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Rationale for signs of transformation in iron near 200°C

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The analysis of the literature data on the properties of iron and steels carried out in this work indicates numerous anomalies of physical and mechanical properties near a temperature of ≈200°C. Based on the thermal effect, changes in magnetic properties, anomalies of shear modulus, oxidizability, heat capacity, diffusion, Lorentz number, the transformation in iron at ≈200°C is justified, which may be the cause of a decrease in the magnetization of perlite, sorbitol and martensite, as well as the performance of high-hard low-tempered steel having almost the same hardness after quenching. The study was carried out on samples of practically pure iron (0.008% C). The experiment (metallographic examination, X-ray diffraction analysis, metal deformation resistance (Gleeble-3800 installation) was carried out every 20–40°C. The experimental results indicate significant changes in the structure, as well as extreme values of the mechanical properties of iron (0.008% C) and steels near a temperature of ≈200°C, which makes it possible to declare the transformation in iron and its derivatives — steels at this temperature. Recognition of the transformation at this temperature allows us to explain: the reason for the decrease in magnetization of perlite, sorbitol and martensite, the maxima of impact strength and hardness of iron, the disappearance of the yield point on the tensile curve of riveted steel after aging, the nature of irreversible tempering fragility (the nature of the latter, as well as reversible is still debatable), etc.

Keywords: iron, steel, magnetic properties, X-ray structural analysis, microstructure.

1. Introduction

The aim of the work is to substantiate the connection of extremes on the curves of the physico-mechanical properties of iron with the transformation in it at ≈200°C, which can also determine anomalies in the mechanical properties of iron derivatives — steels.

The term "Transformation" is explained by the example of Fe. Both transformations at A_2 (so-called magnetic) and A_3 (so-called polymorphic) are thermal, accompanied by thermal effects and anomalies of properties: peak heat capacity, acceleration of diffusion, bending of the thermopower curve — at A_2; compression during heating, minimum thermopower, arch-fragility on impact, peak creep — at A_3. Therefore, the term "transformation" refers to a change in the interaction between Fe atoms, which generates anomalies in the properties of iron — derived steels.

The methodology is based on the following judgments: B.G. Livshits: "In the study of phase equilibrium, you can use any property"; A.A. Vertman, A.M. Samarin: "As structurally sensitive properties, you can choose any of about 50 properties currently used in physico-chemical analysis"; A.A. Bochvar: "As a measurable physical property, you can take hardness, electrical conductivity, density, coefficient of linear expansion, etc."

Magnetic analysis is used to study low tempering (≈200°C), the results of which G.V. Kurdyumov recommends "approaching with caution" [1].

A sharp and significant decrease in the magnetization of I martensite at ≈160–220°C (Fig. 1, cr. 1) V.D. Sadovsky (1986) calls "some" [2], and A.M. Belous et al. [3] it is associated with the release of an unknown non-magnetic or low-magnetic phase [4,5,6]. The authors [7,8] associate the decrease in the I of the tempering products at 275–350°C after quenching with the Curie point of cementite, which is hardly true, since the I of isolated cementite, according to B.G. Livshits [9] grows to 180°C (Fig. 1, cr. 2). The same decrease in I of isothermal tempering products at 250°C of steel U12A (Fig. S1, supplementary material), quenching of steels with a carbon content of 0.5, 0.84, 1.0 and 1.23% (Fig. S2 a, supplementary material), annealing, quenching and tempering at 570°C with cold deformation by 12–70% and without it, which excludes the influence of the structure

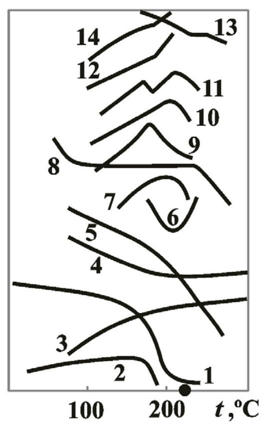


Fig. 1. Schematized dependence of the properties of iron and steel on the heating or tempering temperature. Explanations in the text. ● — thermal effect of iron (Roberts-Austen). The effects of one type are represented by one curve in Fig. 6.

(Fig. S2 b, supplementary material) [3]. All *I-t* curves are called "of the same type" [3]. Therefore, they are all depicted in Fig. 1 by one curve 1. Let us turn to the properties of iron-based steels.

The most expressive effect — the bending of the curve of the temperature (0 – 1100°C) dependence of the Lorentz number — is at ≈200°C (Fig. 1, cr. 3) (R. Powell) [10]. This is confirmed by a sharp decrease in the residual induction of perlite and sorbitol at 180°C, which R. Bozort [11] called "unexpected". On the curve of coercive force, maximum induction and hysteresis bending losses at ≈200°C (Fig. 1, cr. 4) [9]. "In the region of 200°C, the nature of the course of the curve of the "diffusion coefficient" changes." (Fig. S3 a, supplementary material) (The authors [12] state someone else's version about "traps" (structural defects) that are unlikely to disappear above 200°C).

The same fracture on the hydrogen solubility curve in α-iron (Fig. S3 b, supplementary material) has been established, but not commented on by the authors of the work [13, p. 8, see experimental points].

"Unexpectedly" [14] the yield point on the tensile curve of riveted steel with 0.2% C (97% ferrite) (Fig. 1, cr. 6, Fig. S4 a, supplementary material) disappears after aging (20 – 650°C) only at 200°C, which, according to B. G. Livshits, is a sign of the absence of deformation aging in Fe.

The peak of Kester's internal friction, "concerning the nature" of which "there are different opinions", almost does not depend on the carbon content (0.7 – 1.25%) and residual austenite (Fig. 1, cr. 7) [3]. It is located at 200°C, i. e. near the characteristic Debye temperature (≈150°C) calculated from the heat capacity. Darken, who destroyed the 200-degree peak of the "hot" hardness (Fig. 1, cr. 7) of iron by annealing at 910°C (54 hours) in hydrogen [11,12,15], did not take into account that it, being in the melt, and then evaporated during hot conversion, leaves a "trace" in reduced plasticity at 20°C [16,17,18]. In the Cu-Fe pair, the thermopower curve "has a turning point at ≈250°C" (Fig. 1, cr. 7, Fig. S4 b, supplementary material). By analogy with the thermal EMF curve of a Fe-Ni pair having a bend at the Curie point of nickel (360°C) [9] (Fig. S4 b, supplementary material), it can be assumed that the transformation into Fe at ≈200°C.

Roberts-Austen showed a distinct thermal effect in Fe not only at A_3, A_1, ≈620, ≈450, but also at ≈220°C (Fig. 1). "The law of growth of the oxide film on Fe is logarithmic (200°C) and becomes parabolic at temperatures exceeding this value." "At a temperature of 200°C, the oxidation mechanism apparently undergoes profound changes" [19, 20]. At ≈230°C, there is a significant bending of the shear modulus (Fig. 1, cr. 8) of mild steel [21, 22]. The second bend at ≈110°C can also be associated with the transformation [23], because in hardened (e. Gudremon) or riveted steels after tempering at 100°C maximum hardness.

"Above 500 K (+223°C), the heat capacity also increases sharply…" [9] (Fig. 1, cr. 7). On the curves of thermal conductivity and heat content [9] of iron bends at ≈200°C (Fig. 1, cr. 13, Fig. 1, cr. 12).

Apparently, these changes in the properties of iron are continued in bends at ≈200°C: elongation during heating of steel with 0.25% C [9] and steel 70, after warm drawing at 300°C [9, 25]; the coercive force curve after tempering at 200°C of hardened steel with ≈1.0% C [26]; in the minimum δ and ψ at ≈200°C of normalized and thermally improved steel with 0.47% C, despite a decrease in σ_S [9]; in the maximum heat capacity of steel with 1.23%C after tempering at 250°C [27]; in the bending of the fundamental dilatogram of hardened steel at ≈180°C (Fig. 1, cr. 14) (Hahnemann and Treger) [9]; in eliminating the brittleness of equidistant hardened low-tempered steel, which, with an increase in t_{temp} >≈250°C, is again subject to irreversible tempering brittleness, the nature of which has ceased to be discussed.

According to V. G. Glushchenko [35], the degree of localization of valence electrons of iron at ≈20°C is 39% [35]. (When "calculating the degree of localization, data from X-ray analysis, results of interpretation of X-ray emission and adsorption bands, information on electrophysical and magnetic properties, electron-positron annihilation and characteristic electron energy losses are used" [35].

The localization of electrons creates a covalent directional bond that hinders plastic deformation, i. e. energy absorption during the destruction of not only iron, but also other d-transition metals.

"Static bending tests are the softest, and impact bending tests of a sample with an incision are the toughest type of tests. Consequently, impact bending tests are more sensitive to the occurrence of rigid directional (covalent) bonds in the metal… and the values of T_X (brittleness temperature, K) will approach 0.225 T_{melt}" [36].

For iron, this temperature is ≈130°C (407 K). This temperature certainly corresponds to a sharp increase in the impact strength of iron, which reaches an absolute maximum at ≈200°C [30 – 34, 36], which may indicate the destruction of the covalent bond.

The maximum is reached after tempering at 200°C not only by the impact strength associated with the movement of dislocations, but also by the critical stress during stress corrosion not associated with this movement [37, 38, 39], since the fracture is macro-brittle.

Electron delocalization when heated above 0.225 T_{melt} cannot explain the brittleness of iron above ≈250°C and the irreversible tempering brittleness (>≈200°C) of hardened steel. The nature of the latter, as well as reversible, is still debatable. But the concept of V. G. Glushchenko is attractive by involving an electronic structure to explain the properties.

2. Materials and methods of research

The study was carried out on samples of practically pure iron with a content of 0.008% C. The samples were quenched in water at temperatures of 1050°C and 1220°C. Then the samples were released (1 hour) in the temperature range of 100 – 350°C every 20 – 40°C (heat treatment was carried out in salt baths of JSC "Obukhov Plant").

After carrying out heat treatment on a general-purpose diffractometer (DRONE-2) according to the standard procedure, X-ray diffraction analysis was carried out on cubic samples with dimensions of 10 × 10 × 10 mm.

The microstructure of the samples after heat treatment was studied using an optical microscope "Watering can" (etching was carried out in 4% HNO_3 in alcohol, the holding time of all samples was 20 seconds).

The metal deformation resistance of the samples (∅10×15 mm) at half the height was determined on the Greeble-3800 installation: heating to the deformation temperature (80–520°C) was carried out by passing an electric current, with a heating rate of 5°C/s, every 20°C. Then deformation was carried out at a rate of 0.5 s^{-1}, followed by 1 min exposure and free cooling due to heat removal into water-cooled copper grips.

3. Results of the experiment

According to the averaged data of X-ray diffraction analysis, graphs of the dependence of the width of X-ray lines (110), (220) and the lattice parameter on the tempering temperature after quenching from 1050 and 1220°C were plotted (Fig. 2–4).

Figure 2 in two series of the experiment observed a maximum of the X-ray line broadening in the (110) after tempering at 210°C (quenching from 1050 (Fig. 2a) and from 1220°C (Fig. 2b)). The error of the experiment was 1.5%.

Regardless of the quenching temperature (1050°C or 1220°C), according to the results of two series of experiments at 180°C tempering, a distinct maximum of the broadening of the line B (220) and the crystal lattice parameter (*a*) is recorded (Fig. 3 and 4).

These results indicate significant changes in the fine structure of iron (0.008% C) near 200°C. As is known, at this temperature, not only self-magnetization of steel occurs [15], a decrease in the magnetization of martensite and ferrite-cementite mixture (annealed and riveted) [3], a sharp decrease in the rate of reduction of coercive force [3].

Metallographic examination of iron grinds (0.008% C) after quenching from 1050°C into water and tempering from 160 to 240°C (2 hours) every 20°C showed that after tempering 200°C, there is an increased etchability of grain boundaries (exposure for all samples in 4% HNO_3 alcohol was 20 seconds) (Fig. 5). We believe that the enhanced etchability of grain boundaries (Fig. 5c,e), observed after tempering at 200°C, may be a consequence of the formation of a carbide phase along the grain boundaries, which indicates an increase in

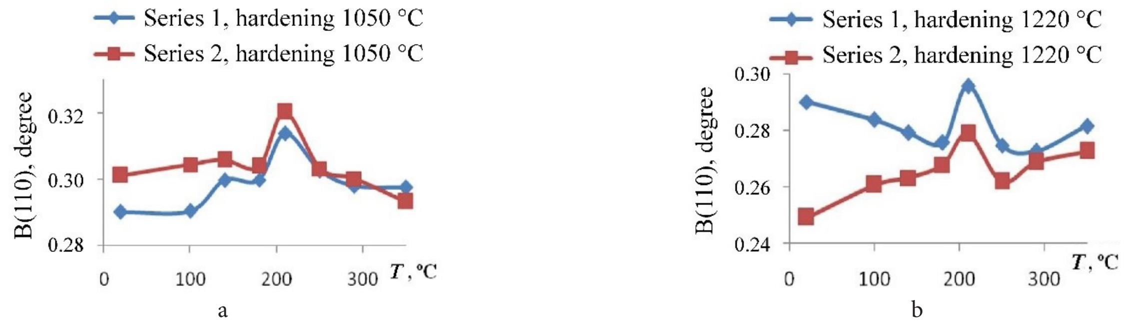


Fig. 2. (Color online) Dependence of the averaged broadening of the X-ray line (110) on the tempering temperature of iron after quenching from 1050°C (a) and 1220°C (b) according to two series of experiments.

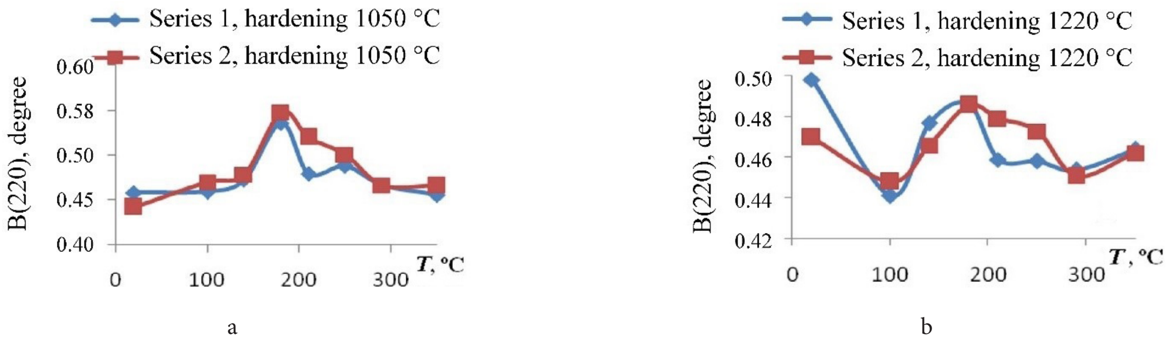


Fig. 3. (Color onine) Dependence of the averaged broadening of the X-ray line (220) on the tempering temperature of iron after quenching from 1050°C (a) and 1220°C (b) according to two series of experiments.

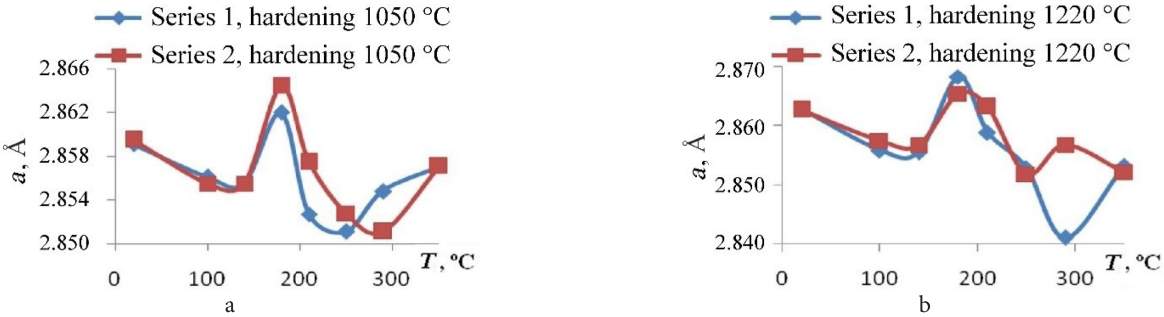
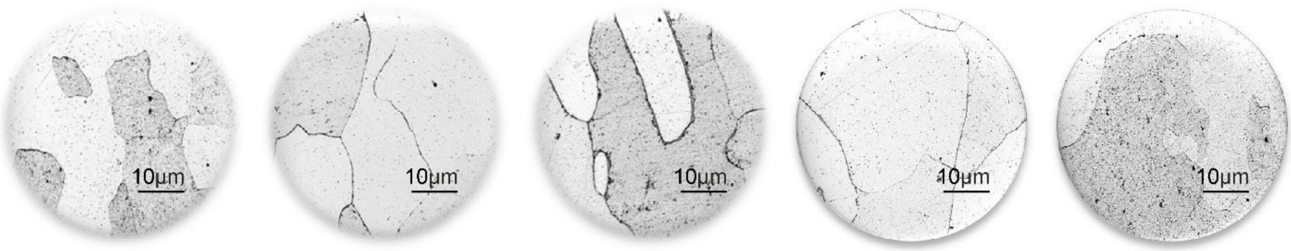


Fig. 4. (Color online) Dependence of the averaged lattice parameter (a) on the tempering temperature of iron after quenching from 1050°C (a) and 1220°C (b) according to two series of experiments.



a b c d e

Fig. 5. Microstructure of iron (0.008% C) after quenching from 1050°C (water) and tempering at 160°C (a), 180°C (b), 200°C (c), 220°C (d) and 240°C (e), ×500.

the diffusion mobility of atoms at a temperature of ≈200°C [40]. Such acceleration of diffusion is possible in cases when the transformation occurs [41], for example, near the Curie point.

Confirmation of the transformation in the fine structure of iron was the hot metal deformation (80 – 520°C) of iron samples with 0.008% C in this work. The maximum at ≈220°C (Fig. 6) indicates a qualitative change in the resistance to deformation. This maximum is similar to the maximum hot hardness of iron M. G. Lozinsky [42]. The nature of this "maximum" M. G. Lozinsky is not disclosed, but is given in the following expressions: "The method for determining the temperatures of phase transformations can be based on the use of the dependence of hardness on temperature" [42]. Thus, the maximum metal deformation at ≈220°C may indicate the expected transformation into iron at a given temperature.

Extrema on the hardness curves are typical not only for iron, but also for other polymorphic metals (cobalt, calcium, strontium, and lanthanum) [42], which allows, using the analogy method, also to assume the transformation in iron at approximately 200°C.

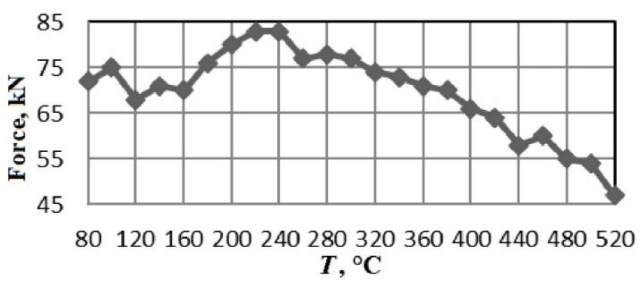


Fig. 6. Dependence of the force during deformation at half the height of the iron sample (0.008% C) at a temperature from 80 to 520°C.

4. Conclusion

Based on literature, as well as our own experimental data (X-ray diffraction analysis, microstructure study, resistance of hot metal deformation of iron samples containing 0.008% C), signs of transformation in iron at ≈200°C are substantiated, which probably determines anomalies in the mechanical behavior of steels. Recognition of signs of transformation at this temperature allows us to explain: the reason for the decrease in magnetization of perlite, sorbitol and martensite, the maxima of impact strength and hardness of iron, the disappearance of the yield point on the tensile curve of riveted steel after aging, etc.

Supplementary material. *The online version of this paper contains supplementary material available free of charge at the journal's Web site (lettersonmaterials.com).*

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