New version of Kurnakov's law about relationship between properties of binary alloys and phase diagrams balance

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Abstract. The representation of the state diagram as a concentration dependence of qualitative changes in crystallization (recrystallization) intervals is introduced for the first time. This makes it possible to connect the phase diagram with inexplicable properties of the phase composition or the structure of the anomaly in the properties of Zn-Cd, Sn-Pb, Cu-Ag, Al-Si, and Fe-C double alloys. A new version of Kurnakov’s law is presented which allows associating the anomalies of binary alloy properties with qualitative changes in crystallization intervals.

1. Introduction
A blatant violation of the additivity rule (Kurnakov’s law) for alloy-mixtures (siluminis) led A. A. Bochvar to a striking conclusion for a metal expert: “There is no single-valued relationship between composition and properties.” The alloys which are different in structure (cast, deformed, annealed, thermo-improved) are not equally subject to the law on property additivity (Kurnakov’s law). An attempt has been made to explain the behavior of the composition-property curves in the Zn-Cd, Sn-Pb, Cu-Ag double bonds that do not obey Kurnakov’s law with qualitative changes in the crystallization intervals, and in steels and silumin with the help of the liquid memory effect (metallurgical heredity).

2. Results and Discussion
Kurnakov N.S. shows the dependence of properties on composition in the form of straight-line segments [1]. The places of their junction will be called a curve band. The refusal of Kurnakov N.S. in 1928 from the “diagrams of properties, established theoretically by Kurnakov N.S. and Zhemchuzhyi S.F.” in 1908, is rarely mentioned [2]. The refusal of the additive (linear) course of the curves was justified by the hardness peak (H) of Zn-Cd, Sn-Pb and Cu-Ag alloys with a eutectic composition after rapid cooling; peak H is eliminated by slow cooling or annealing [1]. (Saldau P.Y., a colleague of Kurnakov N.S. at the Mining Institute, in 1916 showed the presence of a hardness peak in the annealed alloy-mixture - eutectoid steel (0.89% C) [2], what was known to Kurnakov N.S. [1]).

From the standpoint of Kurnakov N.S. (1915), it follows that peak H is a characteristic not only of the eutectic alloy (~ 80% Cd + 20% Zn), but also of the alloy with ~ 20% Cd [2]. Peak H at ~ 20% Cd is represented by Kurnakov N.S. under a very expressive liquidus curvature at ~ 20% Cd [1], which for eutectic systems (solidus-horizontal) means a qualitative change in the crystallization interval.
(CIALS, where \( L \) is the liquidus, \( S \) - solidus, \( \Delta LS \) - the difference between them in degrees) with an increasing (decreasing) proportion of Cd. Since the CIALS in the eutectic point is self-evident, both hardness peaks are related to CIALS.

In slowly cooled Cu-Ag alloys, there are two powerful bends of the curve \( H \) at \( \sim 8 \) and \( \sim 92\% \) Ag [3], which roughly correspond to the ends of the eutectic horizontal [3], where the CIALS are self-evident. It should be noted that at \( 20^\circ \) C all alloys with \( \sim 8\sim92\% \) Ag consist of a mixture of almost pure Cu and Ag crystals.

In Sn-Pb system, annealing or slow cooling destroy peak \( H \) (but not the electrical resistivity) in the eutectic composition (~35% Pb) [1]. However, two bends on the curve \( H \) are preserved at \( \sim20, \sim70\% \) Pb. They correspond to the onset of the transformation of the curvilinear liquidus into rectilinear liquidus [4], which for the eutectic system means CIALS.

The question of the lack of additivity in the change in hardness for Si> 85% in alloys with aluminum is discussed in [5] as follows:

"The microhardness of silicon is 1200 kg / mm\(^2\), and the eutectic is only 80 - 85 kg / mm\(^2\)." One could expect that the hardness will increase steadily in the hypereutectic alloys of this system (Al-Si) with the increasing silicon content, approaching the hardness of silicon ... However, the hardness of alloys containing 12 to 90% of silicon increases insignificantly with an increase in the silicon content (silicon content in % of this alloy, compared with the eutectic one, increased 7 times, and the hardness - only 3.5 times) and reaches 200 kg / mm\(^2\) ... The hardness of alloys with 95% silicon is 3 times higher than that of the alloy with 90% silicon " [5].

"Such a sharp increase in hardness, measured by pressing the winning cone, is explained by the fact that only in an alloy with 95% silicon, eutectic inclusions do not fill the grain boundaries of silicon due to its small number" [1].

If this explanation satisfied the authors of [1], they would not have made unsuccessful attempts to obtain alloys with a different distribution of structural components when the conditions of casting, prolonged annealing, and deformation were changed. Thus, the hardness of a hot-pressed alloy with 55% silicon hardly changed compared to a cast alloy and amounted to 90 kg / mm\(^2\) (for a cast alloy of 86 kg / mm\(^2\)) [1].

This absence of a difference in the hardness of the cast and deformed states that differ greatly in the structure and properties of the cast and deformed states is another illustration of BelyaevN.I. and GudtsovN.T. conclusion on a similar problem: "The apparent elastic limit has no connection with the structure of steel, but introduces only confusion in the general understanding of the technical properties of steel "[6].

Properties are determined by something else and expressed as follows: "The physical properties of steel depend not only on the composition, but, perhaps, even more on the physical state of the substance" [7].

Although some basis for trying to relate the non-additive curve of the hardness-% Si curve is another experiment by the same authors who prepared cermet alloys by pressing a mixture of Al and Si powders at 500 ° C. The hardness of benign samples with 60, 75 and 85% Si [5] increased sharply, approximately 3 times, for the alloy with 85% Si it was 400 kg / mm\(^2\), "whereas the hardness of the cast alloy of the same composition was only \( \sim 100 \) kg / mm\(^2\) [5].

This is already close to the additive [5] course of the hardness curve, that is, to Kurnakov's law for alloy-mixtures. At the same time, let us note that the microhardness of the structural components (solid and soft) coincides with the microhardness of their constituent in the cast alloy [5].

Let us emphasize separately: the pressing temperature is below the eutectic temperature (577 ° C), that is, the Al and Si powders, more precisely, the atoms that make up them never coexist in the melt.

The most important characteristic of the melt is the form of the liquidus.
For example, the extremes of the electrical resistivity and the magnetic susceptibility of the melt (and austenite at ~ 1100 °C) correspond to the bending at the peritectic point B of the Fe-C system [9, 10]. To the same point, solid groups (clusters, cybotactic grouping) of different nature [9] or structural forms of dissolved carbon [11] are anchored.

There are two bending points in the Al-Si system: at the eutectic point, which corresponds to the simultaneous maximum of σ and δ [12], and at ~ 85% Si [13], when Kurnakov's law for alloys-mixtures is very violated [5].

Supra-eutectic melt is a chemical compound [14], that is, in a "special" way organized by matter. At the bending point (~ 85% Si), one can also expect a special interaction of Si and Al atoms in the melt. After crystallization, the alloy consists of almost pure Si and Al, that is, very dilute solid solutions with respect to the melt with ~ 85% Si.

For further reasoning, one will use the effect of "liquid memory", which consists in preserving the characteristic individual properties very strongly (~ 10^{120}) by dilute solutions [14]. Of course, the authors do not know the encoding mechanism and the preservation of information. But its carriers can be Si and Al atoms that were in contact in the melt and retained a "memory" of this, although at 20 °C they are separated into silicon and aluminum crystals, which are almost completely detached from foreign atoms.

The consequence of the effect of "fluid memory", in another terminology - the effect of metallurgical inheritance, but with a very large dilution of the solid solution, can be a completely identical course of the curves for the dependence of the eutectic carbon concentration, the duration of the peritectic and eutectic transformations, the temperatures of the beginning and the end of the eutectoid transformation upon heating, the parameter Lattice of the α-solid solution from the duration (5-150 minutes) of holding at 1480 °C of the synthetic pig iron (3.5% C) from waste steel A 570 Grade and grits graphitized electrodes. The extremum of all dependencies is located on 120 minutes. [11]

Since the samples for determining the lattice parameter were obtained by cooling the melt in a copper ingot, it is difficult to judge the content of carbon in the α-solid solution, but, when heated, the α-solid solution was almost completely freed from carbon by the beginning of eutectoid transformation, being, in relation to the melt, a very dilute solution. However, its response to the holding time at 1480 °C is the same as the melt reaction with 3.5% C.

Let us assume that the anomalous path of the hardness curve in the Al-Si system, which is not obeying Kurnakov's law, is a consequence of the "memory" of the interaction of aluminum and silicon atoms that took place in the melt. The nature of the interaction at both sides of ~ 85% Si was obviously different, if there is a bend of the liquidus at this content.

In the Fe-C system, with an increase in% C of annealed steels, the bending occurs at ~ 0.5% C and the maximum at 0.89% C [7, 8] on 14 electrical resistivity curves at 25-600 °C. With 0.5% C, the liquidus is bent (ABC) at point B and the GOS line — at point 0. With 0.89% C (eutectoid content), the GOSE line bends at point S. There are no grounds for anomalies with ~ 0.5 and 0.89% C, since with the increase of % C, the proportion of high-resistivity (and high-hardness) cementite increases monotonically. Therefore, the anomalies can be "tied" to points B (and O - they have the same abscissa) and S, remembering that the over eutectoid austenite above the point S is a chemical compound [14].

Below point B, there may well be an incongruently melting phase or superstructure, which is often the case in other systems. The first is evidenced by the extremes of electrical resistivity [9], magnetic susceptibility [10] and the true coefficient of linear expansion [16] of austenite at ~ 1100 °C, and the second - bends in the electrical resistivity curves at 25-600 °C [7].
The expected intermediate phase of Fe$_{42}$C (0.5% C) manifests itself in the anomaly on the yield strength curve—the percentage of carbon of annealed or normalized steels: a maximum with ~ 0.55% C [15-17], which is not grounded since the interphase boundary of ferrite-cementite is impenetrable for dislocations. Moreover, with ~ 0.6% C, the shape of the stretching curve changes and it is necessary to determine not the physical but the conditional yield strength [18].

To the "metallographic" structure, these maxima are irrelevant, since the absolute maximum of the yield strength is established also for the highly quenched steel of ~ 0.55% C [18], in which there is no free ferrite. The maxima of the yield stress can be due to the "special" behavior of the solid solution-ferrite, which is very diluted with respect to the parent phases (melt and austenite), which has somehow preserved the memory of the once-existing interaction of iron and carbon atoms.

3. Conclusion

Thus, the proposed new version of Kurnakov’s law sounds as follows: the additive (linear) sections of the curve properties in the eutectic systems are limited by the abscissa of the points, including the eutectic point where the CIALS occur.

The proposed version of Kurnakov's law is needed, by analogy, to explain the bending of the curve of hardness of annealed steels with ~ 0.5% C. The bend of the curve follows from Brinell’s data (HB steels with 0.1, 0.2, 0.25, 0.35, 0.45, 0.66, 0.78, and 0.92% C are 97, 115, 143, 156, 194, 202, 231 and 258) [19] and Boynton (H by Jaggar(It is determined by the number of revolutions by cores well), where steels with 0.2, 0.35, 0.45, 0.48, 0.58, 0.68 and 0.86% C are 842, 1745, 1957, 2046, 2090, 2147, 3129) [7]). The bending of the H curve with ~ 0.5% C can be related to the KIALS, which is self-evident due to the bending of the liquidus at the peritectic point B (0.5% C) of the Fe-C diagram [20].

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