohydride' hydrogen saturation or, in common terms, the hydrogen embrittlement of the ferritic grain boundaries occurring as the material ages, is in many cases limited by the diffusion mass transfer of the necessary amount of carbon from the ferritic grains to their boundaries. Obviously, this process is conducive to intergrain stresscorrosion cracking (see Figs 11 and 12), embrittlement, and delayed fracture (see Figs 9 and 10) of pipeline steels. The process is characterized by the diffusion (aging) time, which in many cases may be as long as 10 years (see Figs 6-8) and depends on the concentration of excess carbon atoms in the ferrite lattice and a number of other factors. Hydrogen embrittlement is the necessary but not sufficient condition for stress-corrosion attack and fracture of the material.

(iii) The diffusion mass transfer of the necessary amount of hydrogen to ferritic grain boundaries is not a limiting process. This fact is confirmed by estimates of the diffusion time for distances corresponding to the pipeline wall thickness (from 9 to 19 mm [23]). If we assume, following the data gathered in [27], that the diffusion coefficient for hydrogen in fractured pipes is $D \approx 1 \times 10^{-6}$ cm² s⁻¹, we find that for 20 mm thick pipes, the hydrogen diffusion time amounts to about 40 days, which is much shorter than the characteristic time for carbon atom diffusion to the ferritic grain boundaries (≥ 10 years).

(iv) Instead of the model of a continuous carbide grid over ferritic grain boundaries [16] (see Figs 14 and 15), we introduce (see Refs [4, 38]) the model of a continuous grid of carbohydride-like (of the Fe₂CH_{0.6-2}) intergrain nanosegregations whose thickness is roughly 1 nm. Obviously, a continuous grid forms in aging pipeline steels, which is the main reason for intergrain hydrogen embrittlement of the material conducive to stress corrosion attack and fracture, including intergrain cracking (see Figs 11 and 12). In pipeline steels that are in the process of aging, which, obviously, runs in the absence of sufficient hydrogen saturation, a grid of carbide-like nanosegregations forms at the boundaries of the ferritic grains in most cases, and this is not as conducive to intergrain embrittlement and stress-corrosion attack of the material as a grid of intergrain carbohydride-like nanosegregations is.

(v) When gas pipelines have been in service and the aging process sets in, the remaining excess carbon with a sufficiently high oversaturation level diffuses from the internal regions of ferritic grains (and/or from pearlitic regions) to their boundaries decorated with nanosegregations, which are ready second-phase nuclei. Here, on the boundaries of ferritic grain, a discrete grid of carbide precipitations may form [16, 24] (see Fig. 11), which may in turn interact with hydrogen [2, 30, 69].

As noted in [18], grain-boundary impurity segregations are capable of inflicting local internal stresses, which can lead to intergrain crack-forming. Local stresses and strain on the boundary of metal grains may possibly emerge because of the excess volume and at the expense of the free energy of topochemical reactions [70]. These may include the formation in ferrite of a grid of intergrain carbohydride-like nanosegregations or an adsorbed two-dimensional phase.

4. Some comparisons and additions

As noted in Refs [4, 38], hydrogen cracking has been observed in substantial volumes (and not only at grain boundaries) in unaged samples of low-alloyed ferrite and pipeline ferritepearlitic steels subjected to tension at a constant rate (up to fracture) accompanied by electrolytic hydrogen saturation (e.g., see Refs [37, 71, 72] and Fig. 17). There are reasons to believe that the data in Refs [37, 71, 72] and Fig. 17 do not contradict the data in [16, 24, 25], and elsewhere (see Figs 11 and 12) on intergrain hydrogen cracking of the material, because they correspond to different testing conditions.

In this connection, we note that the data in [2] on a disastrous rupture of a steel vessel used to transport gaseous



Figure 17. Microstructure of a strip sample (unaged, using the terminology in [16]) of 08FYuP steel near a fracture after being subjected to tension (along the denoted axis σ at the constant rate 6×10^{-5} s⁻¹ up to fracture) and accompanied by electrolytic hydrogen saturation (with the current density 10 mA cm⁻²). The etched metallographic section is in the strip plane [37]: (a) ×240, the arrows point to cleavage facets, which are parallel to the microcracks in the sample and are located primarily inside ferritic grains being almost perpendicular to the tension axis σ ; (b) ×1350.

hydrogen, caused by hydrogen cracking and initiated by pitting corrosion, and also the data in Ref. [2] (see Fig. 2) on the explosion type of a disastrous rupture caused by intergrain (hydrogen) cracking are in fairly good agreement with the data of in [16] and [25] (see Figs 11 and 12) on the intergrain stress-corrosion cracking of pipeline steels. Recent report [73] gives an exhaustive picture of the data in Ref. [2], including those used in the present review (see Figs 1-3).

We also note that the data in [2] on the hydrogen cracking of a stainless-steel pipeline leading to a vessel used for cryogenic hydrogen storage agree, for instance, with the data on the destructive effect of gaseous molecular hydrogen on a 12Kh18N9T austenitic steel pipeline in conditions typical of the space industry [5]. The pipeline was 40 mm in diameter, its wall was 1 mm thick, the hydrogen pressure was 90 bar, the temperature varied between 230 and 270 K, and the time during which hydrogen acted on the pipeline was $10^2 - 10^3$ s. The destructive effect of hydrogen (throughthickness microcracks) manifested itself in the hydrogen pipeline sections that were prestressed (due to bending) at liquid-nitrogen temperatures; in the process, the initial austenitic structure substantially transformed into a martensitic structure. The emergence of microcracks considerably accelerated the diffusion aging process [73, 74] and the related process of local hydrogen embrittlement of the material caused by the formation of adsorbed nanophases of the carbohydride-like and/or intermetallic-compound hydride-like type [4, 38].

The data in [24] (see Fig. 16) on the localization of tritium in aged samples of Kh16N15M3T1 stainless steel on dislocation subboundaries, on dislocations surrounding inclusions, and around grain-boundary precipitations of the Ni₃Ti intermetallic compound agree with our data [44, 45] on the role of intermetallic-compound hydride-like nanosegregations (Ni₃TiH_{1±δ}, etc.) in dislocations and grain boundaries in the embrittlement and delayed fracture of aged samples of the N18K9M5T stainless steel. Our results (see Refs [44, 45]) can be used to solve the problem of 'open' questions (physical problems) concerning anomalies in the solubility and diffusion of hydrogen in stainless steel [75].

At this point, we note that the interaction of hydrogen, e.g., with titanium alloys may lead not only to hydrogen embrittlement and cracking [7, 76] but also (in certain technological conditions) to the opposite result, their plasticizing (softening) up to the point where the hydrogen superplasticity manifests itself [8, 77]. A similar situation occurs for some other metals and alloys [78-82], including iron (hydrogen plasticizing of a material of the transformation superplasticity type). There are indications (Refs [48, 84-86] and others) that in many cases [37], the hydrogen superplasticity of the material is caused by a periodic formation of a liquid-like state in the nanoregions of grain boundaries due to 'bombardment' by dislocations carrying hydrogen [48], deformation vacancies, and hydrogenvacancy clusters (the dynamic effect of local clusterization of vacancies and hydrogen atoms [87] corresponding, to a certain degree, to the Frenkel mechanism of vacancy melting of grain boundaries).

We note the important question formulated in [87], of the fugacity of molecular hydrogen in metals and alloys during their electrolytic saturation with hydrogen (in the process of molarization of atomic hydrogen in micropores and/or microcracks of the material (see Fig. 17), or hydrogen attack, according to the terminology used in [2, 73]); incidentally, this question has been studied in Refs [37, 45, 54].

The participants in the discussion at the Fourth Russian Conference: Physical Problems of the Hydrogen Energy Industry remarked on the proximity of the methodological approaches and ideas related to the problems of aging, embrittlement, and fracture of metallic materials used in the hydrogen energy industry and gas mains and the problem of degradation processes in solid-oxide fuel cells [88].

We believe it is now advisable to discuss the results in [89], which are mentioned in Kahn's classic monograph [90] devoted to a review of the achievements in physical material science and its history. The segregation capacity of, apparently, mainly screw dislocations in the martensitic matrix (α -Fe) in relation to carbon atoms, $n_{C\perp} = 21 \pm 1$, were experimentally determined in [89] (Figs 18a-e). The obtained value is close, by an order of magnitude, to those given in Section 3.1, $n_{C\perp} \approx 40-90$ [32, 28], for mostly edge dislocations in ferrite, whose segregation capacity may (theoretically [32, 33]) be much higher than that for screw dislocations. Nevertheless, if we use the value $n_{C\perp} \approx 22$ [89]



Figure 18. ECOPoSAP (energy compensated optical position-sensitive atom probe) results [89] of an analysis of the regions of the material directly above a dislocation (a-e) and regions outside the dislocation (f-j). The micrographs taken at 12 kV in Ne at 50 K show the analyzed areas (a and f). Four consecutive sections, (b-e) and (g-j), each containing five atomic planes, were analyzed. In each case, the width of the analyzed regions was 10 ± 1.5 mm. The initial dislocation position is shown by a circle in (a) and (b).

to estimate the possible carbon content in segregations on edge dislocations in ferrite (controlled-rolling pipeline steels), the value $\sim 1 \times 10^{-2}$ mass% C (~ 0.05 at.% C) corresponds to the dislocation number density $\sim 2 \times 10^{10}$ cm⁻², which is possible for such steels [16].

It is shown in [89] that in samples containing 0.85 at.% C, most carbon ($\ge 4/5$) is localized in the segregation nanoregions along dislocations (Figs 18a-e and 19). In the martensitic matrix of α -Fe, there is only a small amount of carbon ($\le 1/5$), which ensures the volume concentration no higher than 0.17 at.% C (≤ 0.036 mass% C). We note that this value is much higher than the concentration of carbon ($< 10^{-4}$ mass% C [17]) corresponding to equilibrium with cementite at room temperature and is close to the concentration (~ 0.03 mass% C) of excess carbon atoms in the ferrite lattice (in pipe steels) suggested by the model in [16]. At the same time, the authors of [89] rather convincingly assume that in martensitic samples containing 0.85 at.%, in experimental conditions at room temperature, a carbon distribution close to the equilibrium one sets in between the martensitic matrix and nanosegregations on dislocations and grain boundaries. However, they ignore the fact that their value of the volume concentration of carbon, which, obviously, characterizes the solubility of such nanosegregations in the stressed martensitic matrix, is relatively high.

In this connection, we note that in Refs [35, 39-42], we thermodynamically justified the possibility of formation of cluster nanosegregations on dislocations in hydrogen solutions in palladium and in iron solutions in aluminum, either oversaturated or unsaturated in relation to precipitations of the corresponding second phase.

We also note that the results in [89] are conducive to a deeper understanding and interpretation [46] of the similar data in [59], discussed in Section 3.1, on the bonding of dislocations in martensitic steels with about 0.2 mass% C (0.92 at.% C). The researchers found (see Figs 18 and 19) that the segregation atmospheres around dislocations have a dispersed anisotropic distribution of carbon atoms that extends to about $\approx 7 \pm 1$ nm from the boundary of the dislocation core with the diameter about 2 nm [91]. Thus, the effective diameter of the segregation atmospheres is $\approx 14 \pm 2$ nm, and their cross-sectional area is roughly 150 nm². This implies that each of the four five-layer regions (i.e., containing five atomic layers of the (110) material), shown in Figs 18b-e, with the cross-sectional area about 100 nm², corresponds to roughly 2/3 of the cross-sectional area of a segregation atmosphere; about 60 carbon atoms have been found in each of the four five-layer regions with the overall thickness about 1 nm. With the experimental value $n_{C\perp} = 21 \pm 1$ in Ref. [89], which is the average number of carbon atoms in the monatomic layer (110) of the cross section of a segregation atmosphere surrounding the dislocation, we may assume that the five-layer cross section of the segregation atmosphere surrounding the dislocation contains about 105 carbon atoms. The remaining $\sim 1/3$ of the crosssectional area ($\sim 50 \text{ nm}^2$) of the five-layer atmosphere contains about 45 carbon atoms. This implies that the local concentration of carbon in all four five-layer analyzed regions (over the entire cross-sectional area of the segregation atmosphere with the diameter about $\approx 14 \pm 2$ nm) varies from several to 8 ± 2 at.% C (peak value). These values correspond with the carbon concentration averaged over the depth of the analyzed material of about 1 nm, i.e., over five adjoining atomic layers of the (110) material in the cross section of a segregation atmosphere (see Figs 18 and 19).

There are reasons to believe that there is a kind of stratification, or clusterization, of segregation atmospheres, i.e., a monolayer carbide-like structure with a high local concentration of carbon ($\sim 15-35$ at.%) forms in a segregation atmosphere. The following facts corroborate this view:

(i) A high local concentration of carbon (from several to 8 at.% C if averaged over the five atomic layers of the (110) material [89]) over the entire cross section of the segregation atmosphere with the diameter $\approx 14 \pm 2$ nm. As noted in [89],



10 nm

Figure 19. ECOPoSAP results [89] of an analysis of the regions of the material directly above a dislocation. Shown are the isoconcentric (4 at.% C) surfaces in the segregation atmosphere for three different positions (angles) of observation. The width of the analyzed region was 10 ± 1.5 nm and the depth of analysis was roughly 4 nm. The circle in (a) shows the dislocation position.

such values of carbon concentration may be achieved in the Cottrell model only near the dislocation core at a distance ≤ 1 nm from it.

(ii) An abrupt decrease (by a factor of 100) in the carbon concentration in the martensitic matrix of α -Fe outside the segregation atmospheres, which is typical of interphase boundaries (interfaces) [89].

(iii) A relatively high volume concentration of carbon $(\sim 0.17 \text{ at.}\% (\sim 0.036 \text{ mass}\%))$ in the martensitic matrix outside segregation atmospheres. This value exceeds the concentration ($< 10^{-4}$ mass% C [17]) corresponding to the equilibrium solubility of cementite in α -Fe at room temperature by several orders of magnitude. According to [92], a characteristic feature of the metastable phase is its higher solubility compared to that of the stable second phase, cementite (in relation to their solubilities in α -Fe). As a metastable state, we can take the cluster carbide-like nanophase, the segregation nanostructure surrounding dislocations in the martensitic matrix. But this does not agree very well with the disintegration of cementite in cold-shaped (up to 90%) steels [43, 60-62] and the transfer of the released carbon from lamellar-pearlite regions into segregation carbide-like nanoregions on dislocations. Hence, it must be assumed that mainly the high level of stress in the matrix causes the high solubility of the cluster carbide-like nanophase in the martensitic matrix. This agrees with the fact, to be mentioned below, that the distance between dislocations $(\sim 18 \text{ nm})$ in martensite [89] is close to the diameter of segregation atmospheres (14 nm).

(iv) The experimental observation in [19] of the formation, in low-temperature aging of low-carbon iron, of a metastable band (cluster, segregation) nanostructure inside ferritic grains (see Section 3.1). This fact can be described by the thermodynamic model of the clusterization of excess carbon in the ferrite lattice (e.g., see Refs [43, 51]). The possibility of clusterization of segregation atmospheres is also corroborated by the formation in bcc lattices (α -Fe, W, Mo) of flat segregations of interstitial impurities (C, N, O) with a diffraction contrast that differs slightly from that of stacking faults (prismatic loops) [91].

(v) The Mössbauer data [60, 61] (discussed in Section 3.1 and in Ref. [43]) on the high values of the segregation capacity of dislocations ($n_{C\perp} \approx 20$) in cold-shaped synthetic steels. What is important here is the experimental fact [60, 61] that the hyperfine structure and characteristics of the Mössbauer spectrum for iron atoms localized in segregation nanoatmospheres of carbon around dislocations differ substantially from those for iron atoms in solid interstitial solutions of carbon in the ferrite matrix, but are close (comparable) to the spectrum characteristics of iron atoms in cementite. This fact agrees with experimental results in [41-43, 50, 65, 66], according to which the Mössbauer spectra for iron atoms localized in segregation nanoatmospheres on dislocations and grain boundaries in dilute solutions of Fe in aluminum differ substantially from those for iron atoms in substitutional solid solutions in aluminum, but are close to the spectra of the second phase (FeAl₆, FeAl₃).

(vi) The data in [93] on three-dimensional atomic force microscopy on cluster segregations of carbon (of the Fe₃C type) in linear nanoregions along dislocations in iron (Fig. 20a) and homogeneous segregations of carbon in planar nanoregions along intergrain boundaries in iron (Fig. 20b).

A critical constructive analysis of the results in [89] and the comparison of those results with other data [17, 19, 41–43, 50, 60, 61, 65, 66, 91–93] demonstrate the possibility of formation, around dislocations in the martensitic matrix, of



Figure 20. Images obtained by using an atomic force microscope equipped with a 3D probe [93]: (a) linear cluster segregations of carbon along a dislocation in iron (Fe₃C nanoclusters, 24 at.%), and (b) planar homogeneous segregations of carbon along a grain boundary in iron. (Figure 20 was obtained together with X. Sauvage.)

high-capacity segregation atmospheres with the diameter $\approx 14 \pm 2$ nm with a dispersed anisotropic distribution of carbon inside the atmospheres and a monolayer carbide-like structure with a high local concentration of carbon ($\sim 5-35$ at.% C). It is obvious that such formations differ substantially from those in the Cottrell atmosphere model [32, 33] used in [16], but are close to those used in the simplified model, considered in this review, of high-capacity carbide-like nanosegregations on edge dislocations and grain boundaries in ferrite [4, 38, 43, 53] (the last model does not take their dispersive nature into account). At the same time, it should be noted that the observed segregation atmospheres on dislocations were named Cottrell atmospheres in [89].

Using the experimental value $n_{C\perp} = 21 \pm 1$ and the data in [89] on the localization of four-fifths of the overall carbon content (0.85 at.% C) in martensitic samples in segregation nanoatmospheres on dislocations, we can estimate (see Section 3.1) the average dislocation number density in these samples (~ 3 × 10¹¹ cm⁻²) and the average distance between them (~ 18 nm), which turns out to be close to the diameter of segregation atmospheres (14 ± 2 nm).

Hence, we can speak of segregation structural-phase nanofragmentation (nanoheterogeneity) of the martensitic matrix of the samples used in [89] and formally think of them as specific nanomaterials [57, 64, 93, 94]. This idea agrees quite well with the rack-like, or lamellar, microstructure of the martensitic samples used in [89], in which the thickness of the plates was about 250 nm and a certain fraction of inter-rack interfaces were highly segregated intergrain boundaries of the large-angle type.

In the justified opinion of Wilde et al. [89], the observed, large-angle grain boundaries, highly segregated by carbon, in the martensite of α -Fe point to a situation in which a carbon distribution close to the equilibrium distribution (with the aging temperatures of hardened samples maintained at 273 K over the course of 24 hours) sets in between the martensitic matrix and the segregation nanoregions on dislocations and grain boundaries. The researchers corroborate their opinion by estimates of the length of the characteristic path of carbon diffusion in the martensitic matrix when the sample is kept at 273 K for 24 hours, $L \sim 15$ nm, which appears to be close to the average distance between dislocations. Independent data on the diffusion coefficient of carbon in martensite, $D_V \approx 3 \times 10^{-17}$ cm² s⁻¹, was used in the estimate. According to [89], this value is close to the one obtained in Section 3.1 by processing the data in [19], $D_V \approx 4 \times 10^{-17}$ cm² s⁻¹, and the value $D_V \approx 5.5 \times 10^{-17}$ cm² s⁻¹ given in Ref. [16].

We also note that the observed (but unexplained in [89]) substantial redistribution of carbon already in the process of hardening the sample (from 1273–1373 K into an ice bath), which, obviously, agrees with the anomalously high diffusion mass-transfer coefficients, can be interpreted on the basis of the known data (e.g., see Ref. [74]) on the effect of high-rate shaping of the material on diffusion and, in particular, in a martensitic transformation.

The gradual decrease in the limit of macroelasticity of pipeline steel with the increase in the service time of the steel in gas mains, noted in [16], may point to a diffusion redistribution of a significant amount of carbon from metastable carbide-like nanosegregation on dislocations to the thermodynamically preferable boundaries of ferritic grains (in the formation of carbide-like grain-boundary nanosegregations). In this connection, we refer to Fig. 21, which illustrates the data gathered in [27].

Remaining within the modified model presented in this review, we can consider the well-known but insufficiently discussed fact [16] that cracks form on the inner surface, rather than the outer surface (as in gas mains) of oil pipelines. These pipelines are subjected to substantial cyclic loads (rather than static leads, as gas pipelines are) and operate at



Figure 21. Temperature dependence of the internal friction of pipeline steel 17GS: (a) emergency reserve, and (b) after 30 years in service [27].

lower (by 10-30 K) temperatures [26]. The formation of cracks on the inner surface can be attributed to obvious differences in the kinetics and degree of hydrogen saturation in gas and oil pipelines.

Our discussion has shown the need for further comprehensive studies [37, 38], including the study of safety problems and the problem of compatibility of hydrogen and metallic materials [1-4]. We believe that the following areas of research are important to investigations of the main fundamental planar nano-object in metals and alloys, the large-angle grain boundaries of the general type:

(i) The physics of grain boundaries with an adsorbed nanophase, including carbohydride-like, intermetallic-compound-hydride-like, and other cluster intergrain nanosegregations, which lead to embrittlement and local stresses in regions of grain boundaries and are conducive to intergrain (hydrogen) cracking and stress-corrosion attack on the material.

(ii) The physics of what is known of nonequilibrium grain boundaries with a high level of local stresses generated, e.g., by intensive plastic deformation of the material [93] or thermomechanical treatment [24] (stepped boundaries). Here, one should consider (see Ref. [86]) the periodic (threelevel cyclic) variation of the state of the nonequilibrium grain boundaries from state I with a negligible number density of captured lattice dislocations (as for 'equilibrium' boundaries) to state II with a very large number density of captured lattice dislocations whose energy is close to the material melting energy (the I \rightarrow II transition), with a subsequent transition to liquid-like state III (the $I \rightarrow III$ transition, of the melting type), and a return to the initial state (the III \rightarrow I transition, of the crystallization type). Obviously, the corresponding periodic volume variations caused by these transitions (especially the III \rightarrow I transition) explain the high local stresses in the regions of grain boundaries [93]. The sequence (in the cycle I \rightarrow II \rightarrow III \rightarrow I . . .), periodicity, and kinetics of these transitions are possibly related to the manifestation of various accommodation processes with a limited intensity (potential capability or productivity) of accommodation of the intergrain structure in the capture and/or absorption by grain boundaries of lattice dislocations and vacancies [86]. Such behavior may in particular lead to stepped boundaries [24], which apparently correspond to the extensive path of their self-organization as the material is being deformed.

5. Conclusion

Effective ways of solving the physical, technological, complex problem of aging, hydrogen embrittlement, and destruction of metallic materials should be sought with allowance for the huge body of empirical knowledge, accumulated over the last several decades, concerning various aspects of the behavior of a large number of material-hydrogen systems operating within a broad range of external conditions. Such information has yet to receive proper acknowledgment, systematization, and use in developing fundamental ideas and understanding the nature (micromechanisms) of hydrogen embrittlement and hydrogen degradation of properties, these ideas being necessary for optimizing the technological process and parameters of structural metallic materials.

We believe that we must use new concepts and methodological approaches, results, and methods of analysis [3, 4, 35– 57], whose effectiveness has been proved in the studies of other pressing physical problems [36, 64, 74, 86, 94]. On the basis of such approaches, which may in a certain sense be called nanotechnological and nanosize approaches [57, 64, 70, 74, 86, 93, 94], results, and analysis methods [3, 4, 35-57], we have developed (see Refs [4, 38]) a model, described in this analytical review, of grain-boundary hydrogen embrittlement of the material due to the formation of a continuous grid of carbohydride-like nanosegregations on ferritic grain boundaries in aging gas mains (as a necessary but not sufficient condition for stress-corrosion attack and the failure of gas mains). This method is a further development of the model in [16].

A similar fine-tuned model can be used for other materials of the hydrogen energy industry [2, 73].

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