Binary phase diagrams based on elements VIIIA and IB periods of the D.I. Mendeleev's table and features of crystallographic parameters

A I Potekaev[1], A A Klopotov[1,2], S A Porobova[3], V D Klopotov[3], T N Markova[2], M I Imanaliev[2]

[1]Tomsk State University, Tomsk, 634050, 36 Lenina str, Russia
[2]Tomsk State University of Architecture and Building, 634003, Tomsk, 2 Solyanaya Sq., Russia
[3]Tomsk Polytechnic University, Tomsk, 634050, 30 Lenina str, Russia

E-mail: klopotovaa@tsuab.ru

Abstract. The data obtained as a result of the analysis of crystallogeometric parameters and the structure of state diagrams of binary systems from elements VIIIA and IB periods of the D.I. Mendeleev's table are presented. It is shown that the classification of the evolution of phase diagrams of binary systems by types, proposed by T.A. Lebedev, correlates with features of concentration dependences of the deviation of atomic volumes in solid solutions from Zen law.

1. Introduction

The data on phase equilibria and structural-phase states in multicomponent systems is of greatest interest from the perspective of the development of functional materials. To identify common patterns in multicomponent systems it is necessary to obtain them in binary systems. Thus, functional materials based on binary alloys from elements VIIIA and IB periods of the D.I. Mendeleev's table are of keen interest. These alloys exhibit weak lattice resistance in temperature ranges preceding structural phase transitions (SPT) [1, 2].

Increasingly stringent requirements to materials for modern engineering structures require targeted search for systems with new functional properties. The conventional method, based on simple search of alloy-forming elements and alloying additives in multicomponent systems and standard technological methods, is no longer effective. Semi-empirical approach, widely developed in the classic materials science, also has limitations in forecasting new materials with a complex chemical composition. Thus, classical conceptual ideas on methods of designing the properties of new metallic and composite materials have exhausted all possibilities.

On the other hand, the search for general laws can be carried out using conventional classifications of binary and ternary state diagrams. This approach is productive since it reveals typical and special state diagrams. Namely, state diagrams that exhibit of a weak stability of the crystalline lattice in pre-transitional regions prior to phase transitions

It should be noted that the existence of a weak stability of the crystalline lattice in pre-transitional regions prior to phase transitions is manifested in features on temperature dependences of physical and

mechanical properties. These weak-stable states affect features of the change in structural and phase states [3].

The aim of the work is to carry out a search for general laws by analyzing the structure of state diagrams of binary systems from elements VIIIA and IB periods of the D.I. Mendeleev's table and deviations of atomic volumes in solid solutions and ordered phases from Zen law

2. Atomic volume and metallic bond

The metallic bond is usually represented as a bond that arises due to interaction forces of positive ions surrounded by gas of "free" electrons. The presence of free electrons, due to their mobility in the interatomic space, results in high thermal and electrical conductivity. The energy of the crystal with a metallic nature of the bond can be written as [4]:

$$U = -Ae^2 \times \Omega^{-\frac{1}{3}} + B \times \Omega^{-\frac{2}{3}} + Ce^2 \times \Omega^{-1},$$ (1)

where Ω is the atomic volume (volume per atom).

$-Ae^2 \times \Omega^{-\frac{1}{3}}$ this term in the equation (1) is the potential energy of free electrons, $B \times \Omega^{-\frac{2}{3}}$ this term is their kinetic energy, and $Ce^2 \times \Omega^{-1}$ characterizes the kinetic energy of electrons occupying lower energy states. The minimum value of the resulting energy can be related to the linear dimension r_0 that can be considered as the atomic radius $\Omega = \frac{4}{3}\pi r_0^3$.

This expression works well for alkali metals of the subgroup IA. However, for metals of the subgroup IB of the Periodic Table (ie, Cu, Ag, Au) an agreement between the theory and the experiment is not observed. The difference between structures and properties of metals of subgroups IA and IB reflects a phenomenon in which the metallic bond does not limit the number of nearest neighbors in nodes of the crystalline lattice, and that the values of the interaction between electrons and ions can be significantly different [4].

The comparison with the covalent bond shows that the metallic nature of the bond is characterized by the collectivization of electrons that become free, but the number of valence electrons is small (one to three), and CN $\geq$ 8,12 (CN - coordination number). This leads to the fact that all valence electrons can become free [4].

These types of bonds do not normally occur in the pure form. In fact, there is a situation where one type of interatomic bond contributes more to the interatomic interaction. A large number of compounds with a mixed type of bond have been revealed.

Thus, it can be stated that the concept of the representation of atoms in the form of non-compressible solid balls during the formation of crystalline structures that can exhibit different ratio between metal and covalent components in the interatomic interaction can be used in the search for general laws on the qualitative level [5]. On the other hand, the atomic volume affects the conditions of formation of solid solutions and intermetallic compounds.

3. Atomic volume. Zen rule

In binary systems with a continuous series of solid solutions it has been established that the atomic volume of the concentration $\Omega = f(C)$ has a functional dependence close to linear. This phenomenon well manifests itself on the example of solid solutions in systems Au-Ni, Au-Cu, and Cu-Ni [2]. This phenomenon has been formulated in the form of Zen rule [1, 2]:

$$\Omega = C_A \Omega_A + C_B \Omega_B$$ (2)

where C_A, C_B and Ω_A, Ω_B are concentrations and atomic volumes of pure components, respectively. The term "atomic volume" refers to the share Ω of the volume of the unit cell V, per atom ($\Omega = V/n$, n is the number of atoms in the unit cell).

In [6, 7] it has been established that atomic volumes of the same element in the FCC and BCC modification have similar values at the same temperature. The atomic volume of pure metals Ω is a

more universal characteristic than the parameters of unit cells of pure metals. This allows the use of atomic volumes in the search for general laws of structural properties of alloys with solid solutions and with intermetallic compounds formed by elements with different crystalline structures. This approach has been successfully applied in the analysis of binary compounds based on Ti-Ni [1].

It has been established that the strict Zen rule is practically not executed, or executed in very rare cases. Despite these shortcomings, this rule is widely used in the analysis of features of the change in structural parameters from the concentration in various binary systems [1, 2, 6]. The experimentally determined values of average volumes per atom in different systems may be greater or less than those calculated by Zen rule. For the majority of ordered phases a negative deviation from Zen rule is observed. The value

$$\Delta\Omega = \Omega_i^{exp} - \Omega_i^{theor} < 0 \tag{3}$$

characterizes the deviation from Zen rule. The value of the deviation from Zen rule is a nonconfigurational effect and plays a significant role in the stabilization of both ordered and disordered solid solutions, as well as intermediate phases due to the gain in the volume energy. The correlation between the value of the deviation of concentration dependences of atomic volumes from Zen law and Hume-Rothery factors is presented in the literature [7]. In the analysis of changes in the interatomic interaction in solid solutions and intermetallic compounds it is convenient to use the relative value of the deviation of the atomic volume from Zen law:

$$\frac{\Delta\Omega}{\Omega} = \frac{\Omega^{exp} - \Omega^{theor}}{\Omega^{exp}} = 1 - \frac{\Omega^{theor}}{\Omega^{exp}} = \frac{\Delta\Omega}{\Omega^{exp}}.$$

4. State diagrams and features of the interaction of Ag with neighboring elements in the Periodic Table

Silver belongs to metals of the group IB, and by the number of valence electrons in the s-shell of the atom to analogous metals of the group IA. An important point here is the fact that metals of the group IB have completely filled *3d, 4d, 5d* - electronic shells with 10 electrons, and atoms of alkali metals do not have d-peripheral shells. This affects features of the structure of atoms of metals and their physical and chemical properties, and features during the formation of state diagrams (Fig. 1). By the type of the interaction with other elements Ag is similar to its neighbor in the Periodic Table − Cu. However, silver forms continuous series of solid solutions with Pd and Au with a crystalline structure A1 (Fig. 1). Limited solid solutions based on silver usually have higher concentrations than solid solutions based on Ag in
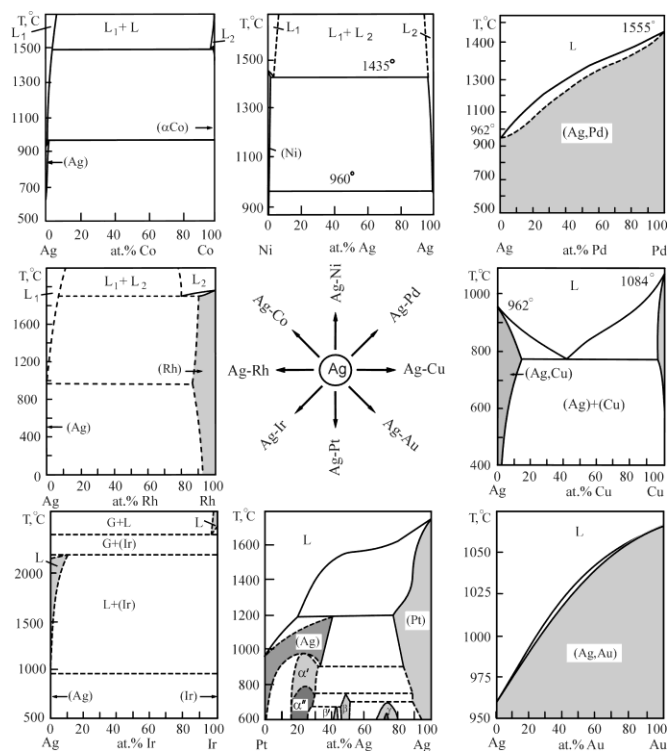

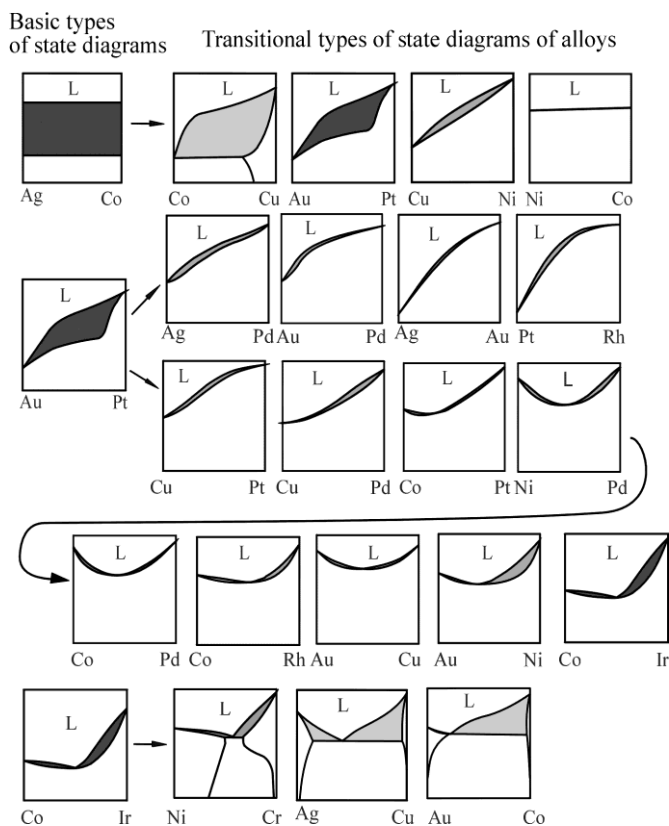**Figure 1.** Phase diagrams of binary compounds based on Ag [4]

Figure 2. The schematic of the evolution of phase diagrams formed by elements VIIIA and IB of the D.I. Mendeleev's periodic table based on the T.A. Lebedev's classification [12]

electronegative metals and nonmetals [10]. Silver practically does not interact with some elements (V, Ta, W, Fe, Ir, C, N).

It is important to note that among all of the systems under consideration only two systems (Ag-Pd and Ag-Au) exhibit the formation of a continuous series of solid solutions during the crystallization from the liquid phase. In these systems, no structural phase transitions are observed at the decrease in the temperature. That is, a disordered solid solution is stable in systems Ag-Pd and Ag-Au in the entire temperature range after the crystallization from the liquid phase.

5. Deviation from Zen law in alloys of binary Ag-based systems

Concentration dependences of the atomic volume in systems Ag-Pd, Ag-Pt, and Ag-Au, obtained from data on lattice parameters of solid solutions and ordered phases, in these systems are shown in Fig. 2. From these diagrams it is evident that in disordered solid solutions in systems Ag-Pd, Ag-Pt, and Ag-Au a slight negative deviation from Zen law is observed. A significant negative deviation of atomic volumes from Zen law is observed in the system Ag-Pt for ordered phases. In Ag-based systems, in which the formation of broad regions of solid solutions is not observed, it is impossible to obtain the dependencies of the atomic volume from the concentration $\Omega = f(C)$ (Fig. 1).

6. Binary state diagrams from elements VIIIA and IB of the Periodic Table and deviations of atomic volumes of concentration dependencies from Zen rule

State diagrams from elements VIIIA and IB of the Periodic Table and deviations of atomic volumes of concentration dependencies from Zen law have been systematized. The analysis of phase diagrams from elements VIIIA and IB periods of the D.I. Mendeleyev's table shall be carried out based on the classification of diagrams proposed by T.A. Lebedev [12]. The classification is based on the change in ratios between the potential energy of interaction U_{AB}, U_{AA}, and U_{BB} between atoms of different types *A* and *B* and the atoms of the same type *AB* and *AB*. Moreover, metallic elements, their solid solutions, and intermetallic compounds typically have two types of bonds: covalent and metallic. It is known that in systems with unlimited solid solutions there are mainly three types of melting curves: 1) with a maximum; 2) monotonically increasing, the "cigar" type; 3) with a minimum (Fig. 1) [1]. A scheme of the evolution of binary state diagrams in solidus and liquidus curves (Fig. 2) has been built in this study (Fig. 1) according to the classification [12].in systems with unlimited solid solutions there are mainly three types of melting curves: 1) with a maximum; 2) monotonically increasing, the "cigar" type; 3) with a minimum (Fig. 1) [1]. A scheme of the evolution of binary state diagrams in solidus and liquidus curves (Fig. 2) has been built in this study (Fig. 1) according to the classification [12].

Moreover, the evolution of binary state diagrams must exhibit a phenomenon caused by a gradual transition from the metallic bond to the covalent bond, depending on the concentration of alloy-forming elements. This reflects the situation that, in most cases, two types of bonds are simultaneously present in the interaction of metal components [4-7]. As consequence, it should appear on concentration dependencies of atomic volumes in binary systems. This is the case in reality (Fig. 3).

The presented in Fig. 2 evolution of state diagrams of the type I under T.A. Lebedev's classification suggests that an increase in the energy of the interatomic interaction between atoms of different kinds *AB* U_{AB} relative to the energy of the interatomic interaction between atoms of the same kind U_{AA} and U_{BB} takes place. At the same time, there is a negative deviation in concentration dependences of atomic volumes from Zen law, which indicates a decrease in the atomic volume in the formation of solid solutions in alloys of the systems under consideration.
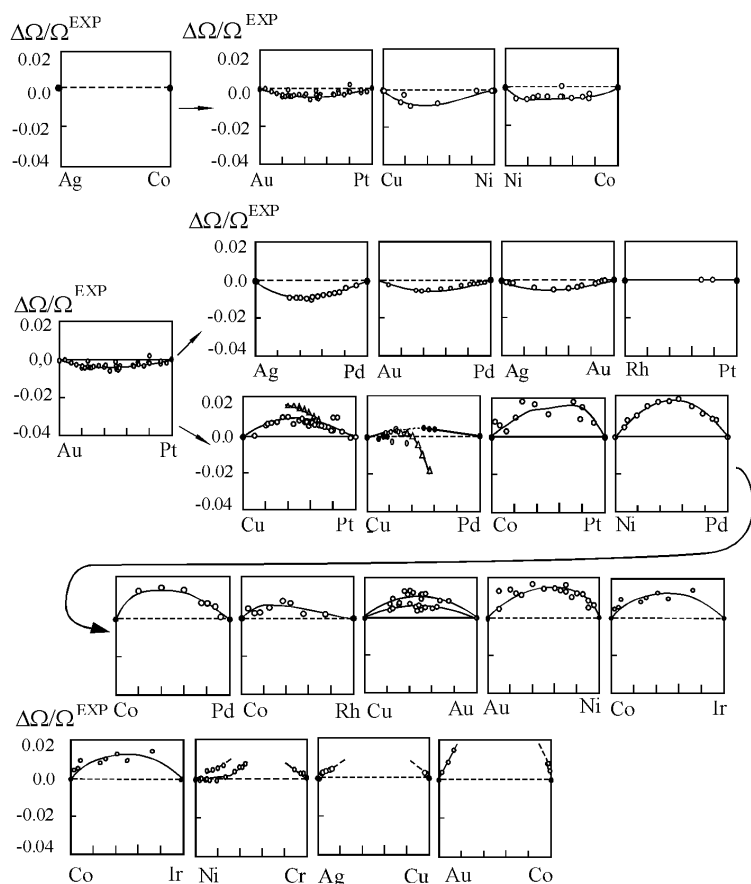

For type II of state diagrams (Fig. 2), the modification of phase diagrams takes place under two scenarios. The first scenario involves the modification of state diagrams due to the fact that the liquidus line goes on rapprochement with the solidus line. In second scenario, the solidus line goes on rapprochement with the liquidus line. Such evolution of state diagrams on solidus and liquidus lines leads to appearance maximum and minimum points.

Type III of state diagrams is represented by a series of state diagrams in which the degree of disintegration of liquid solutions increases to produce, in the end result, a mechanical mixture of pure components.

It is important that the minimum on the diagram of continuous solid solutions (Co-Ir, Fig. 2) cannot be mixed with the eutectic point on phase diagrams. The fact that at the beginning of the given diagram with the eutectic point there is a diagram with the minimum point on solidus and

Figure 3. 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

liquidus curves does not give grounds to identify the minimum point on this diagram with the eutectic point. There is a trend that reflects the process of a possible eutectic formation. This phenomenon is associated with the appropriate prerequisites that a eutectic transformation in the following systems may occur at the place of the unstable.

The distribution of concentration dependences of deviations of atomic volumes in solid solutions and in ordered phases from Zen law in the systems under consideration (Fig. 3) has been built according to the presented location of state diagrams (Fig. 2).

For diagrams of the type I under T.A. Lebedev's classification, only negative deviation of concentration dependences of atomic volumes from Zen law is observed (Fig. 2, 3).

Type II of state diagrams under T.A. Lebedev's classification, is 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 state diagrams (Fig. 3).

Type III of state diagrams, for which the diagram of the system Co-Ir is the basis, is characterized by a positive deviation of atomic volumes in solid solutions from Zen law in places of their existence on state diagrams. At the same time, there is a significant increase in the deviation of atomic volumes from Zen law in regions presiding ruptures of the solubility on phase diagrams (Fig. 3).

7. Conclusion

The analysis of the structure of state diagrams and crystallogeometric parameters has allowed revealing a clear correlation between the type of the evolution of phase diagrams under T.A. Lebedev's classification, depending on the nature of deviations of atomic volumes in solid solutions and in ordered phases from Zen law in systems formed from elements VIIIA and IB periods of the D.I. Mendeleev's table.

Acknowledgement

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