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HYDROGEN AND FLAKES IN STEEL

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Flakes are special discontinuities in steel parts that have the form of silver-colored spots on fracture surfaces or thin hair-like cracks on a ground and etched template. They appear and grow after a considerable incubation period, often in the operation of the part, which makes them a dangerous defect. Depending on the dimensions, number, and position in the metal, flakes can decrease the toughness and ductility of steel to zero and reduce markedly the service life of steel parts and structures, causing unexpected and serious failures. The present review briefly generalizes recent works devoted to the formation of flakes in steel.

Metallurgists encountered flakes as early as in the first world war in mechanical treatment of large preforms for gun barrels. Thousands of research papers and several monographs [1 – 5 and other works] have been published by Russian specialists since that time but the problem has not ceased to be important. For a long time metallurgists could determine neither the mechanism nor the causes of the formation of flakes. Lengthy and intense discussions of the causes of their formation have shown that this phenomenon should be associated with the effect of hydrogen and internal stresses.

States of hydrogen in steel. It has been established that hydrogen in steel can be present in various states, namely, atomic-protonic hydrogen dissolved in the crystal lattice ("free," diffusion mobile), atomic hydrogen bound to defects of the crystal structure (dislocations, vacancies, intergrain and interphase boundaries), molecular hydrogen bound with micro- and macrovoids, hydrogen bound chemically to hydride-forming metals (Ti, Nb, V, Zr, rare-earth metals), hydrogen bound chemically to nonmetals (C, O, S, N), for example in an oxidized state in the form of water vapor adsorbed in pores and hydroxyl groups incorporated in nonmetallic inclusions. There are data that hydrogen forms compounds of the solid-solution type with some alloying elements in steels and can be dissolved in the carbide phase, i.e., can have the form of hydrocarbides [1, 2, 5 – 7].

It is assumed that the process of formation of flakes is caused only by the portion of hydrogen that can move over the volume of the metal, i.e., is in an atomic-protonic state. However, at present there are no reliable methods of fractional separation of different forms of hydrogen [1].

The authors of [8, 9] studied the forms of existence of hydrogen in metals of the Fe group by the method of degassing specimens in heating. The hydrogen content in the specimens and the distribution over its various forms were determined by integrating the corresponding curves describing the dependence of the rate of emission of H_2 on the temperature. The specimens had various initial states (cast, forged, hydro-extruded) and the corresponding amounts of structural defects. The thermokinetic heating curves of all the metals had two well-defined groups of peaks corresponding to low-temperature (at 100 – 650°C) and high-temperature (at 600 – 1100°C) forms of emission of hydrogen. The relative distribution of the dissolved hydrogen over the forms of its emission depended on the nature of the metal and the prehistory of the process (the initial state). An analysis of the data on the thermokinetics of the desorption of hydrogen from specimens subjected to various holds after hydrogen saturation (up to 90 days) has shown that reversibly dissolved hydrogen (emitted at room temperature – "free") corresponds predominantly to low-temperature emission, whereas irreversibly dissolved hydrogen corresponds to high-temperature emission only. The high-temperature group of peaks of emission of H_2 is of the same type for all the specimens and consists of two components. It has also been established [8, 9] that free hydrogen in metals of the Fe group exists in three main forms, namely, a single-atom cation H^{d+} protonized to a different degree at $d < 1$ (H^+ in the limit), a molecular cation H_2^+, and molecular hydrogen H_2 (although the molecular forms of hydrogen cannot be treated as free in the sense of their diffusion mobility). The form H^{d+} corresponds to the low-temperature group of peaks under the conditions of thermally activated desorption. The value of d is determined by the size of the void filled by the H atom in an interstice or in a defect of the crystal lattice and is maximum for the minimum volume of the void (octahedral in α-Fe and tetrahedral in γ-Fe). The charge of the H^{d+} cation is minimum when the hydrogen is positioned in vacancies, dislocations, and grain boundaries. Only two of the several low-temperature peaks of hydrogen emission corre-

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spond to disposition of single-atom cations in tetrahedral and octahedral positions of the regular lattice, the other correspond to their disposition in imperfections of the structure. The existence of hydrogen in the form of H_2^+ and H_2 corresponds to the high-temperature group of peaks on the thermokinetic curves. The first peak corresponds to the process of dissociation and emission of H_2^+ from the metal, the second corresponds to that of H_2. The most favorable variants for deposition of H_2^+ are bivacancies, dislocations, and grain boundaries; H_2 is deposited predominantly in polyvacancies (micropores) and macropores.

At the present time three groups of methods are used to determine the total content of hydrogen in steels, namely, methods related to the transformation of hydrogen dissolved in the metal into a gaseous state in heating or melting in vacuum or in an inert atmosphere, methods based on measurement of physical characteristics of the metal that depend on the hydrogen content in it, and chemical methods based on anodic dissolution with the use of three variants of final determination of hydrogen, namely, volumetric, photometric, and titrimetric. The chemical methods are low-efficiency and therefore hydrogen is most often determined by extraction in vacuum, the method of a carrier gas, electrochemical monitoring, and spectral analysis. Modern methods of hydrogen monitoring in steels and diagrams of installations used for this purpose are considered in detail in monograph [1].

The Ural Research Institute of Ferrous Metallurgy is a base organization for the development and fabrication of standard specimens for metallurgy. It has produced standard industrial specimen SOP 10 – 81 with a certified mass fraction of hydrogen equal to $2.0 \times 10^{-4}\%$ (2.24 cm^3 per 100 g of metal), which can serve as a standard in analyzing the hydrogen content. The mass fraction of hydrogen has been determined with an error not exceeding $\pm 0.2 \times 10^{-4}\%$ or 0.20 cm^3 per 100 g (at a confidence level of 0.95).

Methods for evaluating the flake sensitivity of steels. In order to study the effect of various process factors on the flake sensitivity (FS) of steels we should have a quite universal and reliable method of quantitative determination of the capacity of the metal for formation of flakes. Until recently only one method for evaluating FS has been suggested [10], in which the relative flake sensitivity is understood as the specific length of flakes related to 1 cm^2 of the area of the microscopic specimen, expressed in mm/cm^2, or the density of flakes in cm^{-2}. This method has disadvantages such as a connection with quenching cracks, low sensitivity, especially in cast specimens, poor reproducibility, high errors, a relatively large size of the requisite specimens (20 × 60 mm), laboriousness, and low efficiency (one determination takes 6 days).

Researchers at the Odessa Polytechnic Institute have suggested a fundamentally new method for determining the FS of steels [9] based on experimental gas-analytical measurement of the relative portions of hydrogen present in the tested metal in various states (see above). This method is more universal, reliable, and efficient and less laborious (3 – 5 h instead of 6 days).

Effect of the charge materials, modification, and melting process on the flake sensitivity. Muradova et al. have conducted a comparative study of a steel with 0.8% C melted in an arc furnace on conventional scrap (steel *1*) and on an original mixture, namely, an iron-rich raw material obtained by solid-phase reduction of coal-ore pellets (steel *2*), for susceptibility to the formation of flakes and have determined the maximum content of hydrogen not leading to the formation of flakes [11]. In all cases the density of flakes in steel *2* was 2 – 2.5 times lower than in steel *1*. After hydrogen charging of steel *1* flakes were formed at a hydrogen concentration of 6 cm^3 per 100 g of metal; in steel *2* this concentration was over 8 cm^3 per 100 g of metal. For specimens of steel *1* with a diameter of 25 mm at a hydrogen concentration of 8.8 $cm^3/100$ g the density of flakes was 0.6 cm^{-2}, in steel *2* the corresponding value was 0.22 cm^{-2}. The flake dimensions in steel *2* were also 2 – 2.5 times smaller than in steel *1*. The chemical compositions of the steels were close but steel *2* had a diminished (by a factor of 4 – 5) content of Cu, Sn, Sb, Pb, and As. The effect of minor impurities on the formation of flakes can be related to their segregation and the reduction of the strength of grain boundaries, as well as to the formation of point defects that embrittle the metal.

Hydride-forming elements (Ti, Zr, Pd, etc.) decrease the FS of steel because of their adsorption on structural defects simultaneously with hydrogen and due to possible formation of hydrides (traps of H) although the latter has not been proved experimentally.

It has been established [12] that the susceptibility of low-alloy steels modified by boron to the formation of flakes is decreased because boron concentrates over grain boundaries and cleans them of embrittling impurities and inclusions.

The flake damage of a steel depends considerably on the sulfur content, which is explainable, among other reasons, by the formation of manganese sulfides, which are collectors of hydrogen. The harmful effect of sulfur can be diminished by thorough desulfuration of the steel or modification of the metal by various elements that promote sulfur segregation in uniformly distributed poorly deformable globular inclusions. The modifying elements can be alkali-earth or rare-earth metals. However, their effect on the morphology of sulfur-bearing inclusions is related to the level of the activity of O_2 in the metal – slag – lining system, because the affinity of these elements to O_2 is higher than to S. Therefore, the FS parameters of a steel modified by alkali-earth and rare-earth elements have unstable values. Se and Te exert a favorable effect on the morphology and deformability of sulfur-bearing inclusions, and the stability of their action depends but little on the activity of O_2. By the data of [13, 14], the flake resistance of ferrite-pearlite carbon steels, used to produce oil and gas pipes, seamless rolled wheels for railroad rolling stock, and other parts, with a relatively high (up to 0.038%) content of sulfur has been increased by modifying the metal with

0.005 – 0.009% Se or Te without thorough desulfuration of the metal. This has been associated with a change in the nature of the sulfur-bearing inclusions. Specimens containing no Se or Te had a considerable number of defects of hydrogen origin in the zones of sulfide accumulation. In specimens with 0.009% Se the predominant inclusions were coarse weakly deformed magnesium sulfoselenides. After hydrogen charging, this metal virtually did not contain hydrogen defects. Hydrogen defects were also absent in a metal with 0.005% Te and heterogeneous inclusions of sulfur. It has been established that sulfoselenides and sulfotellurides interact with hydrogen contained in the metal. Se and Te not only have a favorable effect on the hydrogen resistance of the steel but also increase its toughness, especially at low temperatures, and machinability considerably.

Although systematic research on the effect of the method of manufacturing the steel on its final FS in the cast and strained states has not been conducted, these data are required for developing methods for manufacturing parts from flake-sensitive structural steels. For this reason, the authors of [9, 15] studied the flake sensitivity of Cr – Ni – Mo – V steels melted initially by the conventional technology in a 10-ton open electric arc furnace (EAR) and then subjected to vacuum-arc remelting (VAR), electron beam remelting (EBR), and electroslag remelting (ESR). The VAR and EBR methods caused a 0.1% decrease in the content of Mn, and the ESR decreased the content of S from 0.008 – 0.016% to 0.004% and the number of nonmetallic inclusions by a factor of 2. All the remelting techniques led to a considerable increase in the FS (after the "provoking" charging of the metal with hydrogen) in the following order: EAR → VAR → EBR → ESR, i.e., the improvement of the metal quality due to the use of vacuum technologies increases its susceptibility to the formation of flakes. The flake sensitivity increases especially markedly (by a factor of 2.5 – 4) after ESR. It is assumed that the considerable growth of the FS of steels subjected to the aforementioned kinds of remelting is caused by reduction of the concentration of crystallization pores, micropores, and the content of nonmetallic inclusions that are sinks of hydrogen, an elevated crystallization rate that leads to retention of a greater amount of hydrogen in the metal, reduction of the temperatures of the phase transformations, and growth of structural stresses.

In ESR the flake sensitivity of the metal is affected markedly by the composition of the flux used [16]. Of all the fluxes studied (ANF-6, ANF-28, ANF-29, and AN-291) the lowest FS in a strained Cr – Ni – Mo – V structural steel is produced by AN-291, and the highest one is produced by ANF-29. It has been established that by adding 0.08 – 0.16% reducers of Al and Ce to the fluxes the FS of the metal can be decreased by a factor of 2 – 3 compared to ESR processes in conventional fluxes. The FS of remelted structural steels is determined predominantly by the retained content of cerium.

The effect of the season of melting in the DSP-100NZA basic arc furnaces of the Donetsk Metallurgical Plant on the hydrogen content in bearing steels with 1.5% Cr has been studied in [17]. It was established that the absolute moisture content in the air and the hydrogen concentration in the metal are correlated quite closely, depending on the season of the year, with the maxima of both quantities corresponding to the summer period. The results obtained make it possible to correct the regime of antiflake heat treatment (AFHT) for the time of year and obtain a considerable economic effect.

The authors of [8] believe that hydrogen and nitrogen are competing horophilic elements and the horophilicity of nitrogen is higher than that of hydrogen with respect to some kinds of defects in the structure of the metal. For this reason, nitrogen can displace hydrogen from some defects by adsorption and increase the relative proportion of "free" hydrogen in them, thus increasing the FS of the steel. On the basis of this assumption they explained the positive effect of sulfur on the FS of steels sometimes observed. With growth of the sulfur content in liquid steel the rate of nitrogen absorption in it decreases proportionally, and when the concentration of sulfur in the metal attains 0.55% the process of dissolution of nitrogen is impeded completely. The FS of steels with an elevated concentration of sulfur can be decreased due to the very low concentration of nitrogen in them, when it already does not hamper much the adsorption fixation of hydrogen on structural defects of the steel.

Effect of the hydrogen concentration on the appearance of flakes in steel. The flake sensitivity of steels has been considered to be diminished by decreasing the total content of hydrogen (in the process of melting, casting, forging, cooling) and the amount of hydrogen in the solid solution by transferring it into a molecular or bound form (by means of heat treatment or introduction of hydride-forming elements) and by improving the quality of the steel by decreasing the segregation. For example, the use of vacuum casting makes it possible to decrease the concentration of hydrogen in the metal by almost a factor of 2 [5].

The critical concentration of hydrogen for the formation of flakes depends on the composition of the steel, its grade, and other factors and commonly amounts to 0.5 – 2 cm^3 per 100 g of metal, i.e., $(0.5 - 1.8) \times 10^{-4}$ % H.

The authors of [18] have studied the effect of the hydrogen content in a rail steel with 0.7% C and 1.3 – 2.3% Mn on its susceptibility to the formation of flakes. The critical content of hydrogen at which flakes have not yet been discovered was 2.5×10^{-4}% in this case. When the melt contained 3.3×10^{-4}% H, flakes were observed in steel with 1.3% Mn. In steels with a higher content of Mn, flakes appeared at a lower hydrogen concentration. No dependence of the incubation period of flake formation on the hydrogen content in the steels has been discovered.

Diagrams in the coordinates "% H – diameter of the specimen" have been plotted in [19] for a Cr – Mn – Si steel with 0.3% C with indication of the surface density of flakes and regions with flakes and without them. When this steel was cooled in air, flakes appeared in small amounts only in specimens 30 mm in diameter at a high hydrogen content

($12\ cm^3$ per 100 g of metal). With enhancement of internal stresses due to cooling of the steel in oil or water after its saturation with hydrogen, flakes can appear at a lower content of H. At a constant cooling rate the region of existence of flakes shifts toward smaller crosssections with growth of the hydrogen content in the specimens, namely, 15 mm in cooling in oil and 10 mm in cooling in water. Such diagrams make it possible to judge the amount of flakes in the steel by its hydrogen content.

It has been shown in [20] that after induction hardening a Cr – Mo tool steel for cold-rolling rolls undergoes hydrogen embrittlement that causes delayed fracture in machining, transporting, and storing the rolls. The susceptibility to the formation of flakes increased markedly with growth of the hydrogen content in the steel, beginning with a threshold value of $1.4 \times 10^{-4}\%$ below which flakes have not been observed.

In most cases the number and dimensions of flakes depend on the hydrogen concentration in the metal after hardening and increase with the latter.

Effect of the structure and heat treatment on the flake sensitivity. Flakes appear at a specific combination of the level of tensile stresses and hydrogen concentration in the steel [1]. The absolute magnitude of these "critical" parameters is difficult to determine. The formation of flakes is assumed to be a consequence of relaxation of stresses that are caused by the presence of hydrogen in the steel and internal stresses that appear as a result of cooling, strain, and phase transformations. The author of [21] has determined the relation between the stress field that appears around inclusions and their type and the susceptibility to the formation of flakes in steels with 0.08 – 0.17% C. The formation of flakes in strained steels is promoted by nondeformable solid inclusions, whereas soft inclusions of any size do not cause flakes. In cast steel, only inclusions of Al_2O_3 with a diameter exceeding 20 μm caused flakes, and the content of S and MnS inclusions did not affect the process.

Segregation regions in a steel that are enriched with C, P, S, and Cr have a higher stability of supercooled austenite, in which the hydrogen emitted in the transformation of the main part of the austenite is concentrated. In transformation of the retained austenite, hydrogen continues to be emitted, giving rise to stresses that cause the formation of flakes in the embrittled metal [5].

The effect of the structure of a high-strength Cr – Mn – Si steel with 0.3% C charged with hydrogen at 1100°C on the mobility of hydrogen is considered in [22]. To obtain different phase compositions after hydrogen charging, the metal was hardened from the austenitization temperature (1100°C) and hardened with cooling in the 550 – 300°C range. The hydrogen dissolved in the steel under high temperatures was redistributed in the process of isothermal phase transformations between austenite and the products of its decomposition. The mobility of hydrogen in the steel depended of the structure and the phase composition. Hydrogen moved most easily in hardened martensite, and a major portion of it was emitted from this martensite at room temperature. In the decomposition products resulting from intermediate transformation the mobility of the hydrogen decreased stepwise. Hydrogen was emitted actively from retained austenite only when the steel was heated to the temperature of its decomposition. The author of [22] believes that the formation of flakes is related to the decomposition of retained austenite saturated with hydrogen and capable of transforming at low temperatures. This is accompanied by a stepwise fall in the solubility of hydrogen, due to which the martensite regions surrounding the retained austenite are supersaturated with hydrogen and become very brittle. In combination with structural stresses this leads to local fracture and the appearance of flakes.

The same author studied hydrogen-charged structural steels and found two kinetic maxima of the stability of supercooled austenite [23]. The beginning of an isothermal $\gamma \rightarrow \alpha$ transformation was accompanied by enrichment of austenite with hydrogen and an increase in the amount of retained austenite at room temperature. The formation of the composite stress state that accompanies the decomposition of the retained austenite and the corresponding redistribution of hydrogen can cause microcracks that grow in the elastically stressed matrix and are believed to be one of the main reasons behind the decelerated formation of cracks in structural steels that contain hydrogen.

The existence of retained austenite in steels is associated in [24] with structural stresses, chemical inhomogeneity of the solid solution, and phase strain-hardening in the martensite transformation. However, the data of [1] on the participation of hydrogen in the martensite transformation allow us to view the nature of the kinetic features of this transformation, in particular, the cause of the incompleteness of its occurrence, a different way, in allowing for rapid enrichment of the retained austenite with hydrogen.

Kinetics of flake formation. It is convenient to determine the moment of appearance of flakes using the nondesructive physical method of acoustic emission [25, 26], which makes it possible to predict the possibility of flake formation in treating the steel [27]. In deformation of non-hydrogen-charged specimens the intensity of acoustic emission behaves smoothly and attains a maximum in the region of the elastic limit; in strongly charged specimens a powerful acoustic signal arises even under low stresses and indicates the formation of a crack. The method of acoustic emission makes it possible to determine not only the dimensions but even the position of flakes. The determination of the coordinates of flakes with the help of acoustic emission is based on the principles of passive radio (sound) detection and ranging. A developed flake radiates pulses of acoustic emission into the surrounding material; by measuring their parameters with the help of several gauges the position of the source of the emission of the ultrasound can be determined by the method of triangulation using the time of the arrival of the signal at the pressure gauge from the coordinates of the source.

There are no reliable quantitative data on the relation between the main characteristics of the steel and the length of the incubation period and the temperature of formation of flakes. The available data are very contradictory (the temperature is reported to be 20°C, < 300°C, > 600 – 650°C at a length of the incubation period of flake formation ranging from several seconds to half a year!).

The authors of [28] used the method of scanning electron microscopy to determine that the initial rate of development of flakes is 10 – 20 μm/sec, whereas after a day it decreases to 1 – 5 μm/sec. A study of the growth kinetics of flakes by the method of acoustic emission [29] has shown that a flake develops by jumps that are much less than its size but catch many grain-boundary facets in a time less than 1 sec. The growth of a flake stops due to exhaustion of the zone that feeds it with hydrogen. Specimens of a Cr – Ni steel with 0.2% C exhibited a new burst of pulses of acoustic emission 15 – 20 h after hardening, which was associated with merging of close flakes. The flakes grew by jumps commensurable with the size of one or several grains in the steel [30].

A physical model of the growth of flakes within the framework of the structural mechanics of materials is suggested in [31]. The jumpwise growth of an internal grain-boundary crack under the pressure of hydrogen flowing into it is described quantitatively as a process of percolation ("soaking through") of grain-boundary facets on a two-dimensional network of bonds. The size of a jump of a crack is determined by the size of the cluster of facets, and the time between jumps is determined by the time of accumulation of hydrogen in the void. The kinetics of flake growth has been calculated under conditions of a stationary hydrogen flow. The size of the jumps increases with time, and their frequency decreases. The total number of jumps changes approximately exponentially with a time constant of 1.2 – 1.35 h, which has been shown by the method of acoustic emission for flakes growing in a Cr – Ni structural steel with 0.2% C. The minimum pressure for the start of flakes on a single facet (in equilibrium with hydrogen in the solid solution) corresponds to the critical concentration of hydrogen required for formation of flakes (0.5 – 2 cm^3 per 100 g of metal).

The duration of the incubation period for formation of flakes decreases with increase in the cross section of the preform. In steels of the pearlitic class the formation of flakes is completed in 3 – 5 days, in steels of the pearlitic-martensitic class it is completed in 2 weeks, and in Cr – Ni – W steels with 0.18% C of the martensitic class it is completed in several months [1].

Mechanism of flake formation. Role of hydrogen redistribution in the $\gamma \to \alpha$ *transformation in steels.* Various mechanisms of formation of flakes have been suggested over the long period of their investigation that were associated with internal stresses due to the heat treatment, plastic deformation, phase transformations, dendrite segregation, nonmetallic inclusions, nitrides, carbon oxides, water vapor, and methane. All of them turned out to be unsound or explained the formation of flakes only partially. Later, flakes were reported to be related to hydrogen and internal stresses, but the problem of the mechanism of their initiation has not been solved yet [1].

The results of an electron microscopic study of the structure of flakes conducted in [32] have shown that the central portion of a flake consists of regions of brittle cleavage (25 – 240 μm) appearing on single grain edges. Flakes grow jumpwise from the source of formation, leaving ridges that resemble low-cycle fatigue striations. A tough zone 10 – 100 μm wide consisting of fine dimples (1 – 5 μm) appears on the periphery, probably in afterbreaking, and passes abruptly into a plastic "healthy" fracture with uniaxial dimples 5 – 50 μm in size. It is assumed that these are traces of cyclic fracture caused by auto-oscillations of the hydrogen pressure that accompany the development of the crack.

At present the mechanism of the appearance of flakes is considered in close relation to structural and phase transformations of supercooled austenite. The negative effect of hydrogen consists in supersaturation of individual internal volumes of the metal with it. At the same time, it has been established in [33] that even at a high initial concentration of hydrogen the pressure created by it in microscopic voids does not exert a sufficiently great effect on the stable growth of microcracks in the absence of other internal stresses. This "retained" hydrogen present in micropores, microcracks, immobile dislocation clusters, and interphase boundaries affects the short-term strength of the steel. In this connection, delayed fracture of castings and forgings in cooling is associated with the presence of diffusion-mobile hydrogen in them. In steels that undergo a $\gamma \to \alpha$ transformation in cooling, hydrogen undergoes local redistribution between the phases due to the difference in its solubility in the α- and γ-lattices of iron.

It is believed that the phase transformations that occur at diminished temperatures and in particular the decomposition of retained austenite accompanied by a volume expansion and a jumpwise change in the solubility of carbon and hydrogen contained in the austenite cause stresses and embrittlement in the transformation zones.

The authors of [34] studied the effect of hydrogen on the kinetics of the decomposition of supercooled austenite and the flake sensitivity of a Cr – Mn – Si steel with 0.3% C. Hydrogen decelerates substantially the decomposition of supercooled austenite in the isothermal transformation in the temperature range of its relative stability and of the retained austenite at room temperature. The flake sensitivity of hydrogen-charged steel is determined by the degree of stability of austenite at a temperature much below M_i. Specimens with a high degree of decomposition of austenite at room temperature that commonly possess a martensitic structure are the most flake-sensitive. The high degree of decomposition of austenite at a temperature exceeding M_i causes removal of flakes even when the decomposition has occurred rapidly, as in an intermediate transformation (400°C); the specimens retain a considerable amount of hydrogen.

The process of emission of hydrogen, at room temperature and in heating, from a Cr – Ni steel with 0.4% C saturated with hydrogen at 1100°C and the distribution of hydrogen between the α- and γ-phases have been studied in [35]. The degree of hydrogen emergence at room temperature depended on the amount of retained austenite, its stability, and saturation of the α-phase with hydrogen. The maximum degree of hydrogen emergence was observed in specimens with a martensitic structure, and the minimum was observed in specimens with a bainitic structure. The decomposition of supercooled austenite in the bainite region was accompanied by redistribution of hydrogen between the α- and γ-phases, which enriched the nondecomposed austenite with it. The maximum enrichment (9.2 cm^3 per 100 g) of the austenite with hydrogen was observed after an isothermal hold of the steel at 500°C. The nature of the maxima on the thermokinetic curves describing the emission of hydrogen from the investigated steel have also been studied. The low-temperature peak (260 – 280°C) was associated with the maximum emission of hydrogen from the α-phase, and the high-temperature peak (360 – 380°C) was associated with the growth of the mobility of hydrogen in the decomposition of retained austenite.

Hydrogen-saturated mobile zones have been discovered on the boundaries separating the phases in polymorphic transformations that occur in metals [36]. The considerable oversaturation of the steel with hydrogen in the zone of the H-layer leads to changes in the physicochemical and mechanical properties, such as a decrease in the yield strength and a self-induced change in shape. The effect of pulsed emission of hydrogen established in pure iron at the moment of the $\gamma \rightarrow \alpha$ transformation is observed in Fe – C alloys, which can be the cause of the formation of flakes in the process of manufacturing steel parts.

A study of the effect of phase transformations and the redistribution of hydrogen in the $\gamma \rightarrow \alpha$ transformation on the mechanism of flake formation has been conducted at the Prometei Research Institute of Machine Materials in Nizhnii Novgorod. It has been shown that the phase transformations can be influenced by a purposeful change in the chemical microinhomogeneity of the steel [37]. A mathematical model has been suggested for the redistribution of hydrogen in phase transformations that takes into account the kinetics of the $\gamma \rightarrow \alpha$ transformation in steels of various structural classes and makes it possible to explain the flake sensitivity of various steels [38]. It has been established that the degree of oversaturation of the α- and γ-phases by mobile hydrogen is determined by the temperature of the transformation, the coefficient of the distribution of hydrogen between the phases, and their amounts. Oversaturation of one of the phases with hydrogen causes hydrogen embrittlement due to irreversible migration of hydrogen atoms to the interphase surfaces and submicrocracks. In addition, an excess content of hydrogen dissolved in the austenite can decrease the temperature of the beginning of the $\gamma \rightarrow \alpha$ transformation to the bainite or martensite region, as well as the M_i temperature. Then the transformation of the last portions of austenite in grains containing effective sinks for hydrogen atoms will occur by a diffusionless mechanism.

A mathematical model has been suggested for thermodiffusion of hydrogen in the two-phase region of Cr and Cr – Ni steels [39]. A correlation has been discovered between the degree of enrichment of the γ-phase with hydrogen and the kinetics of the $\gamma \rightarrow \alpha$ transformation in isothermal holds and in the process of continuous cooling in air. The degree of saturation of supercooled austenite with hydrogen in the process of its decomposition increases with decrease in the amount of austenite, the distribution coefficient of hydrogen, and the rate of the $\gamma \rightarrow \alpha$ transformation. Therefore, to choose correctly the regime of antiflake heat treatment it is necessary to optimize not only the content of diffusion-mobile hydrogen but also the ratio of nondecomposed austenite to the hydrogen content in it. A numerical computation of hydrogen diffusion in grain bodies [40] has shown that the degree of oversaturation of austenite with hydrogen is connected with the kinetics of the $\gamma \rightarrow \alpha$ transformation in steels of pearlitic and bainitic classes. A mechanism has been suggested for the redistribution of hydrogen and the initiation of flakes in the process of phase transformations. It has been shown that the $\gamma \rightarrow \alpha$ transformation at an excess concentration of hydrogen occurs jumpwise with intervals determined by diffusion redistribution of hydrogen in the α- and γ-phases and the rate of its flow into submicrocracks. Jumpwise transformation of retained austenite by a bainitic or martensitic mechanism causes marked local growth of the hydrogen concentration on the interface of the α- and γ-phases and leads to the appearance of microcracks. Flow of excess hydrogen into the volumes of the emerging microcracks promotes completion of the transformation of the austenite and development of the microcracks to the size of flakes [41].

However, an analysis of all the available information shows that there is no unique mechanism of flake formation and the process consists of several elementary links [1].

New regimes of antiflake heat treatment. The main operation in heat treatment aimed at decreasing the flake sensitivity of steels consists in an isothermal hold at 640 – 660°C that diminishes the hydrogen content in segregation regions and the content of dissolved hydrogen by means of its diffusion into discontinuities of the metal with transformation of the hydrogen into a molecular form that is inactive with respect to flake formation [5].

The difference in the purposes of the preforms, the wide range of the steels used, and the various methods of their melting complicate the choice of the optimum variant of antiflake heat treatment by the enterprise. This explains the existence of various regimes of such heat treatment, which are often based only on the practical experience of the enterprise and thus are far from being optimum, which is explainable by inadequate development of the theory of antiflake heat treatment and the use of out-of-date equipment [42]. The widely used technology of antiflake heat treatment of large forgings is characterized by a long duration (up to 15 – 16 days, i.e., 380 h), which decreases the efficiency of thermic furnaces and increases the consumption of fuel [43]. Generalization of experience in antiflake heat treatment of large forgings in Russia allows us to consider critically the regimes used and outline ways for their optimization and standardization.

A basic evaluation of existing regimes of AFHT of large forgings used by domestic plants and an optimum regime of such heat treatment are given in [42 – 44]. The latter consists in accelerated cooling of the forging after the forging operation (in air or an air-water mixture), an antiflake isothermal hold, and cooling with the furnace to 350 – 450°C followed by cooling in air. The existing regimes are shown to have the disadvantage of accumulating the forgings in the furnace heated to 600 – 650°C with a hold at this temperature after the charge is completely formed, followed by slow cooling to temperatures at which the austenite has minimum stability. This affects negatively the uniformity of the obtained structure, promotes formation of high-alloy austenite, and causes reverse thermodiffusion of hydrogen from the surface layers into the central, more heated layers. In delayed cooling from Ac_3 to the temperature of supercooling, conditions are created for excess isolation of ferrite, pearlite, and retained austenite. The amount of A_{ret} is not high, but it has an elevated content of C, H, and the alloying elements, which makes it more stable [45]. Decomposing in storage and in operation of the parts, the retained austenite causes formation of flakes. This can be avoided by using rapid supercooling after forging (in water, an air-water mixture, or air), in which decomposition of the supercooled austenite begins and proceeds at low temperatures, the decomposition products possess elevated homogeneity, and the chemical composition of the austenite is close to the initial one. This austenite is less stable and decomposes more intensely and completely in subsequent heating than that in slow cooling to 200 – 250°C. Industrial tests of an AFHT regime involving accelerated supercooling of pilot and full-scale forgings of Cr – Ni steels with 0.4% C have given positive results (the cooling cycle has been shortened tenfold).

Another shortcoming of the existing method of AFHT is that it includes the operation of recrystallization, which lengthens considerably (by about two days) the heat treatment process, although it decreases the flake sensitivity somewhat. It is expedient to eliminate this operation from the AFHT and conduct it during the subsequent final heat treatment aimed at improving the grains and attaining the corresponding mechanical properties.

The AFHT regimes used by the enterprises are often characterized by an unjustifiably low supercooling temperature. In order to choose correctly the temperature and time of supercooling it is necessary to know the kinetics of the transformation of austenite and the temperature field in the melt and over the cross section of the forging. Taking them into account, we can guarantee that the austenite transformation will be complete in all forgings of the melt and reduce the time of their hold at the supercooling temperature to a minimum.

Monitoring of the hydrogen content in 20 heats of a Cr – Mn – Si – Ni – Mo open-hearth steel with 0.3% C at one enterprise has shown that 80% of all the heats had a hydrogen content of 5 – 8 cm^3 per 100 g and in only 20% did it exceed 8 cm^3 per 100 g, i.e., 80% of the forgings could have been treated by a regime shortened by 20 – 50%. Since monitoring of the hydrogen content is not conducted in the heat, the enterprise msut treat all forgings by a regime with a maximum hold and the time reserve is not realized.

The final cooling from the temperature of the isothermal hold (620 – 680°C) is conducted in order to reduce the internal stresses as much as possible (because they cause the formation of flakes), and therefore it is envisaged that the temperature should be decreased at a minimum rate. This cooling process lasts 2 – 3 days. Research conducted at the Novokuznetsk Metallurgical Plant has shown that forgings 600 mm in diameter of Cr – Ni steel with 0.4% C cooled with the furnace to 400°C with a 3-h hold at this temperature have the same level of tensile stresses in the center (30 – 40 N/mm^2) as in complete cooling with the furnace. Since such cooling takes at most one day, it is expedient to use it instead of the existing operation.

Thermocycling is an interesting new variant of antiflake heat treatment. It consists in that the forgings accumulated in the furnace and supercooled are subjected to triple cyclic heating to $Ac_1 + (20 - 50)$°C with cooling to 640 – 680°C (with isothermal holds and an accelerated final cooling). This provides fuller decomposition of austenite and accelerates diffusion emission of hydrogen from the forging into the atmosphere, because the periodically formed austenite "jacket" acts as a diffusion pump. As a result, the total duration of the AFHT is decreased by 16 – 18%, i.e., by 4 days [43].

The authors of [46] have suggested an equation that makes it possible to evaluate the hydrogen content at any moment of time in the process of the AFHT and choose the optimum regime with the help of Bessel functions with allowance for the initial hydrogen concentration, the radius of the forging, the activation energy of degassing (the diffusion of hydrogen from the metal into the atmosphere), and the temperature, time, and rate of the cooling. By increasing the cooling rate to 5.3 K/h forgings 150 – 250 mm in diameter are degassed to a safe hydrogen content (1 – 2 cm^3 per 100 g) in virtually 72 h, which shortens the duration of the AFHT.

In order to refine the AFHT regime for seamless forged railroad wheels, the behavior of hydrogen in their production has been studied [47]. It has been shown that hydrogen is removed intensely from massive preforms even in the stage of high-temperature heating for rolling, and therefore the AFHT of race parts should be conducted at 1000°C.

The technology of the production of rails under the conditions of the Azovstal' Plant envisages prolonged AFHT of the rolled stock independently of the hydrogen saturation of the initial metal. Therefore, continuous and reliable rapid analysis of hydrogen in steel is required in the casting process, which makes it possible to correct the duration of the AFHT. It has been shown in [48] that the existing regime results mainly in relaxation of stresses after pressure treatment, because this is accompanied by emission of about 0.5 cm^3 H per 100 g of metal. A major portion of the hydrogen is released from the metal in the process of its crystallization and hold in the molds, in heating the ingots in the heating wells, in blooming rolling, in heating the blooms for rolling, and in plastic deformation. It has been shown that it is possible to optimize the regime of antiflake cooling of rails in relation to the initial saturation of the steel with hydrogen by determining experimentally the temperature dependence of the diffusion coefficient of hydrogen in steel.

The Élektrosila Production Association (St. Petersburg) has reconsidered the regimes of AFHT for preforms of shafts of two-pole rotors of electric generators from ingots of a Ni – Cr – Mo – V steel with 0.35% C with a mass of 100 – 205 tons [49]. Immediately after the forging is finished (about 980°C) the preform should be placed in the furnace heated to 650°C, which is the optimum temperature for the pearlite transformation and the antiflake hold. In order to decompose the retained austenite in the process of the hold, the preform is subjected to intermediate cooling to about 300°C. The new regime of the AFHT differs from the existing regime by the absence of austenitization before the antiflake hold, which shortens the total duration of the treatment by 1.5 – 3 days.

The Prometei Research Institute of Machine Materials in Nizhnii Novgorod has suggested a method for cooling ingots and castings from the austenitization temperature that increases the quality of the preforms by preventing saturation of the γ-phase with hydrogen above the maximum solubility in the bainitic region [50]. This method makes it possible to decrease the level of residual stresses and eliminate the formation of flakes in the preforms.

CONCLUSION

The problem of the mechanism of the nucleation and growth of flakes has not been solved completely. The published data on the forms of existence of hydrogen in steels and the corresponding terminology are contradictory, as is the effect of the production process of the steel on the formation of flakes, including vacuum evaporation, the phase transformations, the presence of pores and nonmetallic inclusions in the metal, the sulfur concentration, etc. The data on the critical concentration of hydrogen, the length of the incubation period and the temperature of flake formation, and the effect of hydrogen on the martensitic transformation in steels are also ambiguous. Therefore, this complex problem that has existed for almost a hundred years needs further theoretical and experimental studies employing modern physicochemical methods of analysis.

We have considered the mechanism of the appearance of flakes in steels, which is connected with the structural and phase transformations of supercooled austenite and the redistribution of hydrogen in the $\gamma \rightarrow \alpha$ transformation. The process of the $\gamma \rightarrow \alpha$ transformation at an excess content of hydrogen occurs jumpwise by a bainitic or martensitic mechanism, which causes marked local growth of the hydrogen concentration on the interface of the α- and γ-phases and the appearance of microcracks. The flow of excess hydrogen through the arising cracks makes them develop to a macrosize, i.e., leads to the formation of flakes.

Standard AFHT technologies used by domestic and foreign enterprises are highly energy-consuming and labor-intensive. However, the classical variants of such heat treatment can be improved considerably on the basis of the methods and ideas described. AFHT technologies can be optimized by using computational methods for diffusion removal of hydrogen from large forgings and for determining the temperature field of the melt in the heat treatment in combination with knowledge of the kinetics of the decomposition of supercooled austenite and monitoring the duration of isothermal holds in relation to the hydrogen content in liquid steel, regulated final cooling, and some other methods. The new variants of AFHT include accelerated cooling of the preforms after the forging and/or thermocycling in the intercritical temperature range with subsequent accelerated cooling. It is also recommended to combine AFHT with the final heat treatment, which provides elevated toughness of the steel.

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