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SUBSTANTIATION OF RELATION BETWEEN ANOMALIES IN PROPERTIES OF STEEL MELTS (AT $\sim 0.5\%C$) AND PRESENCE OF INTERMEDIATE PHASE $\sim Fe_{42}C$

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ABSTRACT

"Phenomenon of structural inheritance" is used by industry, although the "transmission mechanism of hereditary characters to melt, their preservation, origination of new features in this melt and their transfer to hard metal are all the complicated, largely unexplored questions" (Baum, Hasin, Tyagunov).

It is shown that transmission of information encoding from the melt to austenite and then to martensite or to ferrite-cementite mixture requires a mechanism, which nature is not clear, although the correlation of properties given in this paper is unambiguous.

Anomalies in the properties of non-alloyed hypoeutectoid steel melts at $\sim 0.5\%C$, established in different studies, are considered as additional arguments for presence of an intermediate phase $\sim Fe_{42}C$, manifesting itself in a well-known qualitative changes of the structure and properties of solid state (martensite, ferrite, austenite, ferrite-cementite mixture). Anomalies in properties is more important practically in comparison with crystal geometrical signs of presence of the third phase. These signs can be very rarely detected, for example, in $InZn_8$ or Pt_4Al phases. (Perhaps " $Fe_{42}C$ phase" is a convenient designation of anomalies in properties of both states at $\sim 0.5\%C$), in the same way as " $FeAl_3$ phase".

An attempt was made to link the significant effects - extremes and bends of the curves of properties at $\sim 0.5\%C$ melt, austenite, ferrite and martensite-cementite mixture. This attempt was undertaken with different genealogy of iron atoms to the left and to the right of point B ($0.5\%C$) and point O ($0.5\%C$) at the diagram $Fe-C$ by D. K. Chernov.

Structural diagrams for liquid $Fe-C$ alloys are word-for-word connected with the peritectic B point ($\sim 0.5\%C$) [1, p. 71].

Several sections of the works [1, pp. 100, 102] and [2, pp. 53–55, 100–102] mentioned carbon content 0.5 or 0.6% rather frequently; the first considers liquid state, and the second – solid state.

It seems to be natural, because "correlation and mutual influence of liquid and solid states" [3, p. 52] and "phenomenon of structural inheritance" [4, p. 4] were established experimentally. However, "transmission mechanism of hereditary characters to melt, their preservation, origination of new features in this melt and their transfer to hard metal are all the complicated, largely unexplored questions" [3, p. 53]. Therefore, the formal approach for searching the causes of "correlation and mutual influence of both states" seems to be suitable.

Let's examine at first the sold state.

The following qualitative changes in structure and properties, known only from the handbooks about metal science, are the formal grounds for recognition of the intermediate phase $\sim Fe_{42}C$ ($\sim 0.5\%C$). When C content is more than 0.5 %, martensite starts to change its morphology from dislocation one to twinning morphology. At that time martensite becomes critically brittle and tetragonal without any reservations for self-tempering during quenching cooling, and it does not strengthen practically, although it is a solid solution. The yield strength of ferrite-cementite mixture even starts to decrease not depending

on cementite form, while the interval of martensite transformation also starts to diminish, and ferrite loses its ability to be characterized as Widmanstätten pattern [5, p. 7]. Such variation of ferrite morphology is explained by absence of "the packages of dislocation sweeping planes" in austenite, that ease "origination of ferrite nuclei inside austenite grains" [5, p. 7]. It is considered to be equivalent to recognition of "different austenites" that cause ferrite of different morphology [6, p. 8] etc.

In spite of these well-known facts, presence (of the phase $\sim Fe_{42}C$ can hardly be substantiated faithfully. The first reason is that "the nature of cementite as the most simple carbide is not still revealed unmistakable until today" [7, p. 27].

Secondly, binary systems are characterized by not large, but enormous amount of compounds with "?" and "???" signs, e.g. there are only 8 lines devoted to Au_3Cu auride, while Cu_3Au and $CuAu$ aurides are described on several pages [8, pp. 82–86], nevertheless to extraordinary large number of investigations of $Au - Cu$ system (345 references, [8, pp. 114–123]). The same situation is observed for the phase $FeAl_3$ examined by N. S. Kurnakov [9, p. 531]. M. Hansen and K. Anderko think that "it is necessary to save the formula of $FeAl_3$ as a suitable designation" [10, p. 109]. Perhaps, the same situation will be also with $Fe_{42}C$.

Thirdly, the $Fe-C$ system can't be classified "to any definite type of liquid systems, which classification is proposed by F. Sauerwald" [11, p. 305]. Classification is based on presence of anomalies on curves of properties of melts and intermediate phases in the solid state [11, pp. 119–123].

Fourthly, “it is rather difficult to reveal chemical composition having corresponding minimal point, or maximal point, or simple turning point... on the curve... However, its exact explanation is principally indifferent for using these curves...” [12, p. 368].

The last opinion of V. S. Meskin is very important because maximal values [3, p. 100], or minimal values [3, p. 101], or bending [11, p. 187] can be observed on the curves “electric resistance – % C” at $\sim 0.5\%C$.

The aim of this work is to find additional formal arguments in favour of presence of the intermediate phase $\sim Fe_{42}C$ in the system Fe – C based on the following maximal, minimal and bending values on the curves of melts at $\sim 0.5\%C$.

1. Kinematic toughness, not depending on overheating temperature above the liquidus line [11, p. 302], activating power of tough flow [1, p. 56], density and surface tension [13, p. 44], electric resistance of melt and austenite at $1200\text{ }^{\circ}C$ [3, p. 100] have maximal values at $\sim 0.5\%C$ (fig. 1).

It allows to declare $Fe_{42}C$ compound is based on the declaration that “Toughness isotherms have often maximal values at concentrations corresponding to composition of an intermetallic compound” [11, p. 232]. The same declaration is proposed for activating power of tough flow [11, p. 232].

2. Magnetic amenability of melt and austenite (see fig. 1), electronic parameters (such as concentration of carriers and frequency of relaxation) and electric resistance of melt and austenite have minimal values at $1000\text{ }^{\circ}C$ and $\sim 0.5\%C$ [3, p. 101]. The last conclusion contradicts evidently to the conclusion mentioned above in the 1st declaration. It is noted by the authors of the work [3, p. 101], but is not commented.

It is important for this work that maximal and minimal values are the singular points – the signs of intermediate phase.

3. Isotherms of dynamic toughness at $1550\text{--}1700\text{ }^{\circ}C$ have dramatic bending at $\sim 0.5\%C$ [1, p. 58], [11, p. 266]. Such shape of curves has led to the following conclusion: “Sometimes the maximal value...is transforming in the flex point on isotherms” [11, p. 232], what can also be considered as a sign of presence of intermediate phase in solid state [11, p. 232].

4. Shape of isotherms of electric resistance at $1550\text{--}1650\text{ }^{\circ}C$ illustrates citation about degradation of maximal value: dramatic growth up to ~ 0.5 , then almost linear sections with small inclination [1, p. 187]. Bending of curves is explained in such way: “there are probably (!– Author) two structurally different carbon solutions in iron, in the framework of these two sections” [11, p. 186] “with large difference of carbon solubility in δ - and γ -phases” [11, p. 187].

The described curves of resistance are quite similar as relationship between martensite hardness and carbon content, where martensite is formed by austenite and melt.

This coinciding can be accidental, but also can be an appearance of existing of the “integrated element of

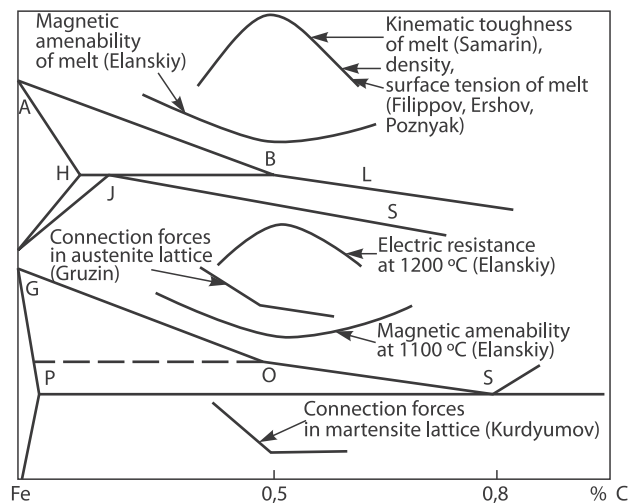


Fig. 1. Schematic dependence between different properties and carbon content

condensed state [3, p. 18], that is integrated for two solutions – melt and martensite. “Association of atoms that are qualitative connected by the same forces at any temperature of existing of the condensed state” can be considered as such element [3, p. 18]. This version is not irreproachable because e.g. the same maximal values of electric resistance of melt and austenite, as well as minimal values of magnetic amenability of electronic melt and austenite parameters “can’t be explained by varying of phase composition” [3, p. 102], i.e. by associations of atoms.

The authors think that a single Fe atom (presented by absolute majority), containing carbon of different genealogy to the left and to the right of B point can be an “integrated element”. It can be expressed as melt $\rightleftharpoons \delta\text{-Fe} \rightleftharpoons \gamma\text{-Fe} \rightleftharpoons \beta\text{-Fe} \rightleftharpoons \alpha\text{-Fe}$ and melt $\rightleftharpoons \gamma\text{-Fe} \rightleftharpoons \alpha\text{-Fe}$ respectively. If it is not true, we need a convincing explanation for the reason, why carbon as interstitial impurity decreases electric resistance to the right of its maximal value at $\sim 0.5\%C$ (as for melt, as well as for solid solution (austenite)). Another question in this case is as follows: why carbon that lowers substantially connection forces in martensite lattice (evaluated via characteristic temperature and elasticity module) and austenite lattice (evaluated via diffusion constants, reference to the experimental points for steels containing 0.43 and 0.77% C, not to the curve drawn aside of them) at its content up to $\sim 0.5\%C$, practically stops its influence when this C content is larger than 0.5% [2, p. 45], [14, p. 18]? This question also relates to influence on both on martensite hardness and melt toughness with $\sim 0.5\text{--}1\%C$ [11, p. 266] (fig. 1).

5. The above-mentioned melt toughness, as well as formation of intermediate phases in solid state, is determined by interaction between particles, “by the same forces that stipulate existence of intermetallics in solid state” [11, p. 232]. These forces, according to [11, p. 232], lead to “creation of preferential groups of atoms inside liquid melt”. Such groups in solid state are not mentioned at all in [2], while in liquid state “the occurring variation of

structure of short-range ordering...” corresponds to transition from body centered cubic (BCC) lattice to more compactly packed face centered cubic (FCC) lattice only by formal signs” (!) [3, p. 102]. And structural diagrams [1, p. 71] of melts, based on the above-mentioned groups, are considered only as “hypothetic ones” [1, p. 105]. By the way, there is also another version “about absence of structural transformations in Fe – C melts” [3, p. 100].

Thereby, the curves of melt electric resistance [11, p. 187] and martensite hardness coincide, as well as the curves of melt toughness [11, p. 266], [1, p. 58] and connection forces in martensite lattice [2, p. 45]. Both these pairs of curves mirror-like each other, what can be connected with intermediate phase Fe_{42}C . Such suggestion is based on the idea, that “chemical interaction can appear in several cases just in liquid state” [13, p. 101]. The authors think that this interaction takes place with ore probability between atoms, not between groups.

6. Relationship between the rate of melt decarburization V_C and carbon concentration in 50 t and 150 t openhearth furnaces is expressed by the curve with flat maximum at 0.25–0.35% C (overheating degree above liquidus is $\sim 100^\circ$) [1, p. 113].

As soon as the rate variation curve of hydrogen concentration V_H has minimal value at $V_C = 0.0065$ %/min [1, p. 130], it is interesting to analyze those values of carbon content when $V_C = 0.0065$ at $V_C - \% C$ curves. It makes ~ 0.2 and $\sim 0.55\% C$ [1, p. 113]. Peritectic points J and B correspond approximately to those values of carbon content, and structural schemes of building of overperitectic compositions, based on anomalies of their properties at ~ 0.2 and $\sim 0.5\% C$ [1, p. 71], are linked to these points.

In the meantime, the extremal values of diffusion coefficient and hydrogen solubility in melt [13, p. 16], correspond to the intermediate phases with open maximum (NiAl) or with maximum forming as a result of ordering in solid solution (Ni_3V , Ni_3Cr). It allows to suggest that the extremal value on the curve $V_H - V_C$ [1, p. 130] is stipulated by the intermediate phase at $\sim 0.5\% C$.

7. If we shall not ignore the experimental points, we can observe the local extremal values at 0.5–0.55% C [1, p. 103] on the 4 curves describing oxygen behaviour during free boiling in the 150 t openhearth furnace. The same extremal values are observed for oxygen activity at $\sim 0.55\% C$ [1, p. 104], and for oxygen concentration and activity values (that are “higher in the interval 0.5–0.6% C compared with the values corresponding to regression lines” [1, p. 102]).

The explanation “the conditions for oxygen accumulation are creating at 0.5–0.7% C, while at carbon content $< 0.5\%$ the conditions for its intensive consumption for decarburization reaction are creating” [1, p. 102] are not satisfactory for then authors: “However, the above-mentioned causes of boiling self-acceleration can’t explain, why this effect occurs not depending on the kind and charge of a furnace, in the carbon content interval 0.6–0.3%. Probably, the data about varying of metal properties and structure have to be attracted for explanation...” [1, p. 102].

The authors think that information about the phase $\sim \text{Fe}_{42}\text{C}$ can help to make another opinion on collision with explanation of slag self-acceleration.

8. Discussing about “self-acceleration of metal boiling at 0.4–0.6% C” [1, p. 102] was conducted without mentioning of Fe atoms [1, p. 100–105] in amount of 97–98 units on 100 melt atoms at $\sim 0.5\% C$. These 97–98 atoms are considered as not only a media where “carbon and oxygen flows in the reaction area” are occurred [1, p. 112], but also as unique aggressive media in the Fe– Fe_3C system: the melt containing 0.5% C (and only it) practically absorbs high-temperature ferrite that has been extracted early at peritectic temperature. The authors think that such melt with $\sim 0.5\% C$ can be named as “independent individual”, in agreement with the opinion of N. S. Kurnakov [9, p. 547].

9. Three curves $V_C - \% C$ (during overheating above the liquidus line by 40–59°, 80–100° and $> 100^\circ$) are crossing in the one point with absciss $\sim 0.55\% C$ [1, p. 116].

Crossing means exclusion of the second influencing factor (overheating temperature), while carbon content at $\sim 0.55\% C$ is the first one. It is possible when the melt with $\sim 0.55\% C$ is a bright individuality (intermediate phase). This argument can be confirmed by two analogies. Two electric conductivity curves (for annealed and cast alloys) are characterized by a bend and touch one another in the single point requesting AuSb₂ phase [8, p. 256], what means absence of difference in electric resistance between both states. This phase is interesting with the feature that liquidus in its surroundings [8, p. 253] is similar to liquidus near B point in Fe–C system. In accordance with opinion of D. K. Chernov, it is required to draw a vertical at 0.5% C (this line is commemorated on his grave monument in Yalta), the picture near the end of peritectic horizontal (B point) will be the same in the systems Au–Sb and Fe–C.

The second analogy: four toughness curves (very different in their shape) for the melts with oxygen content 0.001, 0.002, 0.003 and 0.006% are crossing at 0.2% C [3, p. 106]. This insusceptibility to the second influencing factor (% O) testifies about bright individuality of melt with 0.2% C. Such carbon content is considered as “critical” one [3, p. 106], what allows to count also $\sim 0.55\% C$ content as critical, when three above-mentioned curves $V_C - \% C$ [1, p. 116] are crossing in one point ($\sim 0.55\% C$).

10. According to the figure 1 [1, p. 104], the melt temperature increases continuously during the period of free boiling, as soon as carbon content decreases. However, it is not true completely: experimental points inside the “linear” scatter band testify about the area at ~ 0.4 –0.6% C. The same almost area, based on the experimental points, is observed for flowability [1, p. 104], melt density (at 1600 °C) and austenite (at 1300 °C) [3, p. 100], as well as for dynamical toughness at 1600 and 1700 °C [1, p. 58].

Almost areas (or almost stability of properties) have been shown by N. S. Kurnakov near FeAl_3 [9, p. 543], Pb_3Na [9, p. 469] and Cu_3Zn [9, p. 39] compounds, i.e. they also can be signs of presence of intermediate

phases, that can be determined not quite surely and that can sometimes be absent on majority of diagrams (e.g., Cu_3Zn).

11. Uncertainty with the absciss of B point will hamper to reliable determination of “tracks” of $\sim\text{Fe}_{42}\text{C}$ phase: it was located at ~ 0.35 , 0.5 and $0.5\% \text{C}$ [15, p. 207, 210] on the official diagrams published in Germany, USA and USSR respectively in 1948-1949.

The German variant, originating to R. Ruer and R. Klesper, the pioneers of peritectics in 1914 [15, p. 101], can be hardly a result of the fantasy, because the maximal value on the curves of density, surface tension, kinematic toughness and magnetic amenability of melts (in the last case — also curves of austenite at 1000°C) is steadily observed at $\sim 0.35\% \text{C}$ [1, p. 56]. Based on this real fact, the vertical is inserted in the “structural diagram” of Fe–C melts at $\sim 0.35\% \text{C}$ [1, p. 71]. It is not connected with none of any structural transformations in the melt [1, p. 71, 72].

The authors suggest carefully, that anomalies of melt properties at $\sim 0.35\% \text{C}$ are reaction on the left homogeneity boundary of Fe_{42}C phase.

This suggestion is based on analogy: the minimal value of melt magnetic amenability at 680°C corresponds to the left homogeneity boundary of Sb_2Te_3 compound, while curve bending in the solid state (at 20°C) does not display any reaction on the left boundary for stoichiometric composition [12, p. 367].

12. The same curves with Sb–Te diagram are presented in the manual [16, p. 72], but without any comments, i.e. about ~ 10 -fold varying of amenability during addition of $\sim 5\% \text{Te}$ to Sb [16, p. 72]. In the meantime, liquidus is almost flat in the interval of Te content 0 – 5% [17, p. 1006; see the experimental points of Fey and Ashley].

As for Fe– Fe_3C system, the most flat liquidus section is located at ~ 0.5 – $1\% \text{C}$ [14, p. 110, 147, 160, 161, 189, 196, 201, 210 et al.], that can be connected (as cause or consequence) with anomalies of the properties in liquid and solid state at $\sim 0.5\% \text{C}$ — as it is observed for the system Sb–Te.

13. The liquidus line in the point B ($0.5\% \text{C}$) is bended, what testifies about connections, according to the Kurnakov pictures [9, p. 29, 32]. This connection is underlined by the title of the work “Definition of composition of the determined connections via meltability method”, dated by 1901, i.e. related with the shape of the liquidus line.

Let’s strengthen the importance of the discussing material by the quotes from A. M. Samarin works together with his co-authors: “Shape of the liquidus line in Fe–C alloys is evidently considered as one of the factors...” [7, p. 27], “Minimal density at $0.5\% \text{C}$ appears in the temperature interval 1550 – 1750°C ” [18, p. 145].

Other binary systems with the liquidus line configuration the same as near the B point of Fe–C diagram are characterized by enormous, not large, amount of intermediate phases. In other words, Fe_{42}C has many analogues.

Conclusions

Presented experimental data from different investigations can testify about presence of intermediate phase $\sim\text{Fe}_{42}\text{C}$, manifesting itself by anomalies of properties at $\sim 0.5\% \text{C}$ in liquid and solid states. Perhaps, the phase Fe_{42}C , as well as the phase FeAl_3 , can be considered as a suitable designation of anomalies of the properties of both states at $\sim 0.5\% \text{C}$.

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