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PLATEAUS ON HARDNESS CURVES OF ANNEALED HYPOEUTECTOID STEELS AT ~0.5 % C AS A CONSEQUENCE OF THE PRESENCE OF ~$Fe_{42}C$ INTERIM PHASE

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The article presents numerous experimental data of different researchers depending on the hardness of annealed steels hypoeutectoid on the percentage of carbon content. In addition to the classical Brinell hardness measurement, data of Jagar hardness, Shore, the width of lines on sclerometry Martens, weight loss during grinding on sandpaper are given.

Selecting tendentiously experimental data we demonstrate the plateaus on the curves of hardness of annealed hypoeutectoid steels vs. % of C at ~0.5 % C. Similar plateaus were discovered by N.S.Kournakov in the curves of properties around $FeAl_3$, Pb_3Na, Cu_3Zn, which enables one to follow the analogy and declare a ~$Fe_{42}C$ phase in the Fe-C system.

The anomalies of properties observed in the presence of interim phase at ~0.5% C are definitely established (such as magnetic susceptibility, electric resistance, density, ductility, etc.) for melts and austenite. Their derivative is a ferrite-cementite mixture, which – due to the experimentally established metallurgic heritage – may inherit the anomalies of properties of its parent phase. For the three states described (melt, austenite, mixed phase) the anomalies of properties at ~0.5 % C should be denoted in some compact way, ascribing them, for example the formula of interim phase of ~$Fe_{42}C$.

The assumed ~$Fe_{42}C$ phase has a specific analog in the In-Zn system consisting of eutectic mixture of pure In and Zn, which form an $InZn_8$ phase with their crystal phase, found, similar to ~$Fe_{42}C$ phase under the liquidus bend.

Key words: hardness, interim phase, crystal grid, eutectics, ferrite, perlite, cementite.

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Introduction. Professor P.Ya.Saldau, a colleague of N.S.Kournakov at the Mining Institute, arrived at s conclusion in the course of his studies of hardness and electric resistance: «It should be concluded from then, that a straightforward scheme is not applicable for characterizing iron and steel in their annealed state» [21, p.122]. Meanwhile, textbooks [10, p.131; 18, p.224] present a linear dependence of hardness of tempered and annealed hypoeutectoid steels on the content of carbon. There is a different version for tempered steels: its is almost a plateau in the curve of hardness at % C > ~0.5 (or ~0.6) [9, p.192, 193] (Fig.1).

Plateaus on hardness curves of annealed steels are less well known since they contradict Kournakov's law on linear (additive) change of properties of alloy-mixtures and the «common sense» reflected in the following formulation: «Growth in the content of carbon (the amount of perlite) results in higher hardness and toughness of steel [referenced from three sources. – Auth. comment]» [2, p.136]. (By the way, according to two of those sources the yield strength has a maximum at ~0.55 % C, i.e. a singularity point typical for interim phases).

Follow the review of numerous experimental data by different researchers to demonstrate that (despite the general opinion) the hardness of annealed steels does not follow the additivity rule for alloy-mixtures. Provide an explanation for plateaus at ~0.5 % C on curves of hardness of annealed steels relating them to the presence of interim phase ~$Fe_{42}C$.

Discussion. We demonstrate the plateaus in the curves of hardness of annealed hypoeutectoid steels using the following examples:

1. According to Saldau (1916), after annealing at 700 °C for the grainy cementite at 0.45-0.54 % C the rate of growth of hardness (HB) drops sharply: for steels of 0.35, 0.45, 0.54, 0.63, 0.81 and 0.89 % C it is: 97.70, 11.,50, 122.50, 129.20, 146.09 and 185.15 [21, p.142], respectively (Fig.1)

2. According to data by Boynton (1906) when carbon reaches the range of 0.48 – 0.68 % C the curve of hardness by Jaggar (HJ) shows a sharp drop in its growth rate with carbon content: for 0.2, 0.35, 0.45, 0.48, 0.58, 0.68, 0.86 and 0.91 % C it yields 842, 1745, 1957, 2046, 2090, 2147, 3129 and 3994 [23, p.120], respectively (Fig.2).

3. According to Saldau (1916), after its annealing at 1050 ºC for plated cementite the rate of growth of HB decreases within 0.54-0.63 % C (steel of 0.45 % C was not studied); for steels with 0.35, 0.54, 0.63, 0.81 and 0.89 % C it was 95.51, 132.62, 142.05, 165.01 and 210.97 [21, p.122], respectively.

4. According to data by Benedicks (1904), HB of steels with 0.45 and 0.55 % C is remained practically unchanged – 179 and 183 [21, p.120] (Fig.1).

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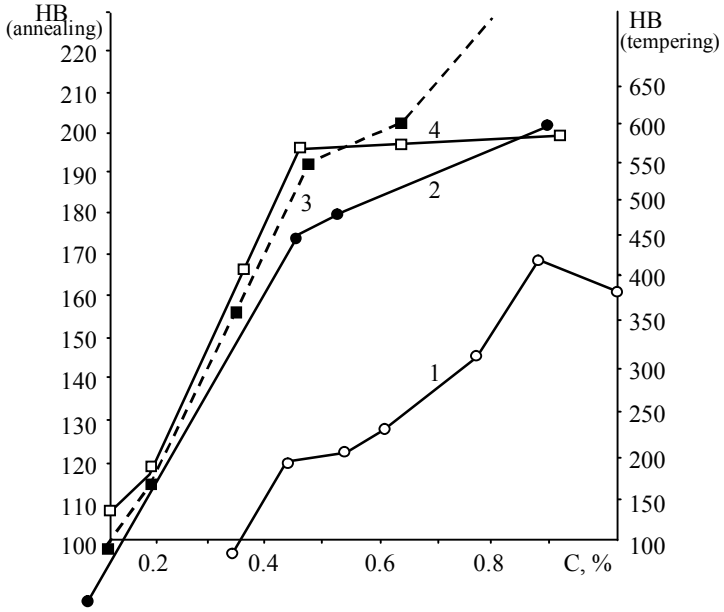


Fig.1. The dependence of hardness on carbon content in annealed and tempered steels
1, 3 – Saldau annealing; 2 – Benedicks annealing; 4 – Brinell tempering

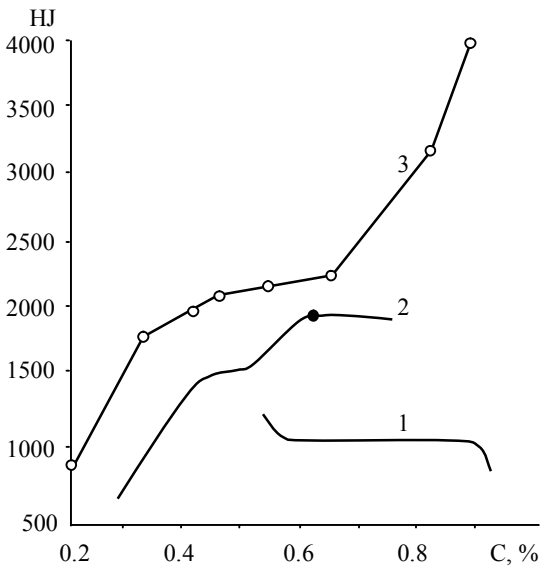


Fig.2. Dependence of hardness on carbon content in annealed steels
1 – groove width at Martens sclerometer anneling; 2 – HB after Robin; 3 – Jiggar hardness

5. According to data by Robin (1911), the rate of growth of HB at 0.4-0.5 % C drops noticeably [17, p.749].

6. According to data by Robin, (1911) the dependence of scratch groove width demonstrated a clear plateau for % C > 0.6 [17, p.749]. (As clear as the one on HRC vs. % C curves for tempered steels [9, p.192, 193]) (shown on Fig.1).

7. According to Wahlberg (1901), steel forgings of 0.4-0.9 % C «freely cooled in the air» showed a growth of hardness (HB) in the range of 0.6-0.65 % C of just a unit, while other ranges (measured each 0.05 % C) it was much higher» [23, p.808].

8. Hardness measured by the groove width using the Martens sclerometer after annealing and tempering at 750, 850 and 950° was the same for 0.65 % C and 0.5 % C [25, p.566] (Fig.2).

From our point of view that result excludes the involvement of «metallographic structure» in the nature of changes of hardness, in the plateaus in the curves at ~0.5% C, to be more exact. Having such plateaus in the curves of hardness and following the analogy technique one may declare the presence of interim phase ~$Fe_{42}C$ (~0.5 % C) if one starts with practically unchanged properties of alloys in the vicinity of compounds ~$FeAl_3$ [15, p.543], ~Pb_3Na [15, p.469] and ~Cu_3Zn [15, p.39], demonstrated by Kournakov (1918-1940).

The concept of «phase $Fe_{42}C$» is, of course, just a «convenient designation» [27, p.109] of qualitative changes in the structure and properties of melt, austenite, ferrite and martensite around ~0.5 % C, that have found their reflection even in textbooks [3, 11].

Ferrite-cementite mixtures to the left and right of points B and O (0.5 % C) are genealogically not equivalent to each other which is self-obvious. Lack of knowledge of the mechanism of transferring hereditary features from the melt to austenite and then to phase mixture does not cancel the importance of genealogy, which E.Houdremont had specially accentuated for the Fe-Cr alloys, writing: «High values of magnetic susceptibility …correspond... to the boundary of compositions, starting from which ... from melting point to room temperature only the volume-centered α-solid solutions exist» [9, p.702].

Claims to introduce the declared phase into common use should be treated with the account of observation by M.Hansen: «the interim phase may manifest expressed chemical properties, similar to properties of typical compounds while not being a compound itself by the character of its crystal structure» [26, p.377].

The listed anomalies of hardness are a particular case, a ‘pale copy’ of glaring violations of additivity rule (Kournakov’s law) in other eutectic and eutectoid mixtures dealt with – to our mind in vain – Kournakov [9, p.59,77], A.A.Bochvar, I.I.Kornilov, E.M.Savitsky and others. Therefore strict identification of the nature of anomalies is hardly possible, in contrast to discussions about them, which assume differing interpretations of the available facts instead of their negation.

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Reasons for the presence of $Fe_{42}C$ phase may be the following:

• The minimum sensitivity of steel with 0.47 % C to dynamic indenting with respect to static one: for steels of 0.17, 0.22, 0.47, 0.63, 1.06 and 1.16 % C these are 1.24, 1.18, 1.15, 1.25, 1,29 and 1.31 [5, p.537], respectively.

• Lack of sensitivity of HB to the form of cementite: at ~0.45 % C the curves of steel hardness cross for plate and granular perlite [21, p.142]. That fact was noticed by Saldau, but is not discussed within the context of the current study

For such a minimal sensitivity to the second affecting factor or lack thereof (the rate of indenting, the form of cementite, the first one being the % of C), an hierarchically higher, stronger, dominating factor is needed. Such a factor may be the chemical composition corresponding to an «autonomous individual» [15, p.547] – the interim $Fe_{42}C$ phase.

An example of such a dominating factor may be the chemical composition of alloy with ~23 % Ni in the Fe-Ni system, its linear expansion coefficients are strictly equal to each other in the range of 500 to 900 ºC temperatures: all 5 curves intersect at a single point [6, p.804]. That alloy is close to the discussable phase Fe_3Ni, its Kournakov point ~320 °C.

Another example is the intersection of 4 viscosity curves of steel melts, very different in their shape, having 0.001-0.006 % of oxygen at 0.2 % C [7, p.106]. That is why such content of carbon is called «critical» for melts [7, p.106]. It corresponds to the peritectic point J and powerful effects in the curves of properties of melts that are found at ~0.5 % C (peritectic point B).

The third example the bend and single touch of the two curves (lack of difference) of electric resistance of cast and annealed alloys with their composition corresponding to the incongruently melting phase $AuSb_2$ [7, p.256]. That phase is interesting in that in its vicinity the liquidus [7, p.253] reminds the liquidus around point B of the system Fe-C. If, following D.K.Chernov one draws a vertical at 0.5% C [10, p.114], the picture by the end of peritectic horizontal (point B) in systems Au-Sb and Fe-C will be the same.

«Simple carbon steel is not worn inversely proportional to the content of carbon», «During polishing with sandpaper the minimum weight loss is observed at 0.4 % C» [19, p.124].

The first conclusion by Robin means unacceptability of operating the shares of ferrite and cementite while explaining the curves of hardness. N.A.Minkevich called the second conclusion «hardly explainable», but never paid attention to the retardation of growth rate of HB for ~0.4-0.5 % C or the plateau in the curve of scratching groove width for % C > 0.6, or an obvious bend in the curve of Shore hardness at ~0.4 % C, though he cited all four curves by Robin for annealed steels in his review [17, p.749].

All four curves at 0.5 ± 0.1 % C have anomalies that may indicate the presence of an intermediate phase with the carbon content. The least expressed is the anomaly in the HB – % C curve.

Thus static indenting is not very helpful in identifying anomalies, but interferes with the practices, as explained by the two examples below.

The statement that «the highest hardness corresponds to the highest wear resistance does not have the nature of a law» [8, p.292].

After annealing tempered steels of 0.12, 0.34, 0.58 and 0.8 % C at 260 °C the loss of mass (in gram per 100000 kg m of work) was1.5, 0.4, 0.12 and 0.08, specimen hardness (HRC) being 32, 47, 50 and 60, respectively [13, p.258]. Therefore, increasing hardness by HRC3 (50 – 47 = 3) resulted in increasing wear resistance by ~3 times, while HRC10 (60 – 50 = 10) only yielded an increase of 1.5 times.

Robin had formulated the detrimental nature of the indenting technique in the following way: «In cases when the hard structural element is encircled by the rather ductile one, test results on hardness by the grinding technique and by penetration appear to be diametrically contrary to each other» [19, p.125].

It is strange that Robin never offered a judgment on the four anomalies 0.5 ± 0.1 % C he had established. He was considered «one of the most productive authors of the current times» [20, p.222] in the beginning of the last century, and his non-trivial reasoning on transformations in iron and steel below A_1 are worth separate overview.

It is hardly possible to clearly determine the $Fe_{42}C$ phase, same as it did not work with Fe_3C: «The nature of even the simplest of carbides, cementite is still not identified clearly» [12, p.27]. «Thus, there is no unity in views on the Fe-C diagram» [12, p.27].

Phases from Kournakov's studies mentioned above also evaded strict determination:

DOI 10.18454/PMI.2016.5.724

• «So far the formula $FeAl_3$ should be retained as a convenient designation» [27, p.109]. Kournakov himself denied that phase, pointing to high brittleness of specimen that «ran fractures and burst» [15, p.546] during indenting. (By the way, martensite is catastrophically brittle at % C > 0.5 where the plateau in the curve of hardness starts. Brittleness does not weaken, though residual austenite appears in the structure).

• «The homogeneity interval does not include the $NaPb_3$ composition… the position and extension of that phase range were studied using the techniques of X-ray and thermal analyses and by measuring its electric resistance and hardness. However the results obtained diverge considerably» [28, p.1057].

• «The ordering of atoms of components in the vicinity of stoichiometric compositions of Cu_9Zn and Cu_3Zn» [1, p.70] is not recognized not only in textbooks but even in a dedicated monograph [3]. Cu_3Zn phase is mentioned in [28, p.696, 697] as a possible or supposed.

Everything said about $FeAl_3$, $NaPb_3$ and Cu_3Zn may be referred to Au_3Cu [16, p.205; 7, p.94], including the plateaus in their curves of properties, though the «system Cu-Au has become a favorite object for experimental and theoretical studies» [27, p.219; 7, p.114-123].

Such a close attention to the described phases is justifiable, since an opinion encountered sometimes that simple reliable techniques are available for detecting interim phases. If it were so, then many diagrams would not feature phases with signs of «?» or «??» by their side. By the way, «far from all the interim phases may be classified [16, p.12].

Phases $Fe_{42}C$, $FeAl_3$, Pb_3Na, Au_3Cu, Cu_3Zn and Fe_3Ni mentioned in the current study are found in the vicinity of bends of liquidus [19, p.128; 15, p.535; 28, p.1057; 26, p.219, see experimental points of Roberts Austen (1900); 3, p.13; 16, p.124], respectively. The importance of that circumstances may be explained by a citation: «The shape of liquidus line in iron and carbon alloys is undoubtedly one of the factors… [12, p.27].

Let us further strengthen the meaning of liquidus by the title of paper by Kournakov (1901): «Retrieving the composition of certain compounds in alloys with fusibility technique» [15, p.19] and his own graphic illustrations on the relation of bends in the liquidus with compounds [15, p.6, 16, 28, 29, 32, 112, etc.]. Illustrations from pages 29 and 32 [15] remind one of the vicinity of point B (~0.5 % C) in the Fe-C diagram. Therefore here is no reason to exclude and incongruently melting phase ~$Fe_{42}C$ from that vicinity. As for the other systems, their number is not simple large but enormous.

The need to introduce the concept of «~$Fe_{42}C$ phase» is defined by numerous anomalies in the structure and physical properties of alloys at ~0.5 % C, as well the wish to offer at least some interpretation to the mysterious observation by Saldau: «Physical properties of steel depend not only on composition, but - maybe even more so- on the physical state of the substance [22, p.54]. This is the conclusion that the researcher from Kournakov's school arrived at, the one who studied not only steels, but non-ferrous alloys too [22].

In his study, presented for publication by A.A.Bochvar, plateaus in the curves of hardness of non-ferrous alloys, are tied to «concentration responsible for composition at the peritectic point» [14, p.117], and unacceptability is stressed of «...using the additivity rule for assessing the properties of phase mixture formed during peritectic crystallization» [14, p.118].

Note that hypoeutectoid steels are partially the product of peritectic crystallization. For our point of view they should be separated into pre- (< 0.5 % C) and post-peritectic (>0.5 % C), since genealogically they are not equivalent to each other, which is fully apparent. However, that issue reaches into the realm of the nature of metallurgic heredity.

So, plateaus in the curves of hardness are observed not only for steels but for non-ferrous mixture-alloys as well. Moreover, one may find examples of even depletion of hardness as the content of the second component, e.g., carbon and zinc increases.

Let us cite one of the observations by Saldau: «According to data by Boynton, the curve of hardness is a broken line with a break at the point, corresponding to 0.58 % C, while the possibility should not be excluded of some maximum existing there» [21, p.129]. «Some such maximum» is found in brass at 10.29 % Zn [15, p.38, 39], i.e. in the vicinity of ~Cu_9Zn.

The reasoning by Saldau on «some maximum» of hardness at 0.58 % C could have been inspired by the very expressive maxima of electric resistance in the annealed and tempered steel at 0.55 % C, which were found by Carl Benediks, a Swedish scientist in 1904, which Saldau believed it necessary to demonstrate in his own study [23, p.123].

DOI 10.18454/PMI.2016.5.724

The maximum means not only a singularity point – an indicator of an interim phase, but also a downtrend, which means softening. It cannot be explained by «metallographic structure», i.e. shares of ferrite and cementite. A new approach is needed, its option outlined in the current study.

The direct line at 0.5 % C on the Fe-C diagram, drawn by Chernov on 1916 has not only made it to a textbook [10, p.114], but was immortalized on his gravestone in Yalta. Saldau's communication circle was noticeable: he expresses his «sincere gratitude for the support provided» to N.S.Kournakov, A.A.Baykov, A.L.Baboshin and P.Herence [21, p.148]. It was in the laboratory of the latter in Germany that Saldau worked until WWI. We believe that it explains the hardly explainable: Saldau did not put any accent on the anomalies at ~0.5 % C neither in 1916 [21], nor in 1952 [22], though one may count up to two dozen anomalies in such properties in the works of Saldau himself.

We believe that the cause was this: being himself a representative of Kournakov's school, Saldau must have gravitated to linking anomalies in properties to critical points. For example, his whole study [21] is dedicated to founding the relation of anomalies of properties at 0.89 % C with eutectoid point S. There was no critical point at 0.5 % C for Saldau in the lower 'steel' corner of the Fe-C diagram that he had plotted in 1914 together with Gerens because the experimentally found point O there sits at ~0.35 % C [22, p.43, 57; 24, p.107]. (By the way, Chernov's point O is positioned at ~0.35 % C [10, p.114; 24, p.25]).

Despite the WWI that broke out at that time, Saldau could know that point B in the peritectic corner plotted for the first time by R.Rhuer (1914) (a co-author of Gerens, same as Saldau) was sitting at ~0.35 % C [24, p.207, 210]. Therefore the anomalies and properties at ~0.5 % C absolutely obvious for Saldau could not be linked with that point.

Point B still remained at 0.35 % C in the official German diagram of 1948-49, while in both the Soviet and American it had already moved over to ~0.5 % C [24, p.207, 210]. Even if Saldau knew about the first and the third of them in 1952, he could have easily made a conclusion in favor of the German diagram since he was an ethnic German himself and used to work in Germany a long time back.

That issue – whether 0.5 or 0.35 % C? – will hardly find its final solution before clearing away the «inconsistency of the results of studies; absolutely similar experiments conducted by two groups of researchers lead to different conclusions» [24, p.239].

Such an «inconsistency of results» is also observed in the system Cu-Sn: «despite especially detailed studies… quite large discrepancies still exist with respect to phase boundaries» [26, p.604]. The Cu-Sn system was studied by researchers whose names have become absolutely common in metal science: Matthiessen, Le Chatelier, Charpy, Hansen, Roberts-Austen [26, p.614].

Something quite noticeable is also associated with the name of Saldau: In his study of 1928 Kournakov, together with N.V.Ageev and R.A.Pogodin disclaims Kournakov's law for eutectic mixtures (1908) referring to study [21] as an example of «deviation… from the diagram of properties established theoretically by N.S.Kournakov and R.F.Zhemchuzhny» [15, p.77].

Conclusion. The data collected by Pyotr Yakovlevich Saldau may be ignored or used to correct the notion of the ostensibly additive change of hardness of annealed hypoeutectoid steels. Most of these data are about one century old. That is why they are even more valuable if one follows the teaching by Bochvar: «At the first glance one gets an impression that older studies diverge with the new ones... there appears a desire to give preference to the new data… one should not draw a general conclusion form that on better truthfulness... » [4, p.194].

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