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(54) **METHOD FOR THERMAL PROCESSING OF ARTICLES CONSISTING OF ALLOYS ON THE BASIS OF IRON (VARIANTS)**

(57) The invention relates to the field of thermal processing of articles consisting of steel and alloys on the basis of iron with a carbon content of up to 4.5% by mass. In order to reduce the duration of the technological processes used for producing articles consisting of alloys on the basis of iron with a set structural state, the first variant of the method comprises heating the articles so as to form austenite and then cooling, which is performed under conditions which ensure the formation, in the structure of the alloy, of regions of austenite with a chemical composition similar to eutectoid with the subsequent formation in said regions of marinite and a set structural state so as to produce perlite with a different degree of dispersion and/or hardened structures. The second variant of the method comprises heating the article, which is performed under conditions which ensure the formation, in the structure of the alloy, of marinite and then cooling with the formation a set structural state so as to produce perlite with a different degree of dispersion and/or hardened structures. When implementing the methods, pulsed cooling, plastic deformation, and the action of a magnetic field are used.

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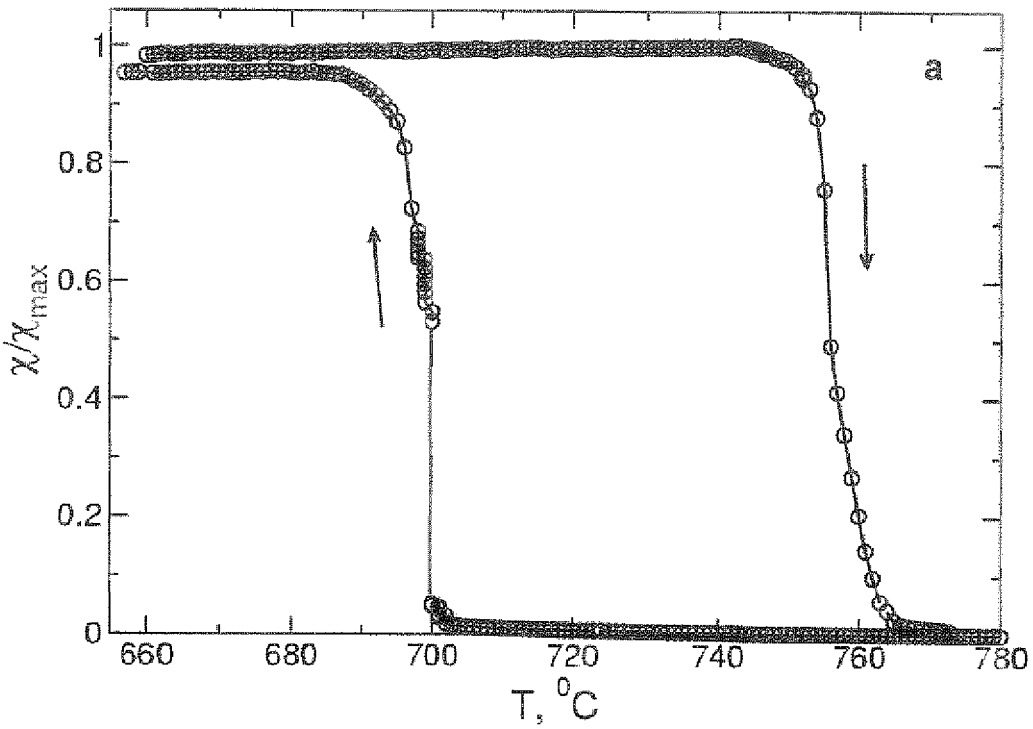


Fig. 1

Description

Field of the Invention

[0001] This invention relates to metallurgy, more specifically, to the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight, and is directed to the production of alloys having the desired structural state and required properties.

Background Art

[0002] A method is known in the art for the heat treatment of articles made of steels, in particular, rolled profiles, this method providing the formation of alloyed construction steels in rolled rods having a long pearlite transformation period or having not the two-layered structure thereof, namely, the ferrite-pearlite structure having low hardness in the surface layer and the sorbite structure having a higher hardness in the central layer. This allows cutting to be used in carrying out subsequent cold working of rods.

[0003] For attaining the aforementioned result, the method for the heat treatment of rolled profiles according to the patent RU 2044779 (which comprises accelerated cooling from the end strain temperature, isothermal exposure at a temperature ranging from 600 to 700°C lasting no longer than 3 h, and subsequent cooling) carries out accelerated cooling until the surface layer at a depth of 5 to 10 mm reaches a temperature below the M_s point.

[0004] A drawback of this prior-art method consists of its low output caused by great time consumption in operations providing the formation of the required structural state.

[0005] As a result of the accelerated cooling of the surface layer 5 to 10 mm deep to a temperature below M_s, the martensite structure appears on the surface of a rod. Upon subsequent heating and exposure at a temperature ranging from 600 700°C, the martensite decomposes to a ferrite-pearlite mixture at far higher rates than the direct austenite transformation occurs over the entire volume of the rod. In this way, a rod acquires a two-layered structure, wherein the surface is ferrite-pearlite having a low hardness, and the central layer is sorbite having a higher hardness. With this, isothermal exposure remains relatively long (up to 3 h).

[0006] A method according to the patent RU 2272080 is known for the heat treatment of articles made of iron-base alloys, in particular, hot-rolled running and railroad rails with profiled parts of various weights, this method comprising the steps of preliminary cooling and final cooling, following the step of roll heating of the profiled parts of various weights to form the desired structure having enhanced strength in the profiled parts of a rail, in particular, in the rail head. The preliminary cooling of the rail after roll heating is carried out until the core of the rail head reaches the temperature of the rail head core, ranging from 750 to 850°C, in order to preclude intermediate overcooling of the surface zone of the rail head and a premature local phase transformation; then, the step of cooling the surface zone of the rail head is carried out to reach at least the core temperature, and the final cooling of the rail is carried out with a heat flux density being so high as the shortest possible cooling time in the phase transformation zone from 800 to 500°C to be reached for the central zone of the rail head. Herein, the final cooling of the rail head in the phase-transformation zone is carried out so rapidly that the desired thin-lamellar pearlite structure is formed and the surface zone is kept from being cooled to below the bainite formation temperature. Drawbacks of this prior-art method consist in the length of the heat treatment process required to produce steel articles with the desired final structural state and a limited range (assortment) of the product steels with the required (desired) properties.

[0007] The most pertinent piece of prior art for the present invention (in its technical essence and the result to be attained) consists of the method according to the patent RU 2266966 for the heat treatment of steel articles, providing the desired final thin-lamellar pearlite or ferrite/pearlite structure. This prior-art method provides heating a workpiece, in particular, a rolled steel profile in the form of a rail, to temperatures of about 850°C, and further cooling the workpiece by individual pulses, these pulses providing the formation of the pearlite or ferrite/pearlite structure without the appearance of quenched structures (in particular, bainite). To accomplish this, a workpiece or a finished article is passed through a cooling section, which comprises individual, autonomous cooling units arranged in series along the length of the cooling section (which is in fact equivalent to pulsed cooling with independently controlled cooling parameters), wherein the cooling units are separated by intermediate regions for releasing structure stresses, these regions being provided with means for the determination of the true temperature of the article, and wherein depending on the true temperature of the part, cooling parameters in the intermediate region, especially cooling intensity, are controlled at least with respect to the subsequent cooling unit to provide the desired temperature of the part during the entire passage through the cooling section, wherein the desired temperature of the part is maintained to be above the critical temperature at which bainite structural components are formed. Further, temporal phases of reheating and/or thermal exposure, and/or temporal phases of slow cooling are employed in pauses between the cooling steps (pulses) to release structure stresses.

[0008] A drawback of this prior-art method consists in the length of the heat treatment process required to produce steel articles with the desired final structural state and a limited range (assortment) of the produced steels with the

required (desired) properties.

[0009] The invention is directed to shortening the timeframe of the technological processes that provide the production of articles made of iron-base alloys having desired structural states and, thereby, having physicomechanical and quality characteristics required in each particular case.

[0010] The further description will operate with the following terms.

Structural state: the state forming as a result of thermal or thermomechanical treatment and characterized by the phase constitution, morphology, and sizes of the structural constituents;

Phase: a thermodynamically equilibrium state of a material, differing in its physical properties from the other equilibrium states of the same material;

Austenite: a solid solution of carbon in FCC iron;

Ferrite: a solid solution of carbon in BCC iron;

Cementite: iron carbide Fe_3C_x, wherein $0,75 \leq x \leq 1$, having an orthorhombic unit cell;

Pearlite: a structural constituent of carbon-iron alloys, steels, and cast irons, which represents a eutectoid mixture of two phases (ferrite and cementite);

Lamellar pearlite: a pearlite variety in which ferrite and cementite dominantly have a lamellar shape;

Granular pearlite: a pearlite variety in which cementite dominantly has a near-spherical shape;

Sorbite: a dispersed variety of pearlite;

Sorbitation time: the time interval from the moment of appearance of sorbite to the moment of the end of formation of the sorbite structure across the cross-section of a workpiece (an article);

Troostite: a highly dispersed variety of pearlite;

Bainite (upper, lower): the quenched structure formed when austenite is overcooled into the temperature range bounded by the starting temperature of bainite transformation and the starting temperature of martensite transformation;

Martensite: the quenched structure formed from austenite by a shear process representing a solid solution of carbon in BCC iron;

Ledeburite: the structural constituent arising as a result of a eutectic reaction in which the carbon-iron melt solidifies to form austenite and cementite, the austenite transforming to pearlite upon further cooling to below 727°C;

Marinite: the structural state of carbon-iron base alloys, characterized by the occurrence, in the FCC iron matrix, of regions wherein quasi-static displacements of atoms transform the lattice from FCC into FCT or BCT (BCC) with a short-range magnetic order, and by the occurrence of regions having the FCT lattice with a short-range order in the arrangement of carbon atoms characteristic of iron carbides of various compositions (see V. N. Urtsev et al., "Relationship between Magnetic and Lattice Degrees of Freedom in the Fe-C System," Stal', 2010, No. 7, pp. 101-106);

Rutite: the structural state of carbon-iron base alloys containing BCT regions with abnormal low tetragonality and dispersed iron carbides of various compositions and having the hardness characteristic of martensite with near-eutectoid carbon concentrations, this state arising upon rapid cooling (quenching) of marinite. Compared to upper and lower bainites and to granular and lamellar pearlites of the same chemical composition, said structural state is distinguished by a higher strength and a higher hardness, and compared to martensite, by an enhanced ductility (see V. N. Urtsev et al., "Relationship between Magnetic and Lattice Degrees of Freedom in the Fe-C System," Stal', 2010, No. 7, pp. 101-106);

Quasi-static displacements: correlated displacements of atoms from their equilibrium positions in the crystal lattice, maintained for a period of time that far exceeds the thermal vibration period;

Curie point of ferrite: the temperature of the ferromagnetic-to-paramagnetic transition upon heating, and the ferrite loses its spontaneous magnetization at this temperature;

Quenching (rapid cooling): cooling at a rate sufficient for diffusion transformations to be inhibited;

Quenched sample: a sample subjected to quenching;

Quenched structures: structures forming as a result of quenching;

Diffusion transformation: a transformation of one phase to another occurring as a result of atomic displacements by means of diffusion;

Shear transformation: a transformation of one phase to another via cooperative atomic displacements, accompanied by distortion of the crystal lattice;

Cooling pulse: the thermophysical process initiated by a short-term impact of the cooling medium on the workpiece;

Residual austenite: the austenite surviving in the structure after cooling to room temperature;

Short-range magnetic order: an order in mutual arrangement of magnetic moments, repeating at distances commensurate with interatomic distances;

Short-range order in arrangement of carbon atoms: an order in mutual arrangement of carbon atoms, repeating at distances commensurate with interatomic distances.

Disclosure of the Invention

[0011] The problem is solved by the method for the heat treatment of articles made of iron-base alloys having carbon

contents of up to 4.3% by weight, the method comprising: heating to provide the formation of austenite and subsequent cooling according to schedules that provide the formation of the desired structural state, wherein the cooling is carried out according to schedules that provide the occurrence of austenite regions with near-eutectoid chemical compositions, followed by forming marinite therein, and wherein the desired structural state is formed so that to obtain therein pearlite with various degrees of dispersion and/or quenched structures.

[0012] Preferably cooling is carried out by schedules that provide the formation of the desired fraction of austenite regions having near-eutectoid chemical compositions, followed by forming the desired marinite fraction therein.

[0013] Preferably the schedules that provide the formation of the desired fraction of austenite regions having near-eutectoid chemical composition, followed by forming the desired marinite fraction therein, are determined by calculations or experimentally.

[0014] Preferably the desired structural state is formed so that to obtain therein desired pearlite fractions of various degrees of dispersion and/or quenched structures.

[0015] When calculations are used to determine the schedules providing the formation of marinite from austenite regions having near-eutectoid chemical compositions, the temperature range of marinite occurrence is set so as to satisfy the condition that $T_{TEX} < T < $, wherein T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations, and T_{TEX} is the temperature selected with account for technological limitations; and the cooling rate is selected such that the cooling temperature versus time T(t) satisfies the condition that T(t) < □(t), wherein the D(t) function is given by the starting lines of the pearlite and bainite transformation in the thermokinetic diagram.

[0016] When experiments are used to determine the schedules providing the formation of marinite from austenite regions having near-eutectoid chemical compositions, samples are quenched from fixed temperatures with various exposure times at these temperatures, and the occurrence of marinite is judged from the occurrence of rutite in the quenched sample.

[0017] Preferably the occurrence of rutite is established by diffraction methods.

[0018] Preferably the schedule for cooling from the prior-formed marinite to form the desired amount of pearlite in the desired structural state is determined by quenching experimental samples followed by the determination of the structural state thereof.

[0019] Preferably the determination of the schedule for cooling from the prior-formed marinite to form the desired structural state comprises: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample; determining the values of thermokinetic constants that would provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i ,$$

wherein:

the operator $\vec{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1};

r is the radius vector of the point to which the calculations refer;

ρ is density measured in kg/m^3;

q_i is the specific enthalpy of formation for the *i*th phase, measured in J/kg;

$f_i(r,t,T)$ is the dimensionless weight fraction of the *i*th phase in the vicinity of point r at moment of time t at temperature T,

$\overline{Q}(r,t)$ is the heat flow measured in $J/(m^2\ s)$;

$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample;

the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT' ,$$

wherein:
$C^i_p(T)$ is the specific heat capacity of the ith phase at a fixed pressure as a function of temperature, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\tau, t, T)}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau ,$$

wherein:
$M_{ik}(T, f_k(\tau), (t-\tau))$ is the function that defines the variation rate of the weight fraction f_i of the ith phase with time t, determined for each phase transformation; and
then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0020] Preferably, after marinite is formed, cooling is carried out according to the schedules that provide the formation of desired fractions of ferrite and iron carbide phases in the desired structural state without formation of quenched structures or .

[0021] Preferably, after the desired pearlite fraction is formed, cooling of alloy articles is carried out at rates sufficient for diffusion transformation to be inhibited.

[0022] Preferably cooling is carried out in pulses.

[0023] Preferably cooling is carried out by pulses alternating with pauses, with lengths selected so that to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of the article made of the alloy.

[0024] The length of each of the cooling pulses is selected such that they would not lead to the formation of quenched structures in the desired structural state.

[0025] Preferably cooling is carried out in pulses, wherein one of the cooling pulses is selected so as to provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures in the desired structural state.

[0026] Preferably, after forming the desired austenite fraction that is sufficient for the desired pearlite fractions to be formed in the desired structural state having various degrees of dispersion and/or quenched structures, the temperature depression required for marinite to be formed is carried out by cooling pulses.

[0027] Preferably after attaining the fractions of ferrite and iron carbide phases that would further provide the appearance of the desired structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

[0028] Preferably after heating alloy articles to temperatures that provide the formation of the desired austenite fraction in the alloy, the alloy articles are subjected to plastic strain.

[0029] Preferably the plastic strain of alloy articles is carried out or finished at temperatures $t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$ is the Curie point of the ferrite, in degrees Celsius.

[0030] Preferably in the course of marinite formation, alloy articles are exposed to a permanent or pulsed magnetic field.

[0031] Preferably water or water-containing media are used for cooling.

[0032] The above-defined problem is further solved by the fact that the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight, comprises heating and subsequent cooling according to the schedules that provide the formation of the desired structural state, wherein heating is carried out according to the schedules that provide the formation of marinite and, the desired structural state is formed to obtain therein pearlite having various degrees of dispersion and/or quenched structures.

[0033] Preferably heating is carried out according to the schedules that provide the formation of the desired marinite fraction.

[0034] Preferably the schedules that provide the formation of the desired fraction of marinite are determined by calculations or experimentally.

[0035] Preferably the desired structural state is formed so that to obtain therein desired pearlite fractions having various degrees of dispersion and/or quenched structures.

[0036] When calculations are used to determine the schedules that provide the formation of marinite, the range of heating temperatures is set so as to satisfy the conditions that

$$T_X < T < T_C^{loc},$$

wherein:

T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations;

T_X is the eutectoid temperature for an alloy of the appropriate chemical composition;

and the exposure time t in seconds, required for the required cementite fraction f_C to dissolve, is determined from the equation

$$f_C = 1.05\, f_{C0} \exp(-kt^n),$$

wherein:

f_{C0} is the dimensionless cementite fraction in the initial moment of time;

n is an exponent, 4 > n > 3; and

k is the parameter that determines the cementite dissolution rate in the alloy of the appropriate chemical composition at temperature T, measured in s^{-n}.

[0037] When experiments are used to determine the schedules that provide the formation of marinite in the alloy, samples are quenched from fixed temperatures with various exposure times at these temperatures, and the occurrence of marinite is judged from the occurrence of rutite in the quenched sample.

[0038] Preferably the occurrence of rutite is established by diffraction methods.

[0039] Preferably the schedule for cooling from the prior-formed marinite to form the desired amount of pearlite in the desired structural state is determined by quenching experimental samples followed by the determination of the structural state thereof.

[0040] Preferably the determination of the schedule for cooling from the prior-formed marinite to form the desired structural state comprises: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample, determining the values of thermokinetic constants that would provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i,$$

wherein:

the operator $\vec{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1};

r is the radius vector of the point to which the calculations refer;

ρ is density measured in kg/m^3;

q_i is the specific enthalpy of formation of the *i*th phase, measured in J/kg,

$f_i(r,t,T)$ is the dimensionless weight fraction of the ith phase in the vicinity of point r at moment of time *t* at temperature T,

$\overline{Q}(r,t)$ is the heat flow, measured in $J/(m^2 \cdot s)$,

$H(r,t,T)$ is the enthalpy distribution, measured in J/m3, over the volume of the sample;

the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT',$$

wherein

$C^i_p(T)$ is the specific heat capacity of the ith phase at a fixed pressure as a function of temperature, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\mathrm{r,t,T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau \ ,$$

wherein
$M_{ik}(T, f_k(\tau), (t-\tau))$ is the function that defines the variation rate of the weight fraction f_i of the ith phase, determined for each phase transformation; and
then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0041] Preferably, after marinite is formed, cooling is carried out according to the schedules that provide the formation of the desired fractions of ferrite and iron carbide phases in the desired structural state either without formation of quenched structures or with formation of fractions thereof not exceeding the desired values.

[0042] Preferably after the desired pearlite fraction is formed, the cooling of alloy articles is carried out at rates sufficient for diffusion transformation to be inhibited.

[0043] Preferably cooling is carried out in pulses.

[0044] Preferably cooling is carried out by pulses alternating with pauses, with lengths selected so that to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of an alloy article.

[0045] Preferably the length of each of the cooling pulses is selected such that they would not lead to the formation of quenched structures in the desired structural state.

[0046] Preferably cooling is carried out in pulses, wherein one of the cooling pulses is selected so as to provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures in the desired structural state.

[0047] Preferably after attaining the fractions of ferrite and iron carbide phases that would further provide the appearance of the desired structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

[0048] Preferably alloy articles are subjected to plastic strain during heating either prior to or in the course of marinite formation.

[0049] Preferably alloy articles are subjected to plastic strain after marinite formation.

[0050] Preferably the plastic strain of alloy articles is carried out or finished at temperatures $t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$ is the Curie point of the ferrite, in degrees Celsius.

[0051] Preferably water or water-containing media are used for cooling.

Brief Description of Drawings

[0052]

Figure 1 represents the plot of magnetic susceptibility as a function of temperature;
Figure 2 represents a fragment of the plot shown in Fig. 1 on an enlarged scale for temperatures ranging from 740 to 800°C;
Figure 3 represents the thermal expansion coefficient as a function of temperature $\alpha(T)$ (arrows indicate the direction of temperature variation);
Figure 4 represents carbon concentration in Fe_3C_X as a function of temperature;
Figure 5 represents the exchange energy J_0 as a function of tetragonal distortion c/a for the volume per atom of V = 11.00 A^3 (curve 1), 11.44 A^3 (curve 2), and 12.00 A^3 (curve 3), wherein negative values correspond with the preference of the ferromagnetic order of moments, and positive values, with the preference of antiferromagnetic order of moments;
Figures 6a, 6b, and 6c represent example microstructures formed in eutectoid steel samples upon exposure at 745°C for about 3 min and subsequent quenching in water (magnification ×30,000);
Figures 7 and 8, respectively, represent an X-ray diffraction pattern for a sample quenched from a temperature of 1100°C and an X-ray diffraction pattern for a sample quenched from a temperature of 745°C after being exposed

at this temperature for about 3 min, wherein dashed lines show the decomposition of the observed profile of the {110} line to constituents;

Figures 9a and 9b represent example microstructures in a eutectoid steel sample heated to a temperature of 745°C, exposed at this temperature for 2 min 55 s, and then cooled in water;

Figures 10a and 10b represent example microstructures in a eutectoid steel sample heated to a temperature of 1010°C, cooled in perchlorate salt having a temperature of 745°C to the temperature of the salt, and then cooled in water;

Figure 11 represents microstructure in a eutectoid steel sample heated to a temperature of 1005°C, cooled in air to a temperature of 745°C, cooled in molten saltpeter having a temperature of 443°C for 10s, and then cooled in water;

Figure 12 represents microstructure in a eutectoid steel sample heated to a temperature of 745°C, exposed at this temperature for 3 min, cooled in molten saltpeter having a temperature of 443°C for 10 s, and then cooled in water.

Embodiments of the Invention

[0053] The variants of the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight providing the attainment of the desired structural state in the articles, corresponding to the present invention, are based on a general concept which consists of providing the conditions for the structural state referred to as "marinite" to form (see V. N. Urtsev et al., "Relationship between Magnetic and Lattice Degrees of Freedom in the Fe-C System," Stal',2010, No. 7, pp. 101-106), this state being characterized by the occurrence, in the FCC iron matrix, of regions wherein quasi-static atomic displacement transform the lattice from FCC into FCT or BCT (BCC) with a short-range magnetic order, and by the occurrence of regions having the FCT lattice with a short-range order in the arrangement of carbon atoms which is characteristic of iron carbides of different compositions, by means of changing (elevating or depressing) temperature and then cooling to attain the desired structural state of the alloy.

[0054] The variants of the method differ from one another in marinite formation conditions. In one variant, marinite is formed upon cooling of the prior-formed austenite; in the second, it is formed upon heating a mixture of ferrite and iron carbide phases.

[0055] The occurrence of such a specific structural state is verified by a number of experimental data obtained by the inventors.

[0056] The marinite formation conditions were elucidated by studying structure-dependent properties.

[0057] One such property is temperature-dependent magnetic susceptibility $\chi(T)$, which was studied at the Institute for Metal Physics (Yekaterinburg) on a magnetometer equipped with a high-temperature unit. In order to ensure a sufficiently high sensitivity and a low noise level, the measurements were carried out in a weak alternating magnetic field (field strength: 10 Oe; frequency: 80 Hz). Temperature was varied at rates of 6 to 12 deg/min. The results obtained for eutectoid steel are displayed in Figs 1 and 2. Temperature-dependent magnetic susceptibility $\chi(T)$ demonstrates a rapid decay upon heating, starting at about 740°C and ending upon reaching the Curie point of α-Fe (T_C = 778°C). Meanwhile, subsequent decrease in temperature from 850°C to a value of about 700°C is accompanied by a slow rise in $\chi(T)$, which changes to a strong rise at 700°C, where α-Fe appears in the structure. The rise in $\chi(T)$ upon cooling to T > 700°C indicates the existence of disperse particles of a magnetic phase or a short-range magnetic order. In this way, the behavior of temperature-dependent magnetic susceptibility $\chi(T)$ indicates that a heterogeneous state is formed within a certain temperature range below the Curie point of α-Fe but above the α-γ transition temperature A_1.

[0058] Measurements of the thermal expansion coefficient as a function of temperature $\alpha(T)$ were also carried out at the Institute for Metal Physics (Yekaterinburg) for steel of eutectoid composition on a high-sensitivity dilatometer over a wide range of temperatures upon heating and cooling at a rate of 3 deg/min. The resulting $\alpha(T)$ dependence has the following extraordinary feature: the thermal expansion coefficient decreases upon heating, starting at T > 500°C, and α (T) strongly decreases above the α-γ transition point within the temperature range from 740 to 850°C (Fig. 3). Upon cooling, the thermal expansion coefficient weakly changes with temperature between 800 and 690°C. At the α-γ transition point, $\alpha(T)$ experiences a jump, and as temperature decreases further, $\alpha(T)$ behaves in an ordinary manner where $d\alpha/dT > 0$.

[0059] The normal behavior of a homogeneous system is known to be a weak rise in thermal expansion coefficient with temperature, namely, $d\alpha/dT > 0$ (see Ch. Kittel, Introduction to Solid State Physics (Wiley, New York, 1976; in the Russian language translation published by Nauka, Moscow, 1978). According to the ideas developed by E. F. Wasserman in Ferromagnetic Materials, ed. by K. H. J. Buschow and E. P. Wohlfarth (North Holland, Amsterdam, 1990, vol. 5, p. 237), the weak variation in $\alpha(T)$ observed in the temperature range between 690 and 800°C is indicative of the existence of a heterogeneous state that represents an ensemble of disperse particles (or clusters) having a smaller specific volume than in the matrix. As a result, thermal expansion is determined not only by lattice anharmonisms; rather, it primarily depends on a variation of the relative fraction of clusters. Upon heating, the $\alpha(T)$ anomaly becomes pronounced far more strongly (Fig. 3). This result implies that kinetic factors play a considerable role in the formation of the aforementioned state. In particular, the rapid decay of $\alpha(T)$ upon heating can arise from the lasting dissolution of carbide particles,

whereas the weak change in α(T) upon cooling can arise from the formation of carbon inhomogeneities having characteristic sizes of 10 to 100 nm.

[0060] Thus, the behavior of magnetic susceptibility and the thermal expansion data both indicate the existence of a specific structural state that appears under near-equilibrium conditions in the temperature range of $A_1<T<T_C$.

[0061] In order to elucidate how the steel structure changes upon slow heating and cooling (where kinetic effects may be ignored), neutron diffraction studies were carried out on an IVV-2M stationary research nuclear reactor at the Beloyarsk NPP. Neutron diffraction patterns were recorded using a high-angle-resolution neutron diffractometer ($\Delta d/d$ = 0.2%). The records were carried out within the temperature range between 20° and 800°C following 1-h pre-exposure at the desired temperature for an equilibrium state to be acquired. The refinement of structure parameters was performed by Rietveld full-profile analysis (see Rietveld, H.M., J. Appl. Cryst. 1969, Vol. 2, p. 65); comparing calculated and measured diffraction patterns, this refinement method allows the determination of atomic coordinates, the overall thermal factor, individual isotropic or anisotropic thermal factors, and site occupancies for different kinds of atoms.

[0062] As a result, it was found that at temperatures below the α-γ transition temperature, samples contained α-Fe and cementite having an orthorhombic unit cell (17% by weight), and at temperatures above the α-γ transition point, they contained γ-Fe, in which carbon atoms are positioned in octahedral interstices. In analysis of site occupancies for Fe and C atoms in cementite, it turned out that the cementite composition is not fixed; rather, it changes considerably depending on temperature (Fig. 4). Its fraction and orthorhombic lattice are preserved up to the α-γ transition point; at higher temperatures, cementite disappears. Thus, the cementite composition may in general be formulated as Fe_3C_X, wherein X decreases, as temperature rises, from $X \approx 1$ at 20°C to $X \approx 0.75$ at temperatures close to the α-γ transition point; therefore, the cementite composition can vary depending on the heat treatment schedule.

[0063] In order to determine in a detailed way what the structural state under study represents, calculations of FCC-Fe were carried out in terms of the electron density functional theory (see Kohn, W., and Sham, L.J., Phys. Rev., 1965, Vol. 140, p. A1133). These calculations showed the existence of several equilibrium states, which differed from each other by the values of magnetic moments, crystal structure types, and specific volumes. Of these states, most essential are a high-spin (HS) ferromagnetic (FM) state (which has a greater energy and a larger volume per atom); and a low-spin (LS) antiferromagnetic (AFM) state (which has a lower energy and a smaller volume per atom). More systematic calculations taking into account the possibility of appearance of non-collinear magnetic structures (which are modeled by spin helices), also lead to two equilibrium states: an HS-FM state (with the spin helix vector q = 0) and a state that represents the combination of energy-degenerate LS states with $0.2 < q \leq 0.5$ (wherein q is expressed in $2\pi/a$ units, "a" is the FCC-Fe lattice parameter measured in nanometers, and q = 0.5 for AFM). An essential feature discovered by these calculations is that the lattice corresponding to the equilibrium state of γ-Fe is FCT rather than FCC. The tetragonality value c/a dependents on the magnetic structure and falls within the range from 4 to 10%.

[0064] It is currently undoubted that magnetism plays the key role in the phase stability of iron and its alloys (see Kaufman, L., Clougherty, E.V., and Weiss, R.J., Acta Metallurg., 1963, Vol. 11, p. 323; and M. Acet, H. Zahres, and B. F. Wasserman, Phys. Rev. B, 1994, Vol. 49, p. 6012). The occurrence of more than one magnetic state creates preconditions for the emergence of heterogeneity in γ-Fe and is the reason for the Invar behavior of its base alloys.

[0065] The possibility for a short-range magnetic order to appear at temperatures close to A_1 (~1000 K) may be judged from estimates of the exchange energy, which is responsible for the appearance of a ferromagnetic state. Figure 5 displays the results of calculations of the parameter J_0, which is measured in eV/atom and characterizes the gain in magnetic energy as a result of formation of a ferromagnetic ($J_0 < 0$) or antiferromagnetic ($J_0 > 0$) order (see A. I. Liechtenstein, M. I. Katsnelson, V. P. Antropov, and V. A. Gubanov, JMMM, 1987, Vol. 67, p. 65). Clearly, this gain amounts to ~1000 K for a volume close to the experimental value (12.2 A^3/atom) and the degree of tetragonal distortion of about -5% ($c/a \approx 0.95$; see curve 3), with the FCC lattice being distorted toward the BCC structure. Thus, tetragonally distorted regions with a ferromagnetic short-range order are expected to appear thanks to the gain in magnetic energy; they are stable at temperatures close to A_1.

[0066] The calculations carried out by the inventors in the frame of electron density functional theory for a partially ordered magnetic state of iron using the disordered local moment (DLM) model (see S. V. Okatov, A. R. Kuznetsov, Yu. N. Gornostyrev, V. N. Urtsev, and M. I. Katsnelson, Phys. Rev. B, 2009, Vol. 79, p. 094111) showed that, when magnetization M is about $0.5M_{max}$ (wherein M_{max} is the maximal magnetization attainable in a ferromagnetic state), the energy minimum is achieved for the FCT lattice having the tetragonality $c/a \approx 0.95$. This result provides direct evidence for the conclusions based on the estimates of the exchange energy J_0, found above.

[0067] Thus, thanks to the strong relationship between the lattice and magnetic degrees of freedom, two stable states can exist in γ-Fe within a certain temperature range of $T > A_3$, namely: a paramagnetic (FCC) state and a tetragonally distorted (FCT) state with a short-range ferromagnetic order. This leads to the specific character of spin-lattice dynamics, the existence thereof explains the observed "anti-Invar" behavior of γ-Fe (see M. Acet, H. Zahres, and B. F. Wasserman, Phys. Rev. B, 1994, Vol. 49, p. 6012) and plays the key role in the nucleation of the new phase upon the α-γ transformation. The structure of spin-lattice excitations at a fixed moment of time may be represented as an alternation of nanosized regions of the FCT and FCC lattices.

[0068] In order to elucidate the role of carbon in the formation of the specific structural state of the Fe-C system under study, the electronic structure and the lattice and magnetic properties of dilute solid solutions of carbon in γ-Fe were calculated in terms of the density functional theory (see D. W. Boukhvalov, Yu. N. Gomostyrev, M. I. Katsnelson, and A. I. Lichtenstein, Phys. Rev. Lett. 2007, Vol. 99, p. 247205). Carbon was found to have a strong effect on the magnetic structure of γ-Fe. The incorporation of carbon into an interstitial position brings about a local magnetic polarization of the γ-Fe lattice and is accompanied by considerable tetragonal distortions of the FCC lattice toward BCC. Moreover, the change in exchange coupling energy appears to be rather great (local spin-flip energy: $J \sim 1100$ K), so that magnetic inhomogeneities in the vicinity of carbon atoms should survive up to rather high temperatures of $T_C^{loc} \approx 1100$K. The occurrence of tetragonal distortions in the vicinity of carbon atoms considerably enhances interactions between them, thereby providing the conditions for decomposition to occur in the γ-Fe-C system as temperature lowers and for a short-range order to form in carbon-rich regions.

[0069] Thus, carbon turned out to be the chemical element enhancing the stabilization (increasing the existence time) of FCT fluctuations with a short-range magnetic order and thereby enhancing the formation of the structural state with quasi-static displacements in the Fe-C system. As the calculations showed, the appearance of a short-range magnetic order brings about a noticeable reduction in elastic modulus C' and, thereby, a reduction in the resistance of the lattice toward the FCC-BCC transformation. As a result, the regions of the FCT lattice can be potential sites for the α phase to nucleate upon cooling.

[0070] Thus, on the basis of experimental facts and the results of the calculations, it is established that the specific structural state referred to as MARINITE appears in the Fe-C system under certain conditions. This state is characterized by the occurrence, in the FCC iron matrix, of regions wherein quasi-static atomic displacements transform the lattice from FCC into FCT or BCT (BCC) with a short-range magnetic order, and the occurrence of regions with the FCT lattice and a short-range order in the arrangement of carbon atoms which is characteristic of iron carbides of various compositions.

[0071] Appropriate experiments were carried out to gain more information about marinite.

[0072] In particular, a sample was heated to a temperature of 745°C, exposed for 2 min 55 s, and then cooled in water, wherein the sample was a steel cylinder 8 mm in diameter of the following chemical composition (hereinafter, weight percent are given): 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance (schedule 1).

[0073] The marinite specific structural state was formed during exposure.

[0074] The electron-microscopic structural study of samples after cooling was carried out at the Institute for Metal Physics (Yekaterinburg) on a JEM 200CX transmission electron microscope.

[0075] Steel microstructure after the above-described treatment, as shown in Fig. 6, is characterized by well-organized colonies of martensite lamellas, each lamella comprising a plurality of parallel microtwins (Fig. 6a). The entire field of vision is covered by characteristic spotty (so-called "tweed") contrast (Fig. 6b), which may be treated as resulting from electron scatter on disperse precipitations having sizes of 2 to 5 nm. Such precipitations can represent carbon-enriched clusters or fine carbide precipitations.

[0076] X-ray diffraction studies of the same sample, which were carried out at the Institute for Metal Physics (Yekaterinburg) on a DRON-1UM X-ray diffractometer using FeK_α radiation, elucidated an unusual specific feature of X-ray lines (Figs. 7 and 8), which was manifested as the violation of the standard intensity ratio of 1 : 2 between the peaks of the (110) doublet prescribed by the geometry of the tetragonal lattice of martensite (see G. V. Kurdyumov, L. M. Utevsky, and R. I. Entin, Transformations in Iron and Steel, Наука, Moscow, 1977). The fulfillment of this ratio is well seen from the decomposition of the X-ray line intensity into the superposition of Lorentzians for a sample quenched from T = 1100°C (Fig. 7). For interpreting the intensity ratio (close to 1:1) observed in samples quenched from 745°C, it is necessary to assume that regions of the cubic phase occur along with the tetragonal phase. The mechanism underlying the formation of the X-ray diffraction pattern in this case is illustrated by Fig. 8, which makes it clear that the 40% volume fraction of the cubic phase gives rise to a peak intensity ratio close to 1:1.

[0077] The samples subjected to neutron diffraction studies were steel samples having the composition of 0.84% C; 0.59% Mn; 0.025% S; 0.24% Si; 0.012% P; 0.07% Cr; 0.08% Ni; 0.0075% Al; 0.05% Cu, and Fe and uncontrollable impurities to the balance, and these samples were studied after being heat treated according to the schedule which consisted in heating in a furnace to 1005°C, cooling in air to 700°C, torsional strain on a torsion-type plastomer (relative strain of the surface layer: $\varepsilon = 0.12$; strain rate: $\zeta = 0.2\ s^{-1}$), cooling in saltpeter (443°C) for 3 s, and further cooling in water; and samples of the same chemical composition having the martensite structure prepared by direct quenching from the austenite region. The neutron diffraction experiment was carried out on an IVV-2M stationary research nuclear reactor at the Beloyarsk NPP using a high-angle-resolution neutron diffractometer. The phase composition was determined and the structure parameters were refined using full-profile Rietveld analysis (see Rietveld, H.M., J. Appl. Cryst. 1969, Vol. 2, p. 65).

[0078] As a result, it was discovered that the degree of lattice tetragonality in the samples in which marinite was formed in the course of heat treatment, was ~0.5%, whereas the lattice tetragonality for martensite of the same chemical composition is ~2%.

[0079] The data obtained confirm the conclusions drawn from the results of the X-ray diffraction experiment, and indicate the abnormal low lattice tetragonality in the structure formed upon rapid cooling of marinite

[0080] In another experiment, a sample of the same shape and the same chemical composition was heated to a temperature of 1010°C, cooled to a temperature of 745°C in a salt melt of composition 41% KCl, 37% NaCl, and 22% BaCl, and further cooled in water (schedule 2). In the course of this heat treatment, the marinite structural state appeared upon cooling in the salt melt.

[0081] Phase composition analysis for samples heat treated according to schedule 1 and schedule 2 was carried out using scanning electron microscopy (SEM) and large-angle electron backscatter diffraction (EBSD). Representative SEM images of etched surface structures are shown in Figs. 9 and 10, respectively. The images in Figs. 9 and 10 are morphologically similar, and in terms of topology they are uniquely interpreted as a projection formed as a result of etching of a complex relief, this relief comprising developed surface elements with a dominant axial orientation and etched pits. A comparison of the SEM and EBSD results for the aforementioned samples implies that the developed surface elements consist of iron carbide, supposedly of composition $Fe_4C_{0.63}$, and the volumes of etching pits are filled with BCC-Fe. Inasmuch as such a structure was generated by quenching marinite, a conclusion is possible that iron carbides are formed from carbon-rich regions whereas carbon-poor regions transform upon quenching into BCT-Fe with abnormal low tetragonality.

[0082] Thus, the comparison of the aforementioned results implies that the appropriate selection of temperature variation schedules would allow forming marinite, the cooling whereof gives rise to a structure containing BCT regions with abnormal low tetragonality and disperse iron carbides of various compositions, this structure being referred to as "quenched marinite " or "rutite" (see V. N. Urtsev et al., "Relationship between Magnetic and Lattice Degrees of Freedom in the Fe-C System," Stal', 2010, No. 7, pp. 101-106),

[0083] In order to elucidate how the kinetics of pearlite transformation changes when the transformation occurs from the prior-formed marinite structural state, the following experiments were carried out.

[0084] The schedule comprised: heating to a temperature of 1005°C, cooling in air to a temperature of 745°C, cooling for 10 s in molten saltpeter having a temperature of 443°C, and further cooling in water. According to this schedule, the sorbite structure is formed in a sample from the marinite structural state that has been formed in the course of cooling, in a volume fraction of near 100% (Fig. 11).

[0085] Experiments were also carried out on heating samples to a temperature of 745°C with exposure for 3 min, cooling them in molten saltpeter having a temperature of 443 °C for 10 s, and further cooling in water. According to this schedule, the sorbite structure is also formed in the sample from the marinite structural state that has been formed by heating (Fig.12).

[0086] In either of the two experiments, the sorbitation time was about 10 s. For a roll of the same diameter, the currently used technologies provide sorbitation times of 20 to 60 s (see V. I. Zyuzin et al., "The Sorbitation Specifics of Rolls from Roll Heating and Wire Made Thereof," Technical Information, Beloretsk, 2001; and Yu. G. Alexeev et al., Steel Cord for Tires, Metallurgiya, Moscow, 1992). Thus, marinite formation allows accelerating the process of sorbite structure formation.

[0087] There is experimental evidence for the existence of a specific structural state (marinite) in the Fe-C system (see V. N. Urtsev et al., "Relationship between Magnetic and Lattice Degrees of Freedom in the Fe-C System," Stal', 2010, No. 7, pp. 101-106). Marinite formation is responsible for the observed specifics of temperature-dependent thermal expansion and magnetic susceptibility, and quenching samples from the marinite state results in rutite formation

[0088] The temperature variations of magnetic susceptibility and thermal expansion (Figs. 1b and 2) indicate that the γ-α transformation upon cooling is preceded by the formation of magnetically ordered nanosized regions. The volume fraction of these regions increases in the course of cooling at temperatures in the range of $A_1 < T < T_C$, and when $T \sim A_1$, these regions are united, finally resulting in the formation of the α phase.

[0089] The calculations show that carbon enhances the stabilization of FCT fluctuations with a short-range magnetic order and, thereby, enhances the formation of the structural state with quasi-static displacements in the Fe-C system. The formation of the short-range magnetic order brings about a noticeable reduction in elastic modulus C' and a reduction in lattice resistance toward the FCC-BCC transformation.

[0090] Given considerable overcooling of marinite, the transformation will develop by the shear mechanism involving the loss of stability by the framework of "soft" FCT regions. As a result, an unusual structure is formed (quenched marinite., i.e., rutite) having abnormal low tetragonality, comprising disperse precipitations of carbides, and having hardness values characteristic of martensite with near-eutectoid carbon concentrations.

[0091] When marinite is cooled at lower rates, the leading process would be carbon redistribution. As a result, the transformation will follow the pearlite mechanism and, depending on the cooling schedule, will lead to the formation of either lamellar or granular pearlite.

[0092] Thus, once marinite is formed, either the structural state referred to as rutite (which differs from martensite and bainite by the combination of performance characteristics, i.e., crack resistance, ductility, hardness, and strength), or ferrite-cementite structures (for example, pearlites of various degree of dispersion) are further formed, depending on the marinite, cooling schedule, within technologically shorter periods of time,.

[0093] Marinite formation can be implemented either by cooling austenite, or by heating a structure whose phase constitution is represented by ferrite and iron carbides. This explains the use of two variants of heat treatment.

[0094] The general feature of the claimed variants of heat treatment of articles made of alloys having carbon contents of up to 4.3% by weight consists in providing the conditions for marinite to form and further cooling it.

[0095] A first variant may be characterized as the heat treatment of an alloy article by means of: forming marinite upon cooling from the austenite region and forming the required structural state, which contains desired fractions of pearlite in various degrees of dispersion and/or quenched structures, in the course of further cooling.

[0096] In this case, heating is carried out to create conditions that provide the formation of austenite for marinite to form further and to provide for further phase transformations as a result of which the required structural state of the alloy would be obtained, and appropriate temperature depression schedules are selected or calculated to attain this purpose.

[0097] As follows from the above-described experiments, the prerequisite for marinite to form from austenite consists in the occurrence of austenite regions having near-cutectoid chemical compositions. Moreover, the greater the volume fraction of these regions, the greater the attainable marinite fraction.

[0098] marinite formation is necessary for providing the conditions for the desired structural state to form, namely, pearlites with various degrees of dispersion (within short times in the flowsheet) and/or quenched structures.

[0099] Inasmuch as rutite is shown experimentally to have a unique combination of properties (hardness, strength, ductility, and crack resistance), the articles obtained as a result of heat treatment will have the set of consumer characteristics hardly attainable by conventional methods.

[0100] After marinite is formed, further cooling an article made of an iron-base alloy having carbon contents of up to 4.3% by weight is carried out according to schedules that provide the formation of the desired fractions of pearlite, rutite, and quenched structures.

[0101] The range of carbon concentrations in the alloy is confined to 4.3% by weight because alloy volumes having near-eutectoid carbon concentrations should be provided in order for marinite to form. In alloys having carbon concentrations below the eutectoid value or in alloys having carbon concentrations above the eutectoid value, conditions for some microvolumes to reach near-eutectoid carbon concentrations can be created by varying temperature. Increasing carbon concentrations to values exceeding 4.3% by weight is inappropriate for the reason that the eutectoid carbon concentration is attained in microvolumes positioned within ledeburite.

[0102] Apart from carbon, an alloy can contain other chemical elements in the form of either alloying additives or uncontrollable impurities, and concentrations thereof should fall within the ranges that allow austenite volumes to form from the alloy upon heating the article, such that the eutectoid decay conditions would appear in certain cooling schedules.

[0103] In practice, the desired structural state is frequently formed with the attainment of the required ratio of volume fractions of the desired structural constituents (pearlite, rutite, and quenched structures). From this, it is appropriate to tailor the fraction of austenite regions with near-eutectoid chemical compositions such that it would be sufficient for the desired marinite fraction to form, that is, fraction necessary for the required structural state to form.

[0104] The schedules providing the formation of the desired fraction of austenite regions with near-eutectoid chemical compositions and then providing therein the desired marinite fraction, sometimes cannot be determined leaning upon the literature data; therefore, it is appropriate to determine these schedules by calculations or experimentally.

[0105] The heating and cooling schedules that would provide the formation of marinite from austenite with a near-eutectoid chemical composition, can be determined by means of calculations. When calculations are used to determine the schedules that provide marinite formation from austenite regions having near-eutectoid chemical compositions, for example, the range of temperatures for marinite to form is set so as to satisfy the conditions that

$$T_{\text{tech}} < \mathrm{T} < T_C^{loc},$$

wherein

T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations and

T_{tech} is the temperature selected with account for technological limitations; and

the cooling rate is selected such that the cooling temperature versus time T(t) satisfies the condition that T(t) < □(t), wherein the □(t) function is given by the starting lines of the pearlite and bainite transformations in the thermokinetic diagram.

[0106] In practice it is appropriate to supplement the calculation methods for determination of the schedules that provide the formation of marinite from austenite with a near-eutectoid chemical composition, with experimental methods, for example, by quenching samples from fixed temperatures with various exposure times at these temperatures. For use in these experiments, suitable are both samples having chemical compositions identical to the composition of the alloy of which the article is made and samples in which alloying elements are present in the same concentration and the carbon concentration corresponds to the eutectoid concentration.

[0107] The occurrence of marinite is judged from the occurrence of rutite in the quenched sample.

[0108] For establishing the occurrence of rutite, it is appropriate to employ diffraction methods, which are most reliable ones. Examples of useful methods comprise electron backscatter diffraction, small-angle neutron scatter, and X-ray diffraction.

[0109] Once marinite is formed, it is necessary to further cool the alloy article for providing the desired structural state containing the desired pearlite and/or rutite fractions. For this purpose, appropriate cooling schedules are to be selected. The cooling schedule that would provide the formation of the desired structural state can be determined experimentally or by calculations. The experimental method comprises quenching samples followed by the determination of pearlite volume fractions therein.

[0110] In particular embodiments of the method, the cooling schedule is determined by means of calculations, wherein the determination of the schedule for cooling from the prior-formed marinite to provide the desired structural state comprises: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample, determining the values of thermokinetic constants that would provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i ,$$

wherein:

the operator $\vec{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1},

r is the radius-vector of the point to which the calculations refer,

ρ is density, measured in kg/m^3,

q_i is the specific enthalpy of formation of the *i*th phase, measured in J/kg,

$f_i(r, t, T)$ is the dimensionless weight fraction of the *i*th phase in the vicinity of point r at moment of time t at temperature T,

Q(r,t) is the heat flow, measured in $J/(m^2 \cdot s)$,

$H(r, t, T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample;

the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT' ,$$

wherein

$C_p^i(T)$ is the specific heat capacity of the *i*th phase at a fixed pressure as a function of temperature, measured in J/(kg·K), and

the kinetic equation

$$\frac{df_i(\mathrm{r,t,T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau ,$$

wherein

$M_{ik}(T, f_k(\tau),(t - \tau))$ is the function that defines the variation rate of the weight fraction f_i of the ith phase, determined for each phase transformation, and

then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0111] In particular embodiments, once the required marinite fraction is formed, cooling is carried out according to schedules that do not comprise quenching to form the desired fractions of ferrite and iron carbide phases in the desired structural state. This treatment scheme allows accelerating the formation of the sorbite structure (for example, for a steel rod 8 mm in diameter having a near-eutectoid chemical composition (0.84% C; 0.59% Mn; 0.025% S; 0.24% Si; 0.012% P; 0.07% Cr; 0.08% Ni; 0.0075% Al; 0.05% Cu, and Fe and uncontrollable impurities to the balance) heated to a temperature of 1005°C and then cooled in air to 745°C, the time within which the sorbite structure is formed upon further cooling in molten saltpeter having a temperature of 443°C is 10 s).

[0112] Cooling an alloy article at rates sufficient for diffusion transformations to be inhibited after forming the desired pearlite fraction, allows the desired fractions of rutite and quenched structures to be formed.

[0113] In some cases it is appropriate to carry out cooling of an alloy article by one or more pulses, for example, in the production of long roll products and wire. In this case, however, there is danger that quenched structures would form in the surface layer. Their formation can be avoided by alternating cooling pulses with pauses during which the surface-layer temperature would increase due to heat transfer from the inner layers of the alloy article to the outer ones, which would result in either the disappearance of quenched structures in the surface layer, or the inhibition of appearance thereof.

[0114] In particular embodiments, the cooling process is organized so that pulses are alternated with pauses, wherein the pause length is chosen to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of the alloy article in order to reduce internal thermal stresses.

[0115] In particular embodiments of the method, the length of each of the cooling pulses is selected such that the pulses do not lead to the formation of quenched structures in the desired structural state. This condition should be fulfilled, because temperature depression can lead to the formation of cooling pulses such that the heat of the central layers of the article would be insufficient for the quenched structures formed in the surface layer to disappear.

[0116] In particular embodiments, it is appropriate to carry out cooling in a way such that one of the cooling pulses would provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures. This is necessary (as experiments showed) for accelerating the kinetics of pearlite formation. For example, when after heating to a temperature of 1005°C and cooling in air to 745°C, further cooling in molten saltpeter having a temperature of 443°C is preceded by water cooling with a single pulse having a length of 0.2 s, the times for the sorbite structure to form are shorter, and for a steel rod of 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance), this time is 4 s.

[0117] In some cases it is appropriate that, after forming the desired austenite fraction in the alloy that is sufficient for obtaining desired pearlite fractions in the desired structural state with various degrees of dispersion and/or quenched structures, the temperature depression required for marinite to be formed is accomplished by cooling pulses.

[0118] Where there is no technological necessity to continue pulsed cooling, after reaching the fractions of the ferrite and iron carbide phases in the alloy that provide the further attainment of the desired content thereof in the final structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

[0119] The kinetics of marinite formation and subsequent pearlite formation can be accelerated by subjecting the alloy to plastic strain after heating it to temperatures that provide the formation of the required austenite fraction therein. The plastic strain can be accomplished over a wide temperature range, but a more efficient result is attained when the alloy is subjected to plastic strain at a temperature of $t_{C\,ferr} \pm 50°C$, wherein $t_{C\,ferr}$ is the Curie point of ferrite, in degrees Celsius (for example, experiments showed that when prior to being cooled in molten saltpeter having a temperature of 443°C, the sample is strained on a torsion-type plastomer with a relative strain in the surface layer of 23% 23% and a strain rate of 0.2 s^{-1} at a temperature of 745°C, then the time within which the sorbite structure is formed is considerably shorter). For example, for a steel rod 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0/07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance), the time within which the sorbite structure is formed according to this treatment scheme is 3 s.

[0120] The greatest acceleration of marinite formation and subsequent pearlite formation is attained by combining the accelerating effects of pulsed cooling and plastic strain in one flowsheet. For example, when heating to a temperature of 1005°C and cooling in air to 745°C is followed by straining a cylinder-shaped steel sample 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0,0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance) on a torsion-type plastomer with a relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a strain temperature of 745°C, and the sample is then

subjected to water cooling by a single pulse having a length of 0.2 s and is placed to molten saltpeter having a temperature of 443°C, then the time within which the sorbite structure is formed is 1 s.

[0121] Experiments showed that the impact of a permanent or pulsed magnetic field on an alloy in the course of the disappearance of austenite and the appearance of marinite also allows shortening the heat treatment time of the alloy. Marinite is characterized by a developed short-range magnetic order. Therefore, the application of an external magnetic field would stimulate its formation.

[0122] In all particular embodiments of the above-described method, water or water-containing media are preferably used for cooling. In principle, cooling can be accomplished by any means of those known to be useful in metallurgical processes (water, oils, air, various emulsions, or molten salts). However, because high cooling rates are required in carrying out some operations, it is appropriate to use media having high heat capacities; such the media are exemplified by water and solutions and emulsions on the basis thereof.

[0123] The second variant of the method can be characterized as the heat treatment of an article made of an alloy by means of: providing marinite upon heating and forming the required structural state that contains the desired pearlite fraction with various degrees of dispersion and/or quenched structures in the course of subsequent cooling.

[0124] In the second variant of the invention, the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight comprises: heating and subsequent cooling according to the schedules that provide the formation of the desired structural state, wherein the heating is accomplished according to the schedules that provide the formation of marinite, and wherein the desired structural state is formed to obtain therein pearlite having various degrees of dispersion and/or quenched structures.

[0125] This method is appropriate when there are not technological requirements for the provision of high heating temperatures (warm drawing, forging, warm heading, or warm compaction).

[0126] The experiments showed that in order for marinite to form in the alloy upon heating thereof from room temperature, the prerequisite is the occurrence of volumes (regions) wherein carbon concentrations are near-eutectoid concentrations (with account for the occurrence of other chemical elements). Thus, depending on the structural state of the alloy, marinite would be formed either upon the dissolution of cementite in pearlite colonies, or within volumes containing sufficient amounts of carbides, or within volumes of quenched structures having appropriate chemical compositions.

[0127] The occurrence of marinite is necessary for conditions to be provided for the formation of desired pearlite fractions in the desired structural state having various degrees of dispersion (within short technological periods of time) and/or quenched structures.

[0128] Inasmuch as rutite has a unique combination of properties (hardness, strength, ductility, and crack resistance) as found experimentally, the articles obtained as a result of heat treatment would have the set of consumer characteristics that are hardly attainable by conventional methods.

[0129] Cooling an article made of iron-base alloys having carbon contents of up to 4.3% by weight following marinite formation is carried out according to the schedules that provide the formation of the desired fractions of pearlite, rutite, and quenched structures.

[0130] The range of carbon concentrations in the alloy of up to 4.3% by weight is due to the fact that alloy volumes having near-eutectoid carbon concentrations should be provided in order for marinite to form. In alloys having carbon concentrations below the eutectoid value or in alloys having carbon concentrations above the eutectoid value, temperature variation can create conditions for some microvolumes to reach near-eutectoid carbon concentrations. Increasing carbon concentrations to values exceeding 4.3% by weight is inappropriate for the reason that, in this case, the eutectoid carbon concentration is attained in microvolumes positioned within ledeburite.

[0131] Apart from carbon, an alloy can contain other chemical elements in the form of either alloy additives or uncontrollable impurities; concentrations thereof should fall within the ranges that allow eutectoid decay to occur in the alloy under certain conditions.

[0132] In practice, the desired structural state is frequently formed with the attainment of the desired ratio of volume fractions of the desired structure constituents thereof (pearlite, rutite, and quenched structures). From this, it is appropriate to tailor the marinite fraction sufficient for the required structural state to form.

[0133] The schedules ensuring the formation of the desired marinite fraction sometimes cannot be determined leaning upon literature data; therefore, it is appropriate to determine these schedules by calculations or experimentally.

[0134] The heating and cooling schedules that would provide marinite formation can be determined by calculations. For example, when calculations are used to determine the schedules that provide the formation of marinite, the following is to be set:

the range of heating temperatures that satisfy the conditions that

$$T_X < T < T_C^{loc},$$

wherein
Q(r,t) is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations and
T_X is the eutectoid temperature for an alloy of the appropriate chemical composition;
the exposure time t in seconds required for the dissolution of the desired cementite fraction f_C, to be derived from the equation

$$f_C = 1.05\ f_{C0} \exp(-kt^n),$$

wherein
f_{C0} is the dimensionless cementite fraction in the initial moment of time,
n is an exponent, 4 > n > 3,
k is the parameter that determines the cementite dissolution rate in the alloy of the appropriate chemical composition at temperature T, in s^{-n}.

[0135] In practice it is appropriate to supplement the calculation methods for determination of the schedules that would provide the formation of marinite from austenite with a near-eutectoid chemical composition, with experimental methods, for example, by quenching samples from fixed temperatures with various exposure times at these temperatures. Suitable for these experiments are both samples having chemical compositions identical to the composition of the alloy of which the article is made and samples in which alloy elements are present in the same concentration and the carbon concentration corresponds to the eutectoid concentration.

[0136] The occurrence of marinite is judged from the occurrence of rutite in a quenched sample.

[0137] As in the first method for the heat treatment of articles made of alloys, in this method, too, diffraction methods are used to establish the occurrence of rutile; the cooling schedules that would provide the formation of the desired amount of pearlite in the desired structural state are determined either experimentally or by calculations.

[0138] The experimental determination of the schedule for cooling from the prior-formed marinite, to form the desired amount of pearlite in the desired structural state is performed by quenching experimental samples, followed by the determination of the structural state thereof.

[0139] When calculations are used, the determination of the schedule for cooling from the prior-formed marinite to form the desired structural state, is implemented by: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample; determining the values of thermokinetic constants that provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising
the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i ,$$

wherein:

the operator $\vec{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1},

r is the radius-vector of the point to which the calculations refer,
p is the density, measured in kg/m^3,
q_i is the specific enthalpy of formation of the *i*th phase, measured in J/kg,
$f_i(r,t,T)$ is the dimensionless weight fraction of the *i*th phase in the vicinity of point r at moment of time t at temperature T,
Q(r,t) is the heat flow, measured in $J/(m^2 \cdot s)$,
$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample;
the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT',$$

wherein
C^i_p (T) is the specific heat capacity of the *i*th phase at a fixed pressure as a function of temperature, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\mathrm{r},\mathrm{t},\mathrm{T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau,$$

wherein
M_{ik} (T, $f_k(\tau)$, (t - τ)) is the function that defines the variation rate of the weight fraction f_i of the *i*th phase, determined for each phase transformation, and
then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0140] In particular embodiments, after the required marinite fraction is formed, cooling is carried out according to schedules that do not comprise quenching to form the desired fractions of ferrite and iron carbide phases in the final structural state. This treatment scheme allows accelerating the formation of the sorbite structure. For example, for a steel rod 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance), heated to a temperature of 745°C and then exposed at this temperature for 3 min, the time within which the sorbite structure is formed upon further cooling in molten saltpeter having a temperature of 443° is 10 s.

[0141] Cooling an article made of an alloy at rates sufficient for diffusion transformations to be inhibited after forming the desired pearlite fraction, allows the desired fractions of rutite and quenched structures to be formed.

[0142] In some cases it is appropriate to perform cooling of an alloy article by one or more pulses, for example, in the production of long roll products and wire. In this case, however, there is danger that quenched structures would form in the surface layer. Their formation can be avoided by alternating cooling pulses with pauses during which the surface-layer temperature would increase due to heat transfer from the inner layers of the alloy article to the outer ones to result in either the disappearance of quenched structures in the surface layer, or the inhibition of appearance thereof.

[0143] In particular embodiments, the cooling process is organized so that cooling pulses are alternated with pauses, wherein the pause length is selected to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of the article made of an alloy in order to reduce internal thermal stresses.

[0144] As in the first method, in particular embodiments of this method, too, the length of each of the cooling pulses is selected such that they would not lead to the formation of quenched structures in the desired structural state. This condition should be fulfilled, because temperature depression can lead to the formation of cooling pulses such that the heat of the central layers of the article would be insufficient for the quenched structures formed in the surface layer to disappear.

[0145] In particular embodiments, it is appropriate to perform cooling in a way such that one of the cooling pulses would provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures. This is necessary (as experiments showed) for accelerating the kinetics of pearlite formation. For example, when after heating to a temperature of 1005°C and cooling in air to 745°C, the cooling in molten saltpeter having a temperature of 443 °C is preceded by water cooling with a single pulse having a length of 0.2 s, the times taken by the sorbite structure to form are shorter, and for a steel rod of 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance), this time is 4 s.

[0146] Where there is no technological necessity to continue pulsed cooling after the fractions of the ferrite and iron carbide phases are achieved in the alloy such that provide the further attainment of the desired content thereof in the final structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

[0147] The kinetics of pearlite formation can be accelerated by subjecting the alloy to plastic strain after marinite is formed. The kinetics of marinite formation and subsequent pearlite formation therein can be accelerated when the alloy is subjected to plastic strain during heating prior to or in the course of marinite formation.

[0148] Plastic straining can be performed over a wide temperature range, but a more efficient result is attained when the alloy is subjected to plastic strain at a temperature of $t_{C\ ferr} \pm 50$ °C, wherein $t_{C\ ferr}$ is the Curie point of ferrite, in degrees Celsius. For example, as experiments showed that, when prior to being cooled in molten saltpeter having a temperature of 443°C, the sample is strained on a torsion-type plastomer with a relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a temperature of 745°C, then the time within which the sorbite structure is formed is considerably shorter. For example, for a steel rod 8 mm in diameter having a near-eutectoid chemical composition (0.84% C; 0.59% Mn; 0.025% S; 0.24% Si; 0.012% P; 0/07% Cr; 0.08% Ni; 0.0075% Al; 0.05% Cu; and Fe and uncontrollable impurities to the balance), the time within which the sorbite structure is formed according to this treatment scheme is 3 s.

[0149] As in the first variant of the invention, the greatest acceleration of pearlite formation is attained by combining the accelerating effects of pulsed cooling and plastic straining in one flowsheet.

[0150] For example, when heating to a temperature of 1005°C and cooling in air to 745°C is followed by straining a cylinder-shaped steel sample 8 mm in diameter having a near-eutectoid chemical composition (0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0,0075% Al, 0.05% Cu, Fe and uncontrollable impurities to the balance) on a torsion-type plastomer with a relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a strain temperature of 745°C, the sample is further water cooled by a single pulse having a length of 0.2 s and is placed to molten saltpeter having a temperature of 443°C, then the time within which the sorbite structure is formed is 1 s.

[0151] In all methods, water or water-containing media are preferably used for cooling. In principle, cooling can be carried out by any means of those known to be useful in metallurgical processes (water, oils, air, various emulsions, or molten salts). However, because high cooling rates are required in carrying out some operations, it is appropriate to use media having high heat capacities; such the media exemplified by water and solutions and emulsions on thereof.

[0152] Further, the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight will be illustrated by examples.

Example 1

[0153] In the very general form, the first variant of the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight was carried out in the following way.

[0154] An article (workpiece) was heated to temperatures providing the formation of the desired austenite fraction sufficient for the desired fractions of pearlite to form in the desired structural state having various degrees of dispersion and/or quenched structures. Should the desired final structural state should not comprise a fraction of the initial structure that existed in the alloy article prior to the start of heat treatment, the austenite fraction in the heated article would be 100%; otherwise, 100% minus the fraction of the initial structure.

[0155] Then, the temperature of the article was lowered according to the schedules that had been determined, either experimentally or by calculations, to provide the formation of the desired fraction of austenite regions having near-eutectoid chemical compositions, followed by providing therein the desired marinite fraction, and cooling was further carried out according to the schedules that provide the formation of the desired structural state to form pearlite therein in various degrees of dispersion and/or quenched structures.

[0156] When the method was carried out using the experimentally determined schedules for providing marinite formation from austenite regions having near-eutectoid chemical compositions, the marinite existence conditions were first determined for each alloy.

[0157] For this purpose, samples (which were round rods having diameters of 6.5 to 8 mm and lengths of 500 to 800 mm) were heated to a temperature of 1050°C; this temperature obviously exceeded the marinite existence temperature and provided austenite formation with a volume fraction of 100%. The samples were exposed at this temperature for a period of about 15 minutes and then cooled to temperatures ranging from 815 to 500°C in 15°C steps so as to provide exposure at the specified temperatures for a period of 0 to 600 s, and quenching was carried out.

[0158] In carrying out the aforementioned operations, a temperature versus time curve was recorded from a thermocouple caulked into the sample to a depth of one-half of the rod radius. Cooling curves were recorded using known techniques, for example, with an analog input module for connecting ADAM 6018 thermocouples. Quenched samples were studied by known methods, in particular, diffraction methods (X-ray diffraction and neutron diffraction). The results of these studies served to conclude whether marinite existed in the sample; in so doing, the occurrence of marinite prior to quenching was judged from the occurrence of rutite in a sample quenched from fixed temperatures with various exposure times at these temperatures.

[0159] The above experiments served to determine the temperature and time frames of the occurrence of marinite in the alloy.

[0160] When calculations were used to determine the schedules that would provide marinite formation from austenite regions having near-eutectoid chemical compositions, the temperature range of marinite formation was set so as to

satisfy the condition that $T_{TEX} < T < T_C^{loc}$, , wherein Q(r,t) is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations, and T_{TEX} is the temperature selected with account for technological limitations; and the cooling rate was selected such that the cooling temperature versus time T(t) satisfied the condition that T(t) < □(t), wherein the □(t) function is given by the starting lines of the pearlite and bainite transformations in the thermokinetic diagram.

[0161] The schedules for temperature depression from the prior-formed marinite to form the desired amount of pearlite having the required degree of dispersion in the desired final structural state, were determined either experimentally (by quenching experimental samples and then determining the structural state thereof), or by calculations.

[0162] When experiments were used to determine the cooling schedules that would provide the formation of the desired amount of pearlite having the required degree of dispersion in the desired structural state, experimental samples were quenched from a temperature ranging between 745 and 400°C, and the structural state thereof was determined. For this purpose, experimental samples (which were shaped as cylinders having diameters of 8 mm and lengths of 500 mm) with thermocouples caulked to a depth of 2 mm, were cooled from a temperature ranging between 745 and 500°C in air or in molten saltpeter having a temperature of 440°C, and quenching was carried out from various temperatures (lying in the range 730 to 440°C), which were determined from the thermocouple reading. The structural state of quenched samples was determined by metallographic and diffraction techniques.

[0163] The experimental cooling curves obtained in this way were used to determine thermokinetic constants, which would allow cooling schedules to be calculated for arbitrary shapes of articles in various cooling media. The determination of the values of thermokinetic constants was carried out so as to reach the coincidence of the experimentally determined temperature versus time dependences with those obtained as a result of solving the set of equations comprising:

the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i ,$$

wherein:
the operator Q(r,t) has a dimension of m^{-1},
r is the radius-vector of the point to which the calculations refer,
p is density, measured in kg/m^3,
q_i is the specific enthalpy of formation of the *i*th phase, measured in J/kg,
$f_i(r,t,T)$ is the dimensionless weight fraction of the *i*th phase in the vicinity of point r at moment of time t at temperature T,
Q(r,t) is the heat flow, measured in $J/(m^2 \cdot s)$,
$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample;
the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT' ,$$

wherein
$C^i_p(T)$ is the specific heat capacity of the *i*th phase at a fixed pressure as a function of temperature, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\mathrm{r,t,T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau ,$$

wherein
$M_{ik}(T, f_k(\tau), (t - \tau))$ is the function that defines the variation rate of the weight fraction f_i of the *i*th phase, determined for each phase transformation, and then calculating the heat flow as a function of time across the surface of the

alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0164] The data obtained in this way were used to embody the method for the heat treatment of articles made of iron-base alloys to produce articles having the desired structural state. For this purpose, the workpiece was first heated to temperatures providing austenite formation. Following this, the workpiece was cooled according to the schedules that provided marinite formation from austenite regions with near-eutectoid chemical compositions. Then, the alloy article was further cooled according to the schedules that provided the formation of the desired pearlite fraction having the required degree of dispersion and/or quenched structures.

[0165] Thus, as a result of the selection of marinite formation (occurrence) conditions and the appropriate schedules (trajectories) of subsequent cooling, performed experimentally and/or by calculations, it becomes possible to produce articles having the desired structural state and with a pearlite content having the required degree of dispersion and/or quenched structures.

[0166] In particular embodiments of the method, for providing the production of articles with the desired structural state and the required mechanical properties and for reducing the times in the flowsheet for forming the pearlite structure, it is appropriate to expose the treated article of workpiece to a magnetic field, subject it to plastic strain, and lower the temperature using pulsed cooling with various pulse times and pauses between them.

Example 2

[0167] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, within short sorbitation times. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0168] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0169] With the goal of determining the schedules that would provide marinite formation from austenite regions with near-eutectoid chemical compositions, according to claim 5, the temperature range within which the occurrence of marinite is possible was determined so as to satisfy the condition that $T_{TEX} < T < T_C^{loc}$, , wherein Q(r,t) (the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom) was determined by quantum-chemical calculations to be ~1100 K or 817°C and T_{TEX} was selected to equal 975 K or 702°C.

[0170] In order to refine the marinite, formation schedules determined by calculations, curves for cooling in air from the specified heating temperatures (~1005°C) were recorded experimentally. The experimental samples were round rods having diameters of 6.5 to 8 mm and lengths of 500 to 800 mm. Cooling curves were recorded from a thermocouple caulked into the sample to a depth of one-half of the rod radius. An analog input module for connecting ADAM 6018 thermocouples was used in recording the cooling curves. In the course of cooling in air, the samples were quenched from various temperatures lying in the range from 700 to 820°C (in 10°C steps). Following this, the samples were studied by various known techniques. In the samples quenched from 730 to 760°C, some structural features intrinsic to rutite were observed, namely, BCT regions with abnormal low tetragonality (about 0.5%) and hardness of ~ 750 HV; therefore, marinite was formed in steel 85 samples in the range of temperatures studied under the specified cooling conditions. The experiment showed that in order for ~100% marinite to form, cooling in air should be accomplished to a temperature ranging from 740 to 750°C.

[0171] Once the marinite, formation conditions were known, the kinetics of formation of the desired final structural state was determined for the cooling schedule selected for the model experiment.

[0172] This purpose was fulfilled as follows: in a model sample, which was a cylinder made of steel grade 85 having a diameter of 8 mm and a length of 500 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, temperature variation upon cooling in air from a temperature of 745°C was recorded from the reading of a thermocouple caulked to a depth of 2 mm.

[0173] The experimentally obtained temperature versus time dependence was used to calculate the coefficients of the computational model, these coefficients characterizing the material and the heat-transfer process (thermophysical and kinetic constants).

[0174] The calculations were performed in the following manner. For the marinite-to-pearlite transformation, the following functional dependence holds (this dependence defines the variation rate with time for the dimensionless weight

fraction of pearlite):

$$\frac{df_i}{dt} = \begin{cases} k_1 + k_2 f_i^{2/3} & \text{- for the case where } \leq 50\% \text{ pearlite was formed;} \\ k_3 (1 - f_i)^{2/3} & \text{- for the case where } > 50\% \text{ pearlite was formed.} \end{cases}$$

[0175] Herein:

$$k_1 = c_1 \times \Delta T_0$$

$$k_2 = c_2 \times \Delta T \Delta T_0^{1/3}$$

$$k_3 = c_2 \times \Delta T \Delta T_0^{1/3}$$

ΔT is temperature deviation from the phase equilibrium temperature, measured in degrees Kelvin,
ΔT_0 is temperature deviation from the phase equilibrium temperature in the starting moment of the phase transformation, measured in degrees Kelvin; and
c_1 (measured in K^{-1}) and c_2 (measured in $K^{4/3}$) are kinetic constants.

[0176] After transition to the finite-difference form, the energy conservation equation for a cell of the difference net will acquire the following form:

$$c_m m_0 \Delta T (1 + f_n (\frac{c_n}{c_m} - 1)) = c_m m_0 \Delta T' (1 + f_n' (\frac{c_n}{c_m} - 1)) - Q - q m_0 (f_n' - f_n)$$

wherein c_m (J/kg·K) is the heat capacity of marinite, c_n (J/kg·K) is the heat capacity of pearlite, m_0 (kg) is the weight of a cell of the finite-difference net, q (J/kg) is the heat of phase transformation, Q (J) is the heat inflow from the outside; and the unprimed and primed values refer to the initial and final time, respectively.

[0177] The heat conductivity equation defines the conductive heat inflow, measured in J/(m^2 s), through the surface of a cell of the finite-difference net:

$$Q_s = -\lambda \frac{dT}{dr}$$

wherein λ is heat conductivity coefficient, measured in J/m·s K (a reference value); and dT/dr is the temperature gradient along the radius of the sample.

[0178] For cooling in air of a model sample with a temperature higher than 600°C, the heat flow on the surface may be regarded as a pure radiation flow, for which the boundary conditions on the surface of the sample are given by the Stefan-Boltzmann law:

$$Q_s = \varepsilon \cdot \sigma \cdot T^4$$

wherein ε is a dimensionless emissivity of steel, equal to 0.8; σ is Boltzmann's constant having a dimension of $J/m^2 \cdot s \cdot K^4$; and T is the surface temperature of the sample.

[0179] The coefficients of the computational model were determined from the condition of coincidence of the experimentally measured and calculated temperature versus time curves in the model sample, and they are displayed in Table 1.

Table 1

Parameter	Exp. no. 1	Exp. no. 2
Critical temperature, °C	755	752
Energy defect, J/kg	8×10^4	7.7×10^4
Induction time, s	24	26
Kinetic constants		
c_1	10^{-7}	10^{-7}
c_2	3.3×10^{-4}	3.5×10^{-4}
Specific heat capacity of the model sample, J/(kg·K)		
Prior to phase transition (at 737°C)	630	630
After phase transition (at 617°C)	700	660

[0180] Then, the coefficients determined as above were used to calculate temperature as a function of time upon cooling the sample from a temperature of 745°C in molten saltpeter. The calculations were carried out for various temperatures of molten saltpeter using reference values of heat-transfer coefficients. As a result, the melt temperature was selected to be 443°C as providing the most complete transformation (the formation. of a finely disperse pearlite structure) within a period of 10 s. Then, rapid cooling in water (quenching) was performed.

[0181] In this way, it was established that cooling in air should be accomplished within the temperature range of from 1005 to 745°C, then cooling in molten saltpeter having a temperature of 443 °C should be accomplished for a period of at least 10 seconds, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C, and cooling thereof was performed according to the specified trajectories. Cooling was performed using molten saltpeter having a temperature of 443°C and technical water. As a result of this, the sorbitation time in the flowsheet was 10 s. Metallographic analysis and diffraction studies of the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~100%, which corresponded to the desired final structural state. The required technical result was thereby attained.

Example 3

[0182] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~80% sorbite within short sorbitation times in the flowsheet and ~20% quenched structures (martensite). For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0183] In order to determine the schedules that provide the formation of the desired marinite fraction from austenite regions with near-eutectoid chemical compositions, cooling curves in air from the specified heating temperature were obtained experimentally. The samples were round rods having diameters of 6.5 to 8 mm and lengths of 500 to 800 mm. The cooling curves were recorded with a thermocouple caulked into the sample to a depth of one-half of the rod radius. An analog input module for connecting ADAM 6018 thermocouples was used to record the cooling curves. In the course of cooling in air, the samples were quenched from temperatures lying in the range from 700 to 820°C (in 10°C steps). Following this, the samples were studied by various known techniques. In the samples quenched from 730 Q(r,t) 760°C, some structural features intrinsic to rutite were observed, namely, BCT regions with abnormal low tetragonality (about 0.5%) and hardness of ~750 HV; therefore, marinite was formed in steel 85 samples in the range of temperatures studied under the specified cooling conditions. The experiment showed that in order for ~80% marinite to form, cooling in air should be accomplished to a temperature of ~750°C.

[0184] Once the marinite formation conditions were known, the kinetics of formation of the desired final structural state was determined experimentally. For this purpose, temperature variation was recorded in the above-described samples upon cooling from a temperature of 750°C in molten saltpeter, having a temperature of 440°C, by the readings of a thermocouple caulked to a depth of 2 mm. The experimentally obtained temperature versus time dependence was used to carry out quenching of the samples in water from various temperatures starting with the onset of heat-evolution features on the cooling curve, these features being associated with the occurrence of the pearlite transformation (approx. 610 to 620°C), followed by the determination of their structural states. As a result of the experiment, it was established that in order for ~80% pearlite (sorbite) to form, the residence time of samples in molten saltpeter should be 7 s and should be followed by quenching in water. In the volume of the sample that remained unconverted to sorbite (~20%) a quenched structure (martensite) was formed.

[0185] In this way, it was established that cooling in air should be accomplished in the temperature range from 1005 to 750°C, then cooling should be accomplished for 7 seconds in molten saltpeter having a temperature of 443°C, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C and cooled according to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C and technical water. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~80%, and the volume fraction of quenched structures (martensite) was ~20%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 4

[0186] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% rutite. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0187] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0188] The schedules that would provide the formation of the desired marinite faction from austenite regions having near-eutectoid chemical compositions in the steel of the specified chemical composition, were first determined by calculations and then refined in experiments, as described in Example 2, for cooling in a salt melt of composition 41% KCl, 37% NaCl, 22% BaCl having a temperature of 740°C. The experiment showed that in order for ~100% marinite to form, cooling in the specified medium should be performed to the temperature of the melt.

[0189] Once the marinite formation conditions were known, the samples were quenched from the above-specified temperatures to thereby provide rutite formation.

[0190] In this way, it was established that cooling should be accomplished within the temperature range from 1005 to 740°C in a salt melt of composition 41% KCl, 37% NaCl, 22% BaCl to the temperature of the salt melt, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C and cooled according to the specified trajectories. Cooling was accomplished using the salt melt of the specified composition having a temperature of about 740°C, and technical water. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the rutite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 5

[0191] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, for sorbitation times in the flowsheet not exceeding 5 s. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0192] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0193] The temperature depression schedules that would provide the formation of the desired marinite fraction in the above-described alloy from austenite regions with near-eutectoid chemical compositions, were first determined by calculations and then refined in experiments, as described in Example 2. The experiment showed that in order for ~100% marinite to form, cooling in air should be accomplished to a temperature ranging from 740 to 750°C.

[0194] After marinite was formed, pulsed cooling was accomplished by a single water pulse having a length of 0.2 s. This pulse length provided the maximal depression of the surface temperature and did not lead to the formation of

quenched structures in the desired structural state. Following this, pulsed cooling was stopped and changed to monotone cooling in molten saltpeter having a temperature of 443°C. The time of occurrence of the pearlite transformation in this method was about 4 s. Then, rapid cooling in water (quenching) was accomplished.

[0195] In this way, it was established that cooling in air should be accomplished within the temperature range of from 1005 to 745 C, then cooling should be accomplished by a single water pulse having a length of 0.2 s followed by cooling in molten saltpeter having a temperature of 443°C for at least 4 seconds, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C and cooled according to the specified trajectories. Cooling was accomplished using molten saltpeter having a temperature of 443°C, and technical water. As a result of this, the sorbitation time in the flowsheet was 4 s. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~1.00%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 6

[0196] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, for sorbitation times in the flowsheet not exceeding 3 s. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0197] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0198] The temperature depression schedules that would provide the formation of the desired marinite fraction in the above-described alloy from austenite regions with near-eutectoid chemical compositions, were determined in experiments as specified in Example 3. The experiment showed that in order for ~100% marinite to form, cooling in air should be accomplished to a temperature of 740 to 750°C.

[0199] After marinite was formed, the steel sample having the specified chemical composition was subjected to plastic strain with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at strain temperatures of $t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$, in degrees Celsius, is the Curie point of ferrite (in the case at hand, at a temperature of 745°C). Further cooling was accomplished in molten saltpeter having a temperature of 443°C. The time of occurrence of the pearlite transformation in this method was about 3 s. Then, rapid cooling in water (quenching) was accomplished.

[0200] In this way, it was established that cooling in air should be accomplished within the temperature range of from 1005 to 745 C, then plastic strain of the sample should be accomplished with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a temperature of 745°C, subsequent cooling in molten saltpeter having a temperature of 443°C should be accomplished for at least 3 seconds, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C, cooled in air to a temperature of 745°C, strained at this temperature, and cooled according to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C, and technical water. As a result of this, the sorbitation time in the flowsheet was 3 s. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 7

[0201] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, for sorbitation times in the flowsheet not exceeding 2 s. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0202] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0203] The schedules that would provide the formation of the desired marinite fraction of austenite regions having near-eutectoid chemical compositions in steel of the specified chemical composition, were determined in experiments as specified in Example 3. The experiment showed that in order for ~100% marinite to form, cooling in air should be accomplished to a temperature of 740 to 750°C.

[0204] After marinite was formed, a steel sample having the specified chemical composition was first subjected to plastic strain with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at strain temperatures of

$t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$, °C is the Curie point of ferrite (in the case at hand, at a temperature of 745°C), and then pulsed heating was accomplished by a single water pulse having a length of 0.2 s. This pulse length provided the maximal depression of the surface temperature and did not lead to the formation of quenched structures in the desired structural state. Following this, pulsed cooling was stopped and changed to monotone cooling in molten saltpeter having a temperature of 443°C. The time of occurrence of the pearlite transformation in this method was 1 s. Then, rapid cooling in water (quenching) was accomplished.

[0205] In this way it was established that cooling in air should be accomplished within the temperature range of from 1005 to 745 C, then plastic strain of the sample should be accomplished with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a temperature of 745°C, then cooling should be accomplished by a single water pulse having length of 0.2 s followed by cooling in molten saltpeter having a temperature of 443°C for 1 second, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 workpiece shaped as a rod was heated to a temperature higher than 1005°C, cooled in air to a temperature of 745°C, strained at this temperature, and cooled according to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C, and technical water. As a result of this, the sorbitation time in the flowsheet was 1 s. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 8

[0206] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% rutite. For this purpose, the workpiece was heated to an experimentally established temperature of 1005°C to form an austenite volume fraction of ~100%.

[0207] For the specified chemical composition, the maximal achievable fraction of austenite regions having near-eutectoid chemical compositions is ~100%.

[0208] The schedules that would provide the formation of the desired marinite fraction from austenite regions having near-eutectoid chemical compositions in the steel of the specified chemical composition, were first determined by calculations and then refined in experiments, as described in Example 2, but after heating the workpiece to the temperatures providing the formation of the desired austenite fraction therein, the workpiece was exposed to a magnetic field.

[0209] For this purpose, the workpiece heated to a temperature of 1005°C was placed into a coil, inside which a permanent magnetic field with strength of 0.5 T was created, and cooled in air. Exposure to magnetic field stimulated marinite formation. Cooling to a temperature of 800°C appeared sufficient for ~100 marinite to form.

[0210] Once the marinite formation conditions were known, the sample was quenched from the above-specified temperatures to provide rutite formation.

[0211] In this way, it was established that in the course of cooling in the temperature range of from 1005 to 800°C, it is necessary to expose the workpiece to a permanent magnetic field, and then cooling should be accomplished to room temperature at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel 85 grade workpiece shaped as a rod was heated to a temperature higher than 1005°C, cooled in air under exposure to a magnetic field having strength of 0.5 T, and rapidly cooled (quenched). Cooling was accomplished with technical water. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the rutite volume fraction was -100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 9

[0212] In the very general form, the second variant of the method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight was carried out in the following way.

[0213] First, the schedules that would provide marinite formation in the course of heating an alloy were recognized either experimentally or by calculations; then an article (workpiece) was heated so as to provide marinite formation. Following this, cooling was carried out according to the schedules that provided the formation of the desired structural state with the desired pearlite fraction in various degrees of dispersion and/or quenched structures.

[0214] When the experimental determination of the schedules to provide marinite formation was used in carrying out the method, formation conditions were first determined for each alloy.

[0215] For this purpose samples (which were round rods having diameters of 6.5 to 8 mm and lengths of 500 to 800 mm) were heated to temperatures ranging from 500 to 800°C in 15°C steps so as to provide exposure at these temperatures of from 0 to 600 s, and quenching was carried out.

[0216] In carrying out the aforementioned actions, temperature was recorded as a function of time from the readings

of a thermocouple caulked into the sample to a depth of one-half of the rod radius. Cooling curves were recorded using a known technique, for example, an analog input module for connecting ADAM 6018 thermocouples. Quenched samples were studied by known methods, in particular, diffraction methods (X-ray diffraction and neutron diffraction). The results of these studies served to conclude whether marinite existed in the sample; in so doing, the occurrence of marinite prior to quenching was judged from the occurrence of rutite in a sample quenched from fixed temperatures with various exposure times at these temperatures.

[0217] The above experiments served to determine the temperature and time frames of marinite formation in the alloy.

[0218] When calculations were used to determine the schedules that would provide marinite formation, the range of heating temperatures was set such that satisfied the conditions that

$$T_X < T < T_C^{loc},$$

wherein

T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations,

T_X is the eutectoid temperature for an alloy of the appropriate chemical composition; and

the exposure time t in seconds was set such that was required for the desired cementite fraction f_C to dissolve, derived from the equation

$$f_C = 1.05\ f_{C0} \exp(-kt^n),$$

wherein

f_{C0} is the dimensionless cementite fraction in the initial moment of time,

n is an exponent, 4 > n > 3,

k is the parameter that determines the cementite dissolution rate in the alloy of the appropriate chemical composition at temperature T, in s^{-n}.

[0219] The schedules for lowering temperature from marinite to the desired state which leads to the formation of the desired amount of pearlite in the desired structural state, were determined either experimentally (by quenching experimental samples followed by the determination of the structural state thereof), or by calculations.

[0220] When experiments were used to determine the schedules that would provide the formation of the desired amount of pearlite having the required degree of dispersion in the desired structural state, experimental samples were quenched from a temperature ranging between 745 and 400 C, and the structural state thereof was determined. For this purpose, experimental samples, shaped as cylinders having diameters of 8 mm and lengths of 500 mm with thermocouples caulked to a depth of 2 mm, were cooled from a temperature ranging between 745 and 500°C in air or in molten saltpeter having a temperature of 440°C, and quenching was carried out from various temperatures (lying in the range of from 730 to 440°C), which were determined from the readings of the thermocouple. The structural state of the quenched samples was determined by metallographic and diffraction techniques.

[0221] The experimental cooling curves obtained in this way were used to determine thermokinetic constants, which would allow cooling schedules to be calculated for arbitrary shapes of articles in various cooling media. The determination of the values of thermokinetic constants was carried out to reach the coincidence of the experimentally determined temperature versus time dependences with those obtained as a result of solving the set of equations comprising:

the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \vec{\nabla} \cdot \vec{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i,$$

wherein:

the operator $\vec{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1},

r is the radius-vector of the point to which the calculations refer,
p is the density, measured in kg/m^3,
q_i is the specific enthalpy of formation of the ith phase, measured in J/kg,
$f_i(r,t,T)$ is the dimensionless weight fraction of the ith phase in the vicinity of point r at moment of time t at temperature T,
$\overline{Q}(r,t)$ is the heat flow, measured in J/(m^2·s),
$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the samples;
the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT',$$

wherein

$C_p^i(T)$ is the specific heat capacity of the ith phase at a fixed pressure as a function of temperature, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\mathrm{r},\mathrm{t},\mathrm{T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau,$$

wherein
$M_{ik}(T,f_k(\tau),(t-\tau))$ is the function that defines the variation rate of the weight fraction f_i of the ith phase, determined for each phase transformation, and
then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

[0222] The data obtained in this way were used to embody the method for the heat treatment of articles made of iron-base alloys to produce articles having the desired structural state. For this purpose, a workpiece was first heated so as to provide the formation of the required marinite fraction. Then, the alloy article was cooled according to the schedules that provided the formation of the desired pearlite fraction having the required degree of dispersion and/or quenched structures.

[0223] In this way, as a result of selecting the marinite formation (occurrence) conditions and the appropriate schedules (trajectories) of subsequent cooling, it becomes possible to produce articles having the desired structural state with a pearlite content having the required degree of dispersion and/or quenched structures.

[0224] In particular embodiments of the method, for providing the production of articles with the desired structural state and the required mechanical properties and for reducing the times in the flowsheet for forming the pearlite structure, it is appropriate to subject the article or workpiece under treatment to plastic strain and to accomplish temperature depression by pulsed cooling with various lengths of pulses and pauses between them.

Example 10

[0225] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, within short sorbitation times in the flowsheet.

[0226] For this purpose, the workpiece was heated to a temperature that satisfied the conditions that

$$\mathrm{T_X} < \mathrm{T} < T_C^{loc},$$

wherein

T_C^{loc} (the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom) was determined by quantum-chemical calculations and was ~1100 K or 817°C, and TX (the temperature for steel of eutectoid composition) was 1010 K or 727°C.

[0227] At a heating temperature lying in the specified range, the workpiece was exposed for a period of time t required for 100% cementite to dissolve, this time being derived from the equation $1 = 1.05 \exp -6\times10^{-10} t^{3,5}$) and equal to ~3 min for the steel of the specified chemical composition.

[0228] In order to refine the marinite formation schedules determined by calculations, the following experiment was carried out. Samples (which were round rods having diameters of 6.5 to 8 mm and lengths of 500 to 800 mm) were heated to various temperatures lying in the range from 720 to 820°C (in 10°C steps), exposed at these temperatures for a period of 1 to 10 min in steps of 10 s, and quenched in water. Following this, the samples were studied by various known techniques. In the samples quenched from a heating temperature ranging between 730 and 760°C and exposed at these temperatures for a period ranging from 2 min 30 s to 3 min, some structural features intrinsic to rutite were observed, namely, BCT regions with abnormal low tetragonality (about 0.5%) and hardness of ~750 HV; therefore, within the range of the temperatures studied, marinite was formed in steel 85 samples provided that appropriate thermokinetic conditions were created. The experiment showed that in order for ~100% marinite to form, it is necessary that an exposure time of ~3 min be provided at a temperature of ~745°C.

[0229] Once the marinite formation conditions were known, the kinetics of formation of the desired final structural state was determined, as defined in Example 2.

[0230] In this way, it was established that it is necessary to heat a steel sample of the specified chemical composition to a temperature of 745°C and provide exposure at this temperature for ~3 min, and then cooling in molten saltpeter having a temperature of 443°C should be accomplished for a period of at least 10 seconds, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the workpiece made of steel grade 85 shaped as a rod was heated to the specified temperature, exposed at this temperature, and cooled according to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C, and technical water. As a result of this, the sorbitation time in the flowsheet was 10 s. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 11

[0231] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% A1, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired final structural state, namely, ~50% sorbite within short sorbitation times and ~50% quenched structures (rutite).

[0232] In order to experimentally determine the marinite formation schedules for steel of the specified chemical composition, samples were heated to various temperatures lying in the range from 700 to 800°C (in 10°C steps), exposed at these temperatures for a period ranging from of 1 to 10 min in steps of 10 s, and quenched in water. Following this, the samples were studied by various known techniques. In the samples quenched from heating temperatures ranging between 720 and 740°C and exposed at these temperatures for a period of time ranging from 2 min 30 s to 3 min, some structural features intrinsic to rutite were observed, namely, BCT regions having abnormal low tetragonality (about 0.5%) and hardness of ~750 HV; therefore, within the range of the temperatures studied, marinite was formed in steel 85 samples provided that appropriate thermokinetic conditions were created. The experiment showed that in order for ~100% marinite to form, it is necessary that an exposure time of ~2 min 50 s be provided at a temperature of ~730°C.

[0233] Once the marinite formation conditions were known, the kinetics of formation of the desired final structural state was determined experimentally as specified in Example 3. As a result of the experiment it was established that in order for ~50% pearlite (sorbite) to form, the residence time of samples in molten saltpeter should be 6 s and should be followed by quenching in water. In the volume of the sample that remained unconverted to sorbite (~50%), some structural features intrinsic to rutite were observed, namely, BCT regions with an abnormal low tetragonality (about 0.5%) and hardness of ~750 HV.

[0234] In this way, it was established that it is necessary to heat a steel sample of the specified chemical composition to a temperature of 730°C and provide exposure at this temperature for -2 min 50 s, then cooling should be accomplished in molten saltpeter having a temperature of 443°C for 6 seconds, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, which corresponded to quenching in water. Following this, the steel grade 85 workpiece shaped as a rod was heated to the specified temperature, exposed at this temperature, and cooled according

to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C, and technical water. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~50%, and the volume fraction of quenched structures (rutite) was ~50%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 12

[0235] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% rutite.

[0236] The schedules that would provide marinite formation in steel of the specified chemical composition, were first determined experimentally and then refined in experiments, as described in Example 10.

[0237] Once the marinite formation conditions were known, the sample was quenched from the heating temperature lying in the range of 745 to 750°C and exposed at this temperature for 2 min 45 s to thereby provide rutite formation,

[0238] In this way, it was established that it is necessary to heat a steel sample of the specified chemical composition to a temperature ranging from 745 to 750°C and provide exposure at this temperature for 2 min 45 s, and further cooling to room temperature should be carried out at rates of 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel grade 85 workpiece shaped as a rod was heated to the specified temperature, exposed at this temperature, and rapidly cooled (quenched). Cooling was accomplished with technical water. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the rutite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Example 13

[0239] The task was to obtain, for a rod made of steel grade 85 having a diameter of 8 mm and having the composition of 0.84% C, 0.59% Mn, 0.025% S, 0.24% Si, 0.012% P, 0.07% Cr, 0.08% Ni, 0.0075% Al, 0.05% Cu, and Fe and uncontrollable impurities to the balance, the desired structural state, namely, ~100% sorbite, for sorbitation times in the flowsheet not exceeding 2 s.

[0240] The schedules that would provide marinite formation in steel of the specified chemical composition were first determined experimentally as specified in Example 11. The experiment showed that in order for ~100% marinite to form, it is necessary that an exposure time of ~3 min be provided at a temperature of ~745°C.

[0241] After marinite was formed, a steel sample having the specified chemical composition was first subjected to plastic strain with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at strain temperatures of $t_{C\ ferr} \pm 50$°C, wherein $t_{C\ ferr}$, °C, is the Curie point of ferrite (in the case at hand, at a temperature of 745°C), and then pulsed heating was accomplished by a single water pulse having a length of 0.2 s. This pulse length provided the maximal lowering of the surface temperature and did not lead to the formation of quenched structures in the desired structural state. Following this, pulsed cooling was stopped and changed to monotone cooling in molten saltpeter having a temperature of 443°C. The time of occurrence of the pearlite transformation in this method was 1 s. Then, rapid cooling in water (quenching) was accomplished.

[0242] In this way, it was established that it is necessary to heat a steel sample of the specified chemical composition to a temperature of 745°C, provide exposure at this temperature for ~3 min, and subject the sample to plastic strain either during or after this exposure, with the relative strain in the surface layer of 23% and a strain rate of 0.2 s^{-1} at a temperature of 745°C, then cooling should be accomplished by a single water pulse having length of 0.2 s followed by cooling in molten saltpeter having a temperature of 443°C for 1 second, and further cooling to room temperature should be carried out at rates ranging from 90 to 110 deg/s, these rates corresponding to cooling in water. Following this, the steel grade 85 workpiece shaped as a rod was heated to the specified temperature, exposed at this temperature, strained, and cooled according to the specified trajectories. Cooling was accomplished with molten saltpeter having a temperature of 443°C, and technical water. As a result of this, the sorbitation time in the flowsheet was I s. Metallographic analysis and diffraction studies for the workpiece sample cooled to room temperature showed that the sorbite volume fraction was ~100%, which corresponded to the desired structural state. The required technical result was thereby attained.

Claims

1. A method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight, comprising: heating to provide the formation of austenite and subsequent cooling according to schedules that provide the formation of the desired structural state, wherein cooling is carried out according to schedules that provide the occurrence of austenite regions having near-eutectoid chemical compositions, followed by forming marinite therein,

and wherein the desired structural state is formed so as to obtain therein pearlite in various degrees of dispersion and/or quenched structures.

2. The method according to claim 1, wherein cooling is carried out according to schedules that provide the formation of the desired fraction of austenite regions having near-eutectoid chemical compositions, followed by forming therein the desired marinite fraction.

3. The method according to claim 2, wherein the schedules that provide the formation of the desired fraction of austenite regions having near-eutectoid chemical compositions, followed by forming therein the desired marinite fraction, are determined by calculations or experimentally.

4. The method according to claim 1, wherein the desired structural state is formed so as to obtain therein the desired pearlite fractions in various degrees of dispersion and/or quenched structures.

5. The method according to claim 3, wherein, when the schedules that provide the formation of marinite from austenite regions with a near-eutectoid chemical composition are determined by calculations, the temperature range of marinite formation is set such that satisfies the condition that

$$T_{TEX} < \mathrm{T} < T_C^{loc},$$

wherein T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations and
T_{TEX} is the temperature selected with account for technological limitations, and
the cooling rate is selected such that the cooling temperature versus time T(t) satisfies the condition that T(t) < □ (t), wherein the □ (t) function is given by the starting lines of the pearlite and bainite transformations in the thermokinetic diagram.

6. The method according to claim 3, wherein in the experimental determination of the schedules that provide the formation of marinite from austenite regions with a near-eutectoid chemical composition, samples are quenched from fixed temperatures with various exposure times at these temperatures, and the occurrence of marinite is judged from the occurrence of rutite in the quenched sample.

7. The method according to claim 6, wherein the occurrence of rutite is established by diffraction techniques.

8. The method according to any of claims 1 or 4, wherein the determination of the schedule for cooling from the prior-formed marinite to form the desired amount of pearlite in the desired structural state comprises quenching of experimental samples followed by the determination of the structural state thereof.

9. The method according to any of claims 1, 2, and 4, wherein the determination of the schedule for cooling from the prior-formed marinite to form the desired structural state, comprises: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample, determining the values of thermokinetic constants that provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising:

the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \bar{\nabla} \cdot \bar{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i,$$

wherein

the operator $\nabla = \frac{\partial}{\partial r}$ has a dimension of m^{-1},

r is the radius-vector of the point to which the calculations refer,

ρ is density, measured in kg/m^3,

q_i is specific enthalpy of formation of the ith phase, measured in J/kg,

$f_i(r,t,T)$ is the dimensionless weight fraction of the ith phase in the vicinity of point r at moment of time t at temperature T,

$Q(r,t)$ is the heat flow, measured in $J/(m^2 \cdot s)$,

$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample,

the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT',$$

wherein

$C_p^i(T)$ is the specific heat capacity *i*th phase at a fixed pressure as a function of temperature, measured in J/(kg·K), and

the kinetic equation

$$\frac{df_i(\mathrm{r,t,T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_{ik}(\tau), (t-\tau))d\tau ,$$

wherein

$M_{ik}(T,f_k(\tau), (t-\tau))$ is the function that defines the variation rate of the weight fraction f_i of the ith phase, determined for each phase transformation, and

then calculating the heat flow as a function of time across the surface of the alloy article, using the above equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

10. The method according to any of claims 1 and 4, wherein after marinite is formed, cooling is carried out according to the schedules that provide the formation of desired fractions of ferrite and iron carbide phases in the desired structural state either without formation of quenched structures or with formation of fractions thereof not exceeding the desired values.

11. The method according to any of claims 1 and 4, wherein after the desired pearlite fraction is formed, cooling alloy articles is carried out at rates sufficient for diffusion transformations to be inhibited.

12. The method according to any of claims 1, 10, and 11 wherein cooling is carried out in pulses.

13. The method according to claim 12, wherein cooling is carried out in pulses, these pulses alternating with pauses having lengths selected to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of an alloy article.

14. The method according to claim 12, wherein the length of each of the cooling pulses is selected such that they would not lead to the formation of quenched structures in the desired structural state.

15. The method according to claim 12, wherein cooling is carried out in pulses and wherein further one of the cooling pulses is selected so as to provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures in the desired structural state.

16. The method according to any of claims 1 and 4, wherein after forming the desired austenite fraction in the alloy that

is sufficient for the desired fractions of pearlite to form in the desired structural state having various degrees of dispersion and/or quenched structures, the temperature depression required for marinite to be formed is provided by cooling pulses.

17. The method according to any of claims 12 and 16, wherein after the fractions of ferrite and iron carbide phases are attained such that that would further provide the appearance of the desired structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

18. The method according to claim 1, wherein after alloy articles are heated to temperatures that provide the formation of the desired austenite fraction in the alloy, the alloy articles are subjected to plastic strain.

19. The method according to claim 18, wherein the plastic strain of alloy articles is carried out or finished at temperatures $t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$ is the Curie point of the ferrite, in degrees Celsius.

20. The method according to claim 1, wherein an alloy article is exposed to a permanent or pulsed magnetic field in the course of marinite formation

21. The method according to claim 1, wherein water or water-containing media are used for cooling.

22. A method for the heat treatment of articles made of iron-base alloys having carbon contents of up to 4.3% by weight, comprising: heating and subsequent cooling according to schedules that provide the formation of the desired structural state, wherein the heating is carried out according to schedules that provide the formation of marinite, and wherein the desired structural state is formed to obtain therein pearlite having various degrees of dispersion and/or quenched structures.

23. The method according to claim 22, wherein heating is carried out according to the schedules that provide the formation of the desired marinite fraction.

24. The method according to claim 23, wherein the schedules that provide the formation, of the desired marinite fraction, are determined by calculations or experimentally.

25. The method according to claim 22, wherein the desired structural state is formed so that to obtain therein desired pearlite fractions in various degrees of dispersion and/or quenched structures.

26. The method according to claim 24, wherein in the determination of the schedules that provide the formation of marinite by calculations, the temperature range of marinite formation is set such that satisfies the condition that

$$T_X < T < T_C^{loc},$$

wherein

T_C^{loc} is the local ferromagnetic ordering temperature in austenite in the vicinity of a carbon atom, determined by quantum-chemical calculations,

T_X is the eutectoid temperature for an alloy of the appropriate chemical composition, and

exposure time t in seconds, required for the required cementite fraction f_C, is derived from the equation

$$f_C = 1.05\ f_{C0} \exp(-kt^n),$$

wherein

f_{C0} is the dimensionless cementite fraction in the initial moment of time,

n is an exponent, $4 > n > 3$, and

k is the parameter that determines the cementite dissolution rate in the alloy of the appropriate chemical composition at temperature T, in s^{-n}.

27. The method according to claim 24, wherein in the experimental determination of the schedules that provide the formation of marinite from austenite regions with a near-eutectoid chemical composition, samples are quenched from fixed temperatures with various exposure times at these temperatures, and the occurrence of marinite is judged from the occurrence of rutite in the quenched sample.

28. The method according to claim 27, wherein the occurrence of rutite is established by diffraction techniques.

29. The method according to any of claims 22 and 25, wherein the determination of the cooling schedule from the prior-formed marinite to form the desired amount of pearlite in the desired structural state comprises quenching experimental samples followed by the determination of the structural state thereof.

30. The method according to any of claims 22, 23, and 25, wherein the determination of the schedule for cooling from the prior-formed marinite to form the desired structural state, comprises: measuring temperature at selected sites of the volume of a model alloy sample having a simple shape upon cooling at rates that lead to the formation of the required structural state in the alloy sample; determining the values of thermokinetic constants that provide (for known heat flows on the sample surface) the coincidence of the temperature versus time dependence obtained in the course of the model experiment with the one obtained as a result of solving the set of equations comprising the heat conductivity equation:

the heat conductivity equation

$$\frac{dH(r,t,T)}{dt} = \bar{\nabla} \cdot \bar{Q}(r,t) + \rho \sum_i \frac{df_i(r,t,T)}{dt} q_i ,$$

wherein

the operator $\bar{\nabla} = \frac{\partial}{\partial r}$ has a dimension of m^{-1},

r is the radius-vector of the point to which the calculations refer,
p is density, measured in kg/m^3,
q_i is the specific enthalpy of formation of the ith phase, measured in J/kg,
$f_i(r,t,T)$ is the dimensionless weight fraction of the ith phase in the vicinity of point r at moment of time t at temperature T,
$\bar{Q}(r,t)$ is the heat flow, measured in $J/(m^2 \cdot s)$,
$H(r,t,T)$ is the enthalpy distribution, measured in J/m^3, over the volume of the sample;
the energy conservation equation

$$H(r,t,T) = \rho \sum_i f_i(r,t,T) \int_0^T C_p^i(T')dT' ,$$

wherein $C_p^i(T)$ (T) is the specific heat capacity of the ith phase as a function of temperature at a fixed pressure, measured in J/(kg·K); and
the kinetic equation

$$\frac{df_i(\mathrm{r,t,T})}{dt} = \sum_{k \neq i} \int_0^t M_{ik}(T, f_k(\tau), (t-\tau))d\tau ,$$

wherein
$M_{ik}(T,f_k(\tau),(t-\tau))$ is the function that defines the variation rate of the weight fraction of the ith phase, determined

for each phase transformation, and
calculating the heat flow as a function of time across the surface of an alloy article, using said equations and the thermokinetic constants thus found, so as to provide the trajectory of temperature variation with time that would lead to the formation of the desired structural state.

31. The method according to any of claims 22 and 25, wherein after marinite is formed, cooling is carried out according to the schedules that provide the formation of desired fractions of ferrite and iron carbide phases in the desired structural state without formation of quenched structures or with formation of fractions thereof not exceeding the desired values.

32. The method according to any of claims 22 and 25, wherein after the desired pearlite fraction is formed, alloy articles are cooled at rates sufficient for diffusion transformations to be inhibited.

33. The method according to any of claims 22, 31, and 32, wherein cooling is carried out in pulses.

34. The method according to claims 33, wherein cooling is carried out by pulses which are alternated with pauses having lengths selected so as to be sufficient for providing the desired reduction of the difference between the maximal and minimal values of temperature across the cross-section of an alloy article.

35. The method according to claim 33, wherein the length of each of the cooling pulses is selected such that they would not lead to the formation of quenched structures in the desired structural state.

36. The method according to claim 22, wherein cooling is carried out in pulses, wherein one of the cooling pulses is selected so as to provide a maximal depression of the surface temperature of alloy articles without formation of quenched structures in the desired structural state.

37. The method according to claim 33, wherein after attaining the fractions of ferrite and iron carbide phases that would further provide the appearance of the desired structural state, pulsed cooling is stopped and changed to monotone cooling and/or isothermal exposure.

38. The method according to claim 22, wherein alloy articles are subjected to plastic strain during heating, either prior to or in the course of marinite formation.

39. The method according to claim 22, wherein alloy articles are subjected to plastic strain after marinite formation.

40. The method according to any of claims 38 and 39, wherein the plastic strain of alloy articles is performed or finished at temperatures of $t_{C\ ferr} \pm 50°C$, wherein $t_{C\ ferr}$ is the Curie point of the ferrite, °C.

41. The method according to claim 22, wherein water or water-containing media are used for cooling.

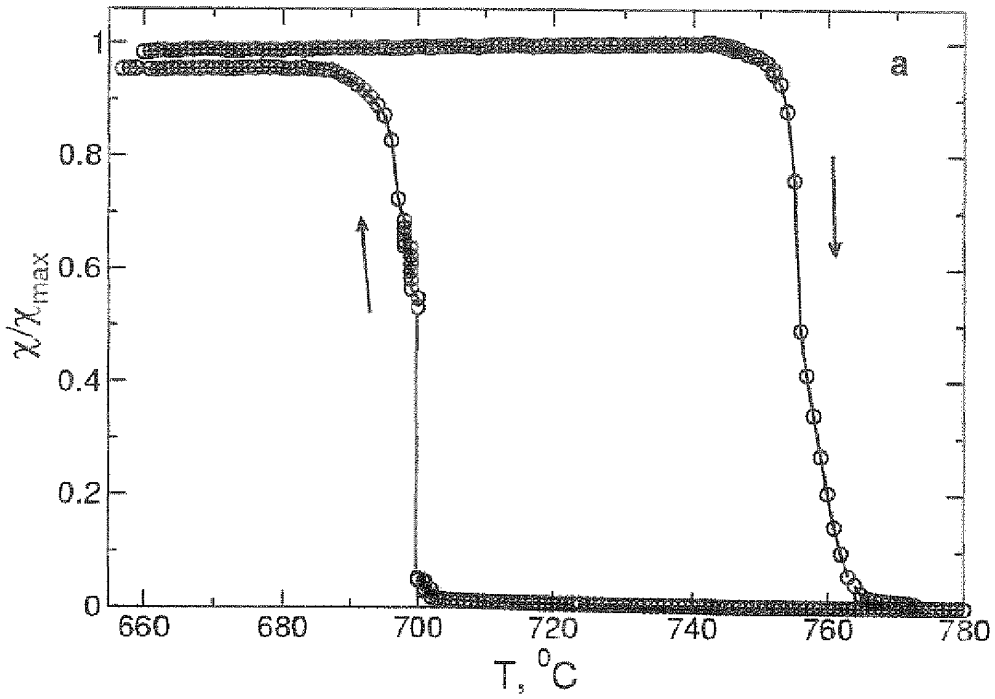

a
1
0.8
0.6
0.4
0.2
0
χ/χmax
660
680
700
720
740
760
780
T, °C

Fig. 1

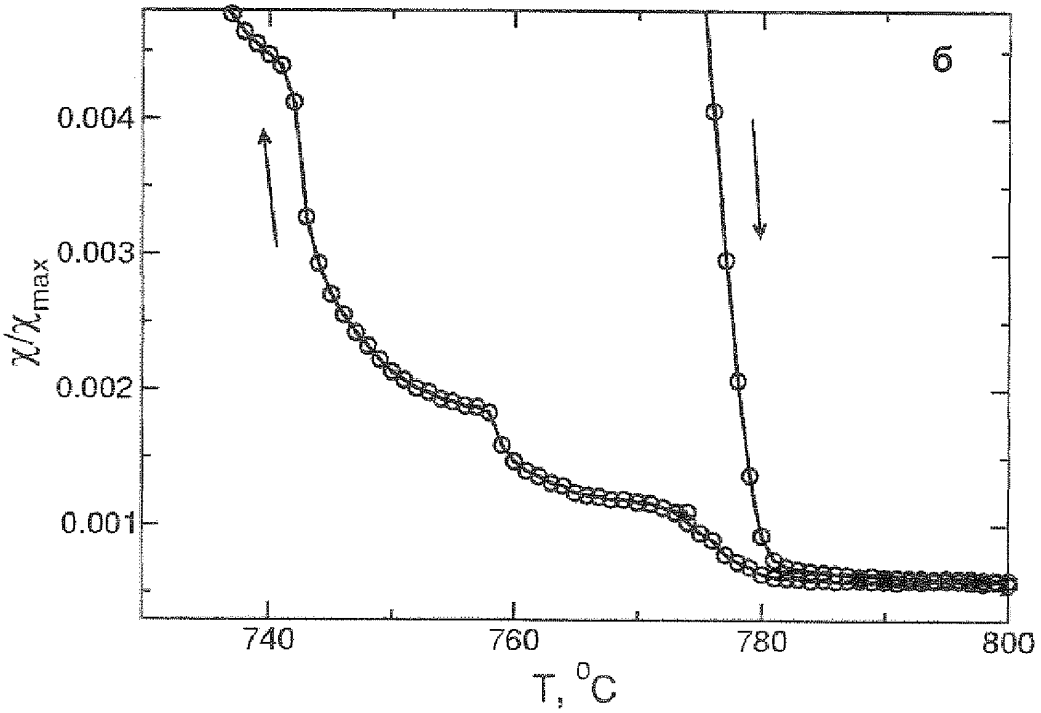

б
0.004
0.003
0.002
0.001
χ/χmax
740
760
780
800
T, °C

Fig. 2

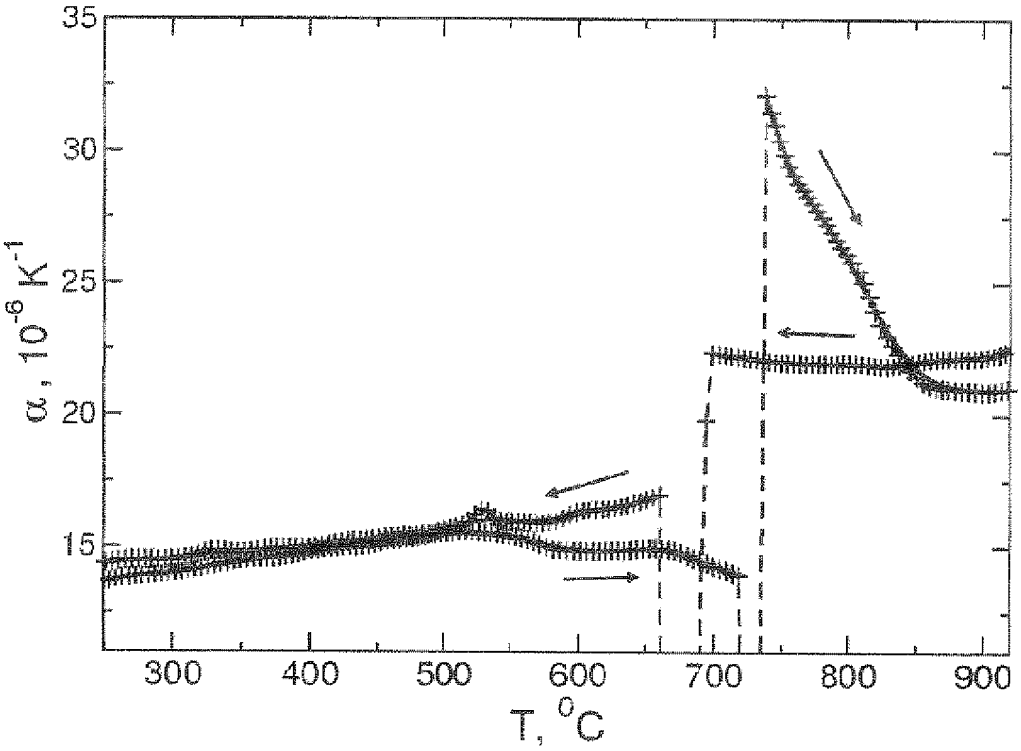

35
30
25
20
15
α, 10^-6 K^-1
300
400
500
600
700
800
900
T, °C

Fig. 3

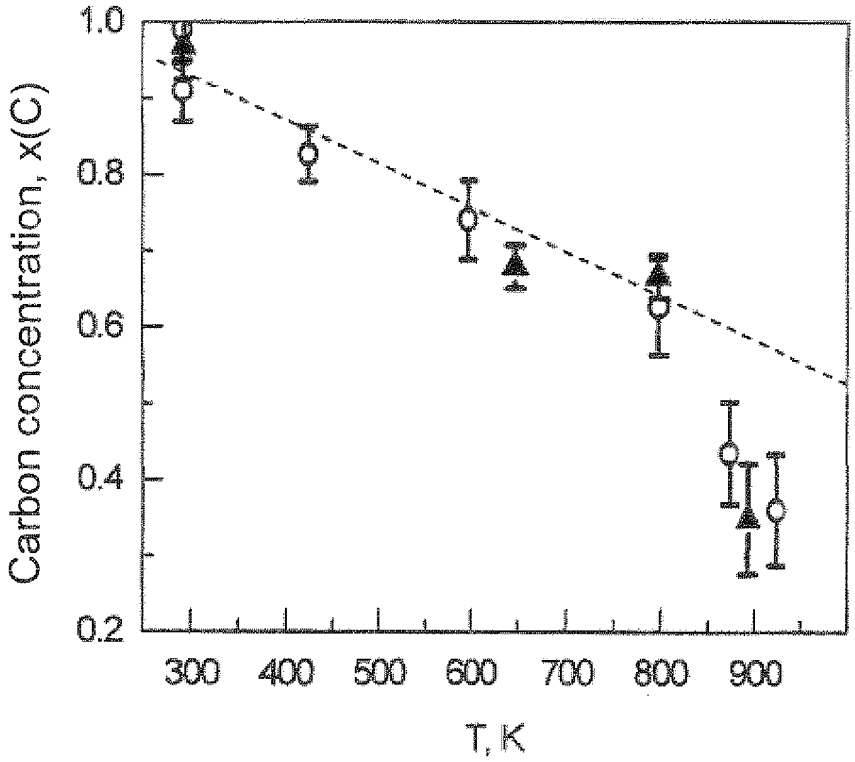

1.0
0.8
0.6
0.4
0.2
Carbon concentration, x(C)
300
400
500
600
700
800
900
T, K

Fig. 4

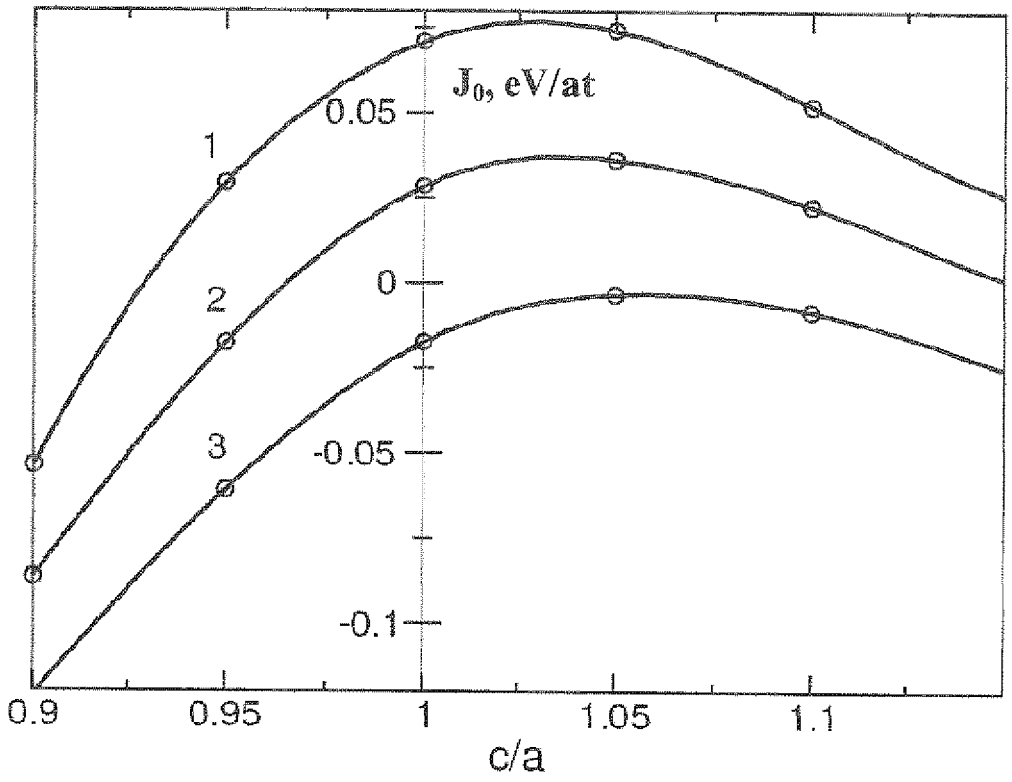


Fig. 5

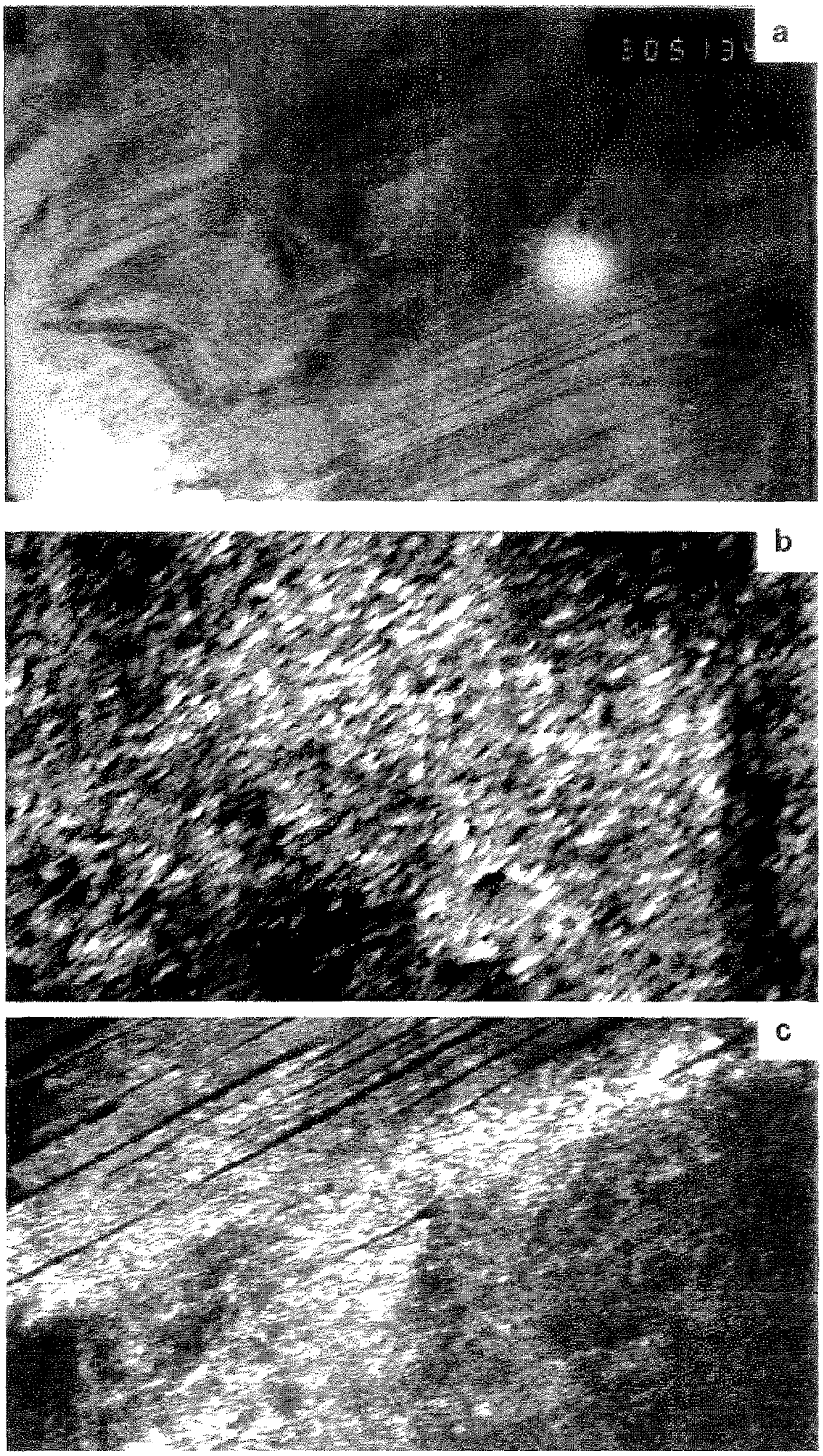


Fig. 6

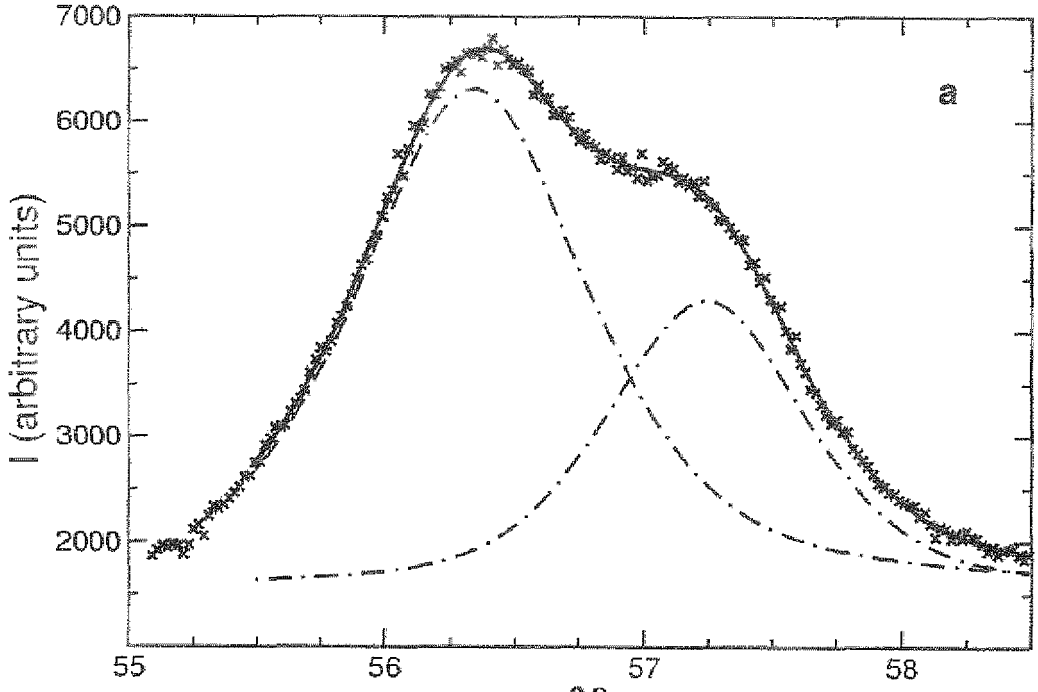

7000
6000
5000
4000
3000
2000
I (arbitrary units)
55
56
57
58
2θ
a

Fig. 7

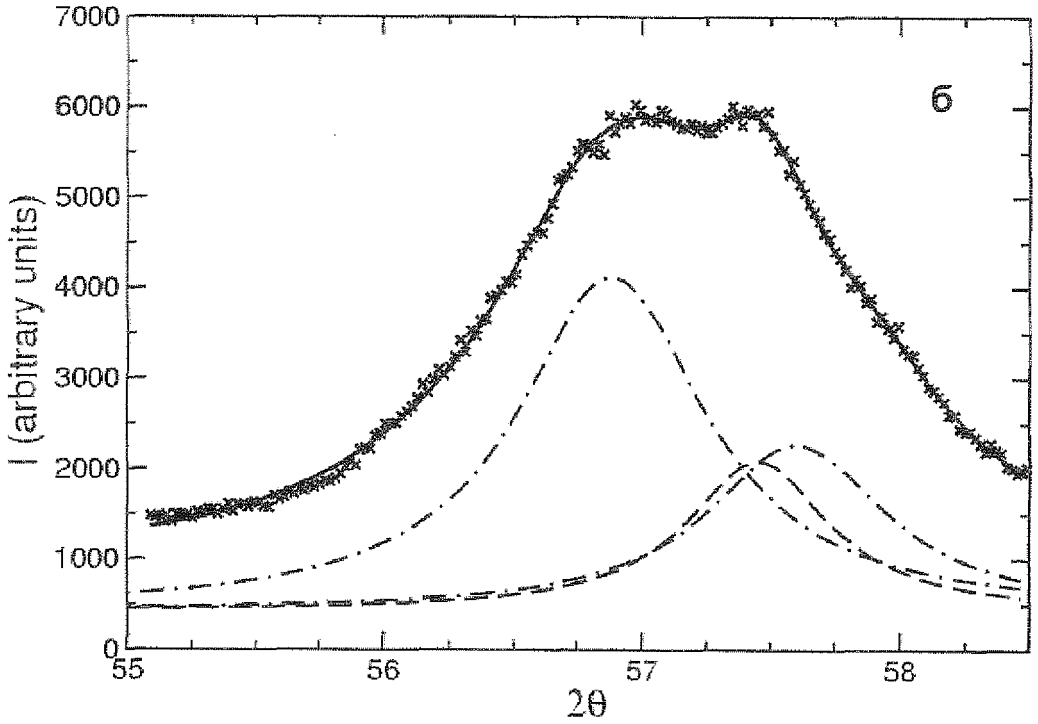
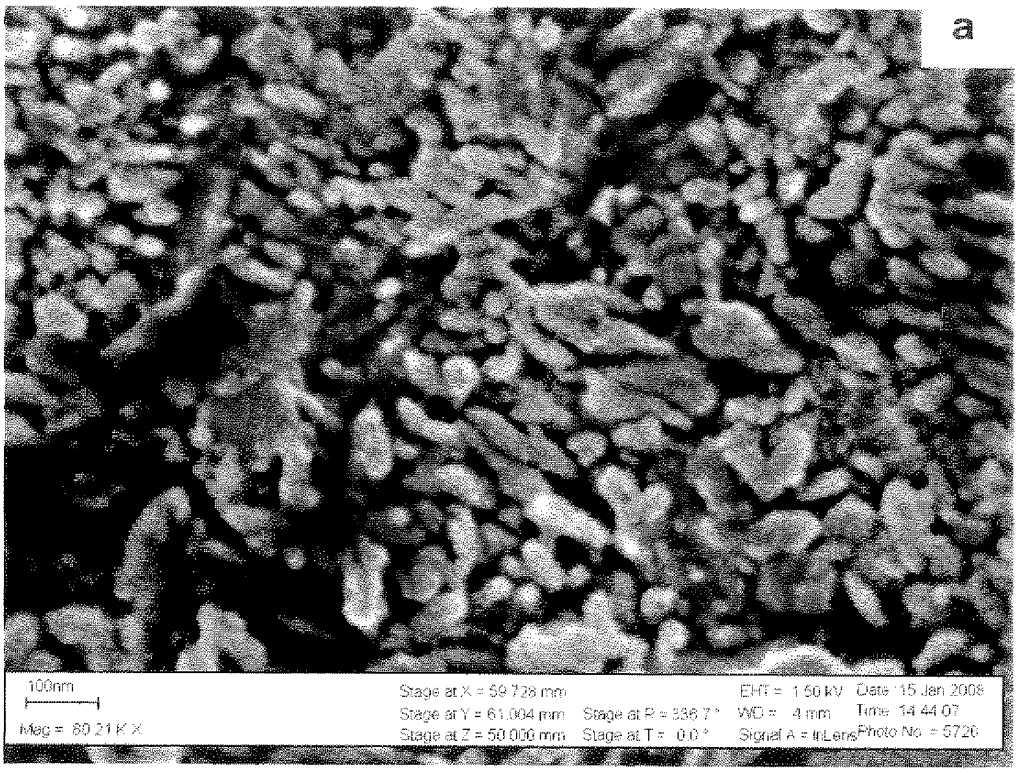

7000
6000
5000
4000
3000
2000
1000
0
I (arbitrary units)
55
56
57
58
2θ
б

Fig. 8


a
100nm
Mag = 80.21 K X
Stage at X = 59.728 mm
Stage at Y = 61.004 mm
Stage at Z = 50.000 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 1.50 kV
WD = 4 mm
Signal A = InLens
Date 15 Jan 2008
Time 14:44:07
Photo No. = 5726

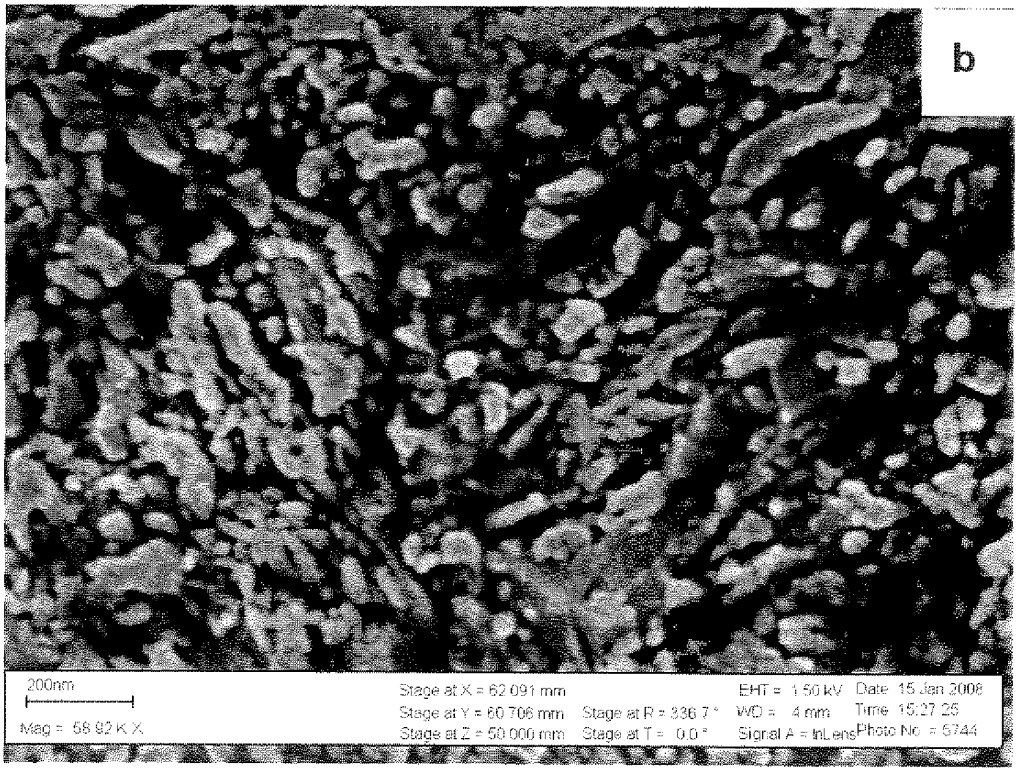
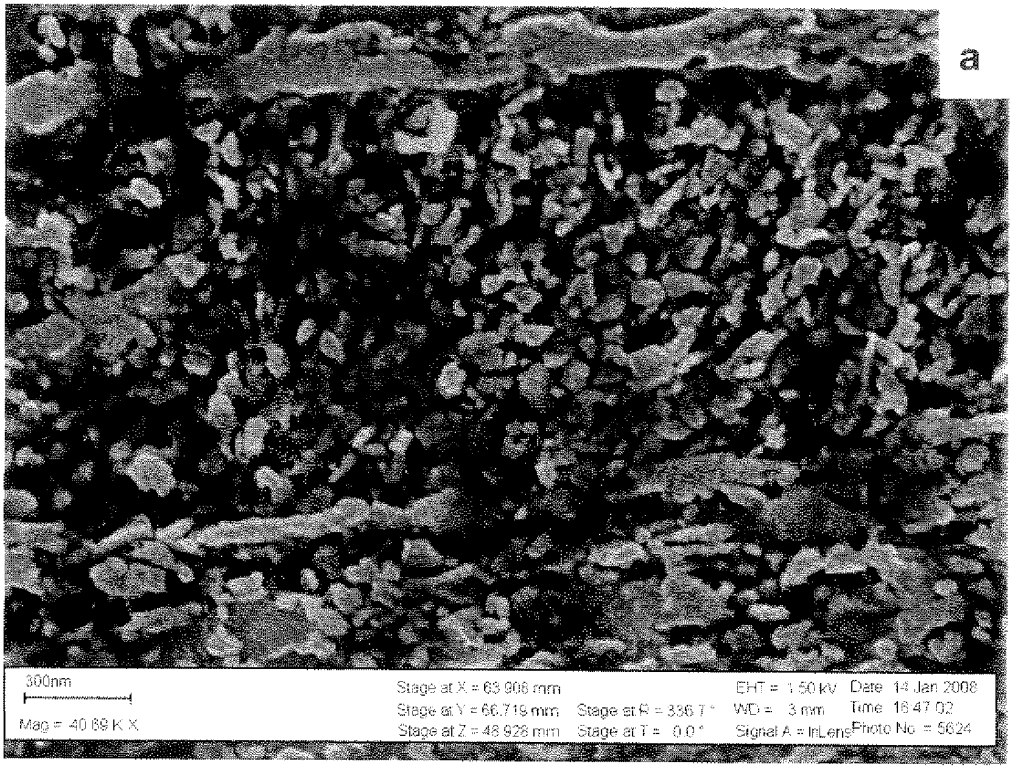

b
200nm
Mag = 58.92 K X
Stage at X = 62.091 mm
Stage at Y = 60.706 mm
Stage at Z = 50.000 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 1.50 kV
WD = 4 mm
Signal A = InLens
Date 15 Jan 2008
Time 15:27:25
Photo No. = 6744

Fig. 9


a
300nm
Mag = 40.89 K X
Stage at X = 63.906 mm
Stage at Y = 66.719 mm
Stage at Z = 48.928 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 1.50 kV
WD = 3 mm
Signal A = InLens
Date 14 Jan 2008
Time 16:47:02
Photo No = 5624

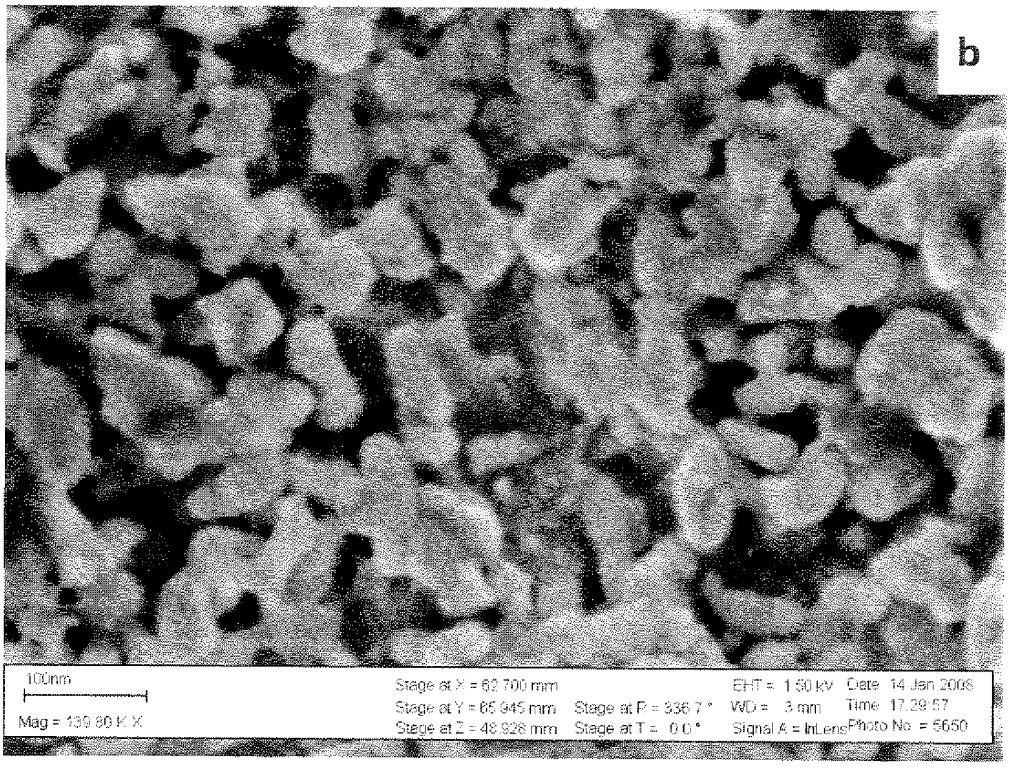

b
100nm
Mag = 139.80 K X
Stage at X = 62.700 mm
Stage at Y = 65.945 mm
Stage at Z = 48.928 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 1.50 kV
WD = 3 mm
Signal A = InLens
Date 14 Jan 2008
Time 17:29:57
Photo No = 5650

Fig. 10

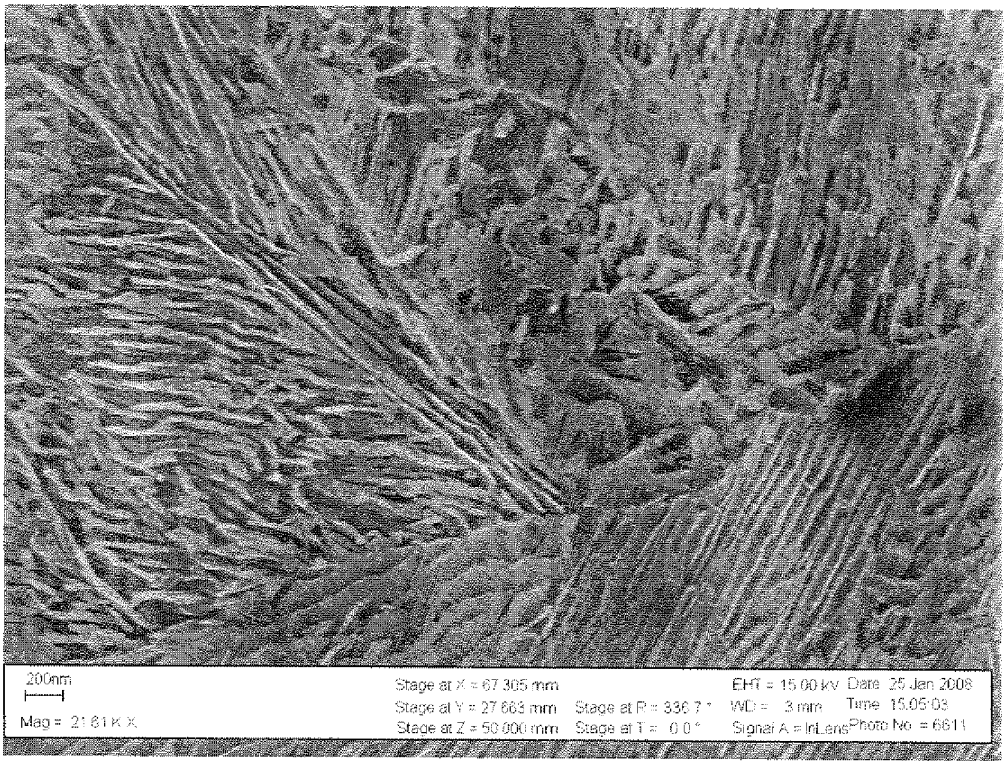

200nm
Mag = 21.61 K X
Stage at X = 67.305 mm
Stage at Y = 27.663 mm
Stage at Z = 50.000 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 15.00 kV
WD = 3 mm
Signal A = InLens
Date :25 Jan 2008
Time :15:05:03
Photo No. = 6611

Fig. 11

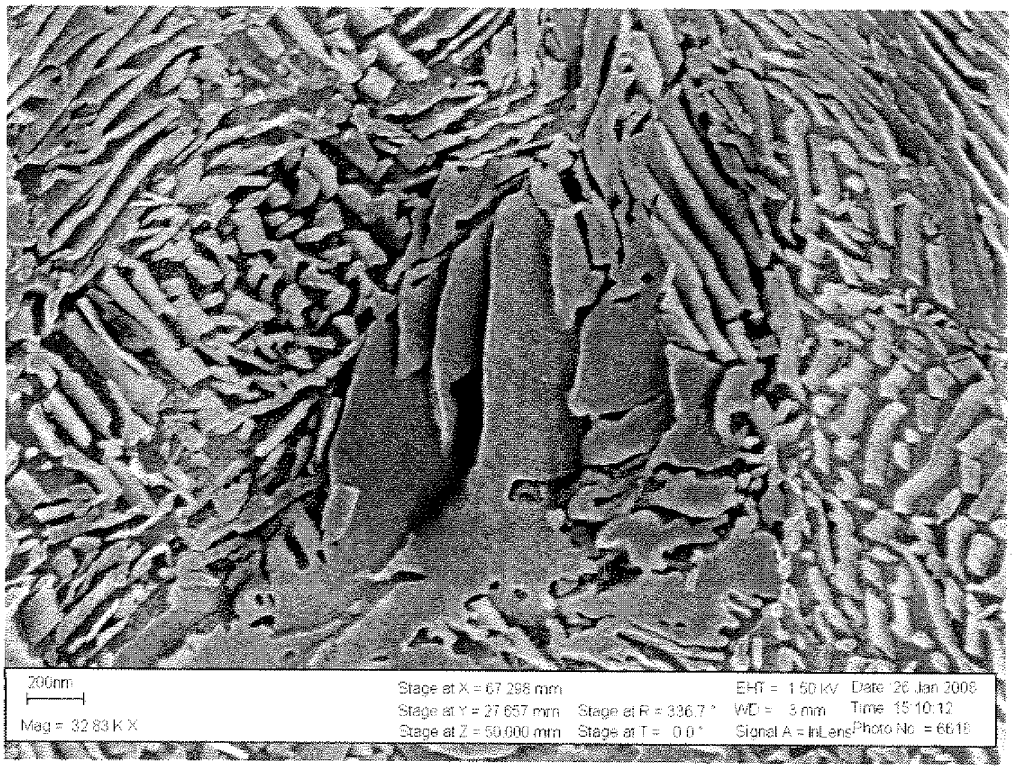

200nm
Mag = 32.83 K X
Stage at X = 67.298 mm
Stage at Y = 27.657 mm
Stage at Z = 50.000 mm
Stage at R = 336.7 °
Stage at T = 0.0 °
EHT = 1.50 kV
WD = 3 mm
Signal A = InLens
Date :26 Jan 2008
Time :15:10:12
Photo No. = 6618

Fig. 12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 2011/000595

A. CLASSIFICATION OF SUBJECT MATTER

C21D 1/19 *(2006.01)*
C21D 6/00 *(2006.01)*
C21D 8/00 *(2006.01)*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21D 1/00-1/25, 1/78, 6/00-6/02, 1/55-1/613, 8/00, 9/00-9/52, G01N 33/00, 33/20

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Esp@senet, PAY, PatSearch

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	**RU 2348701 C2 (GOSUDARSTVENNOE OBRAZOVATELNOE UCHREZHDENIE VYSSHEGO PROFESSIONALNOGO OBRAZOVANIA "ALTAISKY GOSUDARSTVENNY TEKHNICHESKY UNIVERSITET IM. I. I. POLZUNOVA" (ALTGTU)) 10.03.2009, claims**	1-41
A	**SU 834154 A (DONETSKY POLITEKHHNICHESKY INSTITUT) 06.06.1981 p. 2, col. 4, claims**	1-41
A	**RU 2186859 C2 (KOMSOMOLSKOE-NA-AMURE AVIATSIONNOE PROIZVODSTVENNOE OBEDNIENIE) 10.08.2002, claims**	1-41
A	**RU 2201460 C2 (RESPUBLIKANSKOE UNITARNOE PREDPRIATIE "MINSKY TRAKTORNY ZAVOD") 27.03.2003**	1-41
A	JP 57134514 A (KAWASAKI STEEL CO) 19.08.1982, **abstract**	1-41

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 Nov 2011 (15.11.2011)	**24 Nov 2011 (24.11.2011)**
Name and mailing address of the ISA/ **RU** Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- RU 2044779 **[0003]**
- RU 2272080 **[0006]**
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