Zen law and features of liquidus–solidus curves in binary state diagrams based on elements VIIIA and IB of the periodic table

A I Potekaev¹, A A Kondratyuk², S A Porobova³, A A Klopotov¹, T N Markova³, Yu A Kakushkin³ and V D Klopotov³

¹Tomsk State University, Tomsk, Russia
²Tomsk Polytechnic University, Tomsk, Russia
³Tomsk State University of Architecture and Building, Tomsk, Russia

E-mail: klopotovaa@tsuab.ru

Abstract. The paper presents the analysis of binary state diagrams based on elements VIIIA and IB of the periodic table and crystal geometry parameters of solid solutions and intermetallic compositions. The analysis shows an explicit correlation between the type of the evolution of phase diagrams classified by Lebedev depending on the nature of atomic volume deviations observed in solid solutions and intermetallic compounds from Zen law.

1. Introduction
An increased interest to state diagrams of binary and ternary systems from elements VIIIA and IB of the D.I. Mendeleyev’s periodic table is caused by the presence in these systems of solid solutions and intermetallic compounds with unique combinations of physical and mechanical properties as well as important magnetic and optical characteristics. The principal distinctive feature of these functional materials is a weak stability of the crystalline lattice in temperature ranges preceding structural phase transitions (SFT). The weak stability and instability of the crystalline lattice in advance of SFT manifest themselves in features of temperature dependences of physical and mechanical properties (the so-called subtransient phenomena [1, 2]). The development of ideas on the nature of the stability of crystalline structures of solid solutions and intermetallic compounds is unthinkable without the research on clarification of features of their crystalline structure [3-9]. Up to the present moment, a purposeful study of the correlation of state diagrams of systems from elements VIIIA and IB of the D.I. Mendeleev’s periodic table with crystal-geometry parameters of solid solutions and intermetallic compounds has not been carried out.

The aim of the work is to carry out a search for common patterns and correlations between the structure of state diagrams of binary systems from elements VIIIA and IB of the D.I. Mendeleev’s periodic table and the deviation of atomic volumes in solid solutions and intermetallic compounds from Zen law.

2. Materials and methods
In [3-8] it is shown that different types of state diagrams of alloys, depending on the alloyability of elements, have certain regularities in their structure (size factor, electronic structure of atoms) that depend on the ratio of values of interatomic interactions of alloying elements.
There is a wide variety of state diagrams depending on the value of the mixing energy \( W \) for a binary alloy: in the approximation of the interaction among nearest neighbors

\[
W = U_{AB} - \frac{U_{AA} + U_{BB}}{2},
\]

where \( U_{AB}, U_{AA}, \) and \( U_{BB} \) are potentials of interatomic interaction among atoms of different kinds \( AB \) and one \( AA \) and \( BB \), respectively \([9]\). The necessary condition for the formation of a solid solution is the proximity of the value \( W \) to zero. To fulfill this condition, two alloying elements in binary alloys must have the structure of electron atom shells, atomic radii, and the energy of chemical bonds close to each other. In this case, the atomic substitution of one another is not associated with difficulties of the structural or the energy nature, thus, continuous solid solutions appear. The mutual solubility of components decreases when \( W \) becomes positive. Chemical compounds in alloys are formed when the numerical value of the mixing energy \( W \) becomes significantly negative. In the case when an intermetallic compound has a narrow homogeneity region and a significant negative mixing energy \( W \), the location of stability regions of crystalline structures depends on the size factor and the external incomplete electron atom shell of the alloying component.

The classification proposed by T.A. Lebedev is promising if to consider the relationship of individual diagrams within a single type \([10]\). In this classification, it is proposed to consider the evolution of diagrams not only within a single type, but bonds of individual types of diagrams as well. Based on this classification of state diagrams we have presented, with some simplifications, the real state diagrams of binary systems from elements VIIIA and IB of the D.I. Mendeleev’s periodic table \([11]\), the order and the arrangement of which allow to clearly classify them by types (Figure 1). The evolution of alloy state diagrams corresponds to the change in the ratio of potential energies of interaction of different types of atoms \( AB \) and the same type \( AA \) and \( BB \).

The diagram of the system Ag-Co is basic for the first type of phase diagrams under the classification of T.A. Lebedev. For this system, there is a limiting case for diagrams of the type I (Figure 1), in which the miscibility is so small that it can be taken as close to zero. An increase in the miscibility for diagrams of the type I leads to the evolution: the following sequence of diagrams for systems under consideration:

\[
(Ag-Co) \rightarrow (Co-Cu) \rightarrow (Au-Pt) \rightarrow (Cu-Ni) \rightarrow (Co-Ni).
\]

Such evolution of phase diagrams of the type I shows that there is an increase in the energy of the interatomic interaction of different types of atoms \( AB \), i.e., \( U_{AB} \), relative to energies of the interatomic interaction of the same type of atoms \( U_{AA} \) and \( U_{BB} \). This is reflected in the change in the evolution of concentration dependences of atomic volume deviations in solid solutions and in ordered phases from Zen law in systems formed by elements VIIIA and IB of the D.I. Mendeleev’s periodic table (Figure 2). It shall be noted that the deviation in concentration dependences of atomic volumes from Zen law is negative, which indicates a decrease in the atomic volume during the formation of solid solutions in alloys of systems under consideration.

In the investigated binary systems the following set of crystallo-geometrical parameters was used \([13]\): the atomic volume of elements \( \Omega \); the value of deviation from the linear dependence of the atomic volume \( \Delta \Omega = \Omega_{\text{exp}} - \Omega_z \) on the concentration \( \Omega_{\text{exp}} \) is the atomic volume in the alloy determined from the experimental values of parameters of elementary cells of the alloy, \( \Omega_z \) is the atomic volume determined by Zen’s law.
The second type of phase diagrams, for which the system Au-Pt is basic, is characterized by modification of phase diagrams under two scenarios. The first scenario proposes modification of phase diagrams due to the fact that the liquidus line goes to a rapprochement with the solidus line. Then, the sequence of diagrams is as follows:

\[
(Au-Pt) \rightarrow (Ag-Pd) \rightarrow (Au-Pd) \rightarrow (Pt-Rh) \rightarrow (Ag-Au).
\]

The second scenario proposes that the solidus line goes on rapprochement with the liquidus line. In this case, the sequence of diagrams is as follows:

\[
(Au-Pt) \rightarrow (Cu-Pt) \rightarrow (Cu-Pd) \rightarrow (Co-Pt) \rightarrow (Ni-Pd) \rightarrow (Co-Pd) \rightarrow (Co-Rh) \rightarrow (Au-Cu) \\
\rightarrow (Au-Ni) \rightarrow (Co-Ir).
\]
Such evolution of state diagrams leads to an appearance of minima points on solidus and liquidus lines (Figure 1). It should be noted that this sequence is the most numerous among all of the considered phase diagrams formed from elements VIIIA and IB of the periodic table.

The third type of state diagrams is presented by a number of diagrams in which the breakdown degree of liquid solutions increases to produce, in the end result, a mechanical mixture of pure components (Figure 1)

$$(\text{Co-Ir}) \rightarrow (\text{Ni-Cr}) \rightarrow (\text{Ag-Cu}) \rightarrow (\text{Au-Co}).$$

**Figure 2.** The schematic of the evolution of concentration dependences of atomic volume deviations in solid solutions and in ordered phases from Zen law in systems formed by elements VIIIA and IB of the periodic table.
It is important that the minimum on the diagram of continuous solid solutions (Co-Ir, Figure 1) cannot be mixed with the eutectic point. The fact that at the beginning of the given series of diagrams with the eutectic point contains the diagram with the minimum point on solidus and liquidus curves does not give grounds to identify the minimum point on this diagram with the eutectic point. There is a tendency that reflects the process of a possible eutectic formation. This phenomenon is associated with the corresponding prerequisites that a eutectic transformation in the subsequent systems may occur at the place of a weakly-stable or an unstable compound.

Atomic volumes in solid solutions and intermetallic compounds (according to lattice parameters) were calculated for all above-mentioned binary phase diagrams [12]). The obtained values of atomic volumes have allowed determining the deviation of concentration dependences of atomic volumes from Zen law [1, 2].

According to the above mentioned distribution of phase diagrams, depending on the features of liquidus and solidus curves, a detailed arrangement of concentration dependences of atomic volume deviations in solid solutions and in ordered phases from Zen law in systems formed by elements VIII A and IB of the D.I. Mendeleev’s periodic table has been carried out (Figure 2). This arrangement has allowed revealing the correlation between liquidus (solidus) curves and concentration dependences of atomic volume deviations in solid solutions from Zen law in systems under consideration.

In diagrams of the type I under the classification of T.A. Lebedev only negative deviation of concentration dependences of atomic volumes from Zen law is observed (Figure 2).

Phase diagrams of the type II under the classification of T.A. Lebedev, for which the diagram of the system Au-Pt is basic, are characterized by both positive and negative deviation of atomic volumes in solid solutions and in ordered phases from Zen law, depending on the scenario of the evolution of phase diagrams (Figure 2). A positive deviation from Zen law leads to modification of phase diagrams due to the fact that the liquidus line goes on rapprochement with the solidus line. The sequence of diagrams of binary systems with a negative deviation of atomic volumes from Zen law results in a sequence of phase diagrams in which the solidus line goes on rapprochement with the liquidus line. Such evolution of state diagrams on the solidus and liquidus line leads to an appearance of the tendency to formation of the minimum (Figure 1).

Phase diagrams of the type III, for which the diagram of the system Co-Ir is basic, are characterized by a positive deviation of atomic volumes in solid solutions from Zen law in places of their existence on diagrams. At the same time, a significant increase in deviations of atomic volumes from Zen law in regions preceding solubility ruptures on phase diagrams is observed (Figure 2).

3. Conclusion
Thus, a clear correlation between the type of the evolution of phase diagrams under the classification of T.A. Lebedev depending on the nature of atomic volume deviations in solid solutions and in intermetallic compounds from Zen law in systems formed from elements VIII A and IB of the D.I. Mendeleev’s periodic table has been revealed.

Acknowledgement
The paper includes the results obtained in the course of the implementation of the project (No. 8.1.42.2015) within the framework of the Program “Scientific Foundation named after D.I. Mendeleev of Tomsk State University” in 2015-2016.

References
[1] Potekaev A I, Klopotov A A, Kozlov E V, et al. 2004 Pretransitional weak-stable structure in NiTi (Tomsk: NTL) p 296 (in Russian)
[2] Potekaev A I, Klopotov A A, Morozov M M, et al. 2014 Structural features of binary systems with weak-stable (Tomsk: NTL) p 304 (in Russian)
[3] Kornilov I I and Budberg P B 1961 State diagrams of binary and ternary titanium systems (Moscow: Nauka) pp 40-41 (in Russian)
[4] Vozdvizhinsky V M 1972 *Forecast of binary state diagrams. According to statistical criteria* (Moscow: Metallurgiya) p 326 (in Russian)

[5] Kornilov I I 1974 *Equilibrium metalloid systems//intermetallic compounds* (Moscow: Metallurgiya) pp. 244-279 (in Russian)

[6] Kaufman L 1970 *Stability of crystalline lattices in transition metals//Phase stability in metals* (Moscow: Mir) pp. 134-161 (in Russian)

[7] Goodman D, Bennett L and Watson R 1986 *Tendencies of mutual solubility in alloys of transition metals//Phase diagrams in alloys* (Moscow: Mir) pp. 25-35 (in Russian)

[8] Watson R and Bennett L 1986 *Structural maps and parameters determining the phase stability in alloys//Phase diagrams in alloys* (Moscow: Mir) pp. 36-44 (in Russian)

[9] Coreno-Alonso O and Coreno-Alonso J 2004 Volume size factor and lattice parameter in cubic intermetallics with L12 or B2 structure derived from the “Macroscopic Atom” model *Intermetallics* 12 117-122

[10] Lebedev T A 1951 *Some questions in the general theory of alloys* (Leningrad: newspaper and magazine book) p 136 (in Russian)

[11] Liakishev N P 1996-2000 *State diagrams of binary metallic systems* (Moscow: Mashinostroenie) 1 – 3 (in Russian)

[12] ViUars P and Calvert L D 1985 *Pearson’s Handbook of Crystallography Data for Intermetallic Phases* (Ohio: Metals Park) 1 1332

[13] Zen E J 1934 Validaty of «Vegard Law», *MSA*. 41 523-524