Structure peculiarities of binary state diagrams of vanadium with neighboring elements of Mendeleev’s periodic table

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Abstract. Data on search for correlations between a structure of state diagrams of binary systems based on V-Me (Me = Ti, Zr, Hf, Nb, Ta, Cr, Mo, W) and crystal-geometric and crystal-chemical parameters were presented. Manifestation of both positive and negative deviations in experimental concentration dependences of the atomic volume in solid solutions in systems V-Me (Me = Ti, Nb, Ta, Cr, Mo) from Zen’s law was established. It was found that in the systems with unbounded regions of solid solutions, the deviation from Zen’s law is insignificant. A correlation was found between the types of state diagrams and the difference in atomic volumes of alloy-forming elements in systems V-Me (Me = Ti, Nb, Ta, Cr, Mo).

1. Introduction
At present, heightened requirements have been imposed on reactor plants of Water-Water Energetic Reactor (VVER) type with the view of increasing the life time [1]. The life time extension leads to considerable degradation of the material owing to a damaging effect of thermal and radiation embrittlement. One of the methods to compensate this effect is based on using promising structural materials. The used multicomponent vanadium-based alloys with transition elements from IVA, VA and VIA groups of the Periodic Table pertain specifically to the class of such structural materials aimed at operation in the active nuclear reactor core. Among these alloys, a special place belongs to alloys based on V–Ti–Cr [2–4].

As a rule, alloys used in the current technology are multicomponent. When creating new vanadium-based materials, their phase composition can be predicted proceeding from analysis of the structure of double or triple state diagrams. Therefore, on the one hand, it is necessary to search for regularities in the binary state diagrams with vanadium in formation of intermetallic compounds, solid solutions, eutectics. On the other hand, such studies are fundamental and are aimed at establishing the regularities of influence of different crystal-geometric and thermodynamic factors on stability of structural and phase states in binary systems. Such approach, based on the search for stability conditions of different phases in coordinates “concentration – temperature” and peculiarities of change
in crystal and physical parameters depending on structural and phase states, is often informative [4-10].

It is these alloys of this system that have a number of advantages: low activation ability during radiation exposure, good thermal conductivity, high strength values at temperatures in the range from 400 to 700 °C, as well as sufficiently high radiation resistance during neutron irradiation.

However, high chemical activity of vanadium causes a number of problems of technological nature; therefore, when choosing alloys with vanadium, it is necessary to know the regularities of the structure, properties, and peculiarities of preparing alloys’ ingots and their treatment.

It should be noted that, as alternative materials, alloys based on the V-Ga system are started to be developed as structural materials for thermonuclear reactors; these alloys possess a higher rate of a decrease in induced radioactivity as compared with the alloys of the V–Ti–Cr system. [11-12]

To search purposefully for an optimal composition with required physical-mechanical properties in multicomponent vanadium-based alloys, knowledge about peculiarities of structural and phase states in binary systems based on vanadium is necessary. The study of peculiarities of formation and stability of compounds and solid solutions in vanadium-based alloys with transition elements from IVA, VA, and VI groups of the Periodic Table can be carried out based on analysis of binary state diagrams and crystal-geometric parameters, and it is possible to reveal general regularities, characterizing peculiarities of structural and phase states of alloys.

The paper presents the results of the search for correlation regularities of interrelation between crystal-geometric and crystal-chemical parameters and the structure of state diagrams in binary systems based on V with elements that are the nearest neighbors in Mendeleev’s Table. (Ti, Zr, Hf, Nb, Mo, Ta, Cr, W) and with Ga – an element from the IIIB group.

2. Peculiarities of Interaction between Vanadium and Neighboring Elements in Periodic Table

Different classifications are usually used to analyze the peculiarities of the structure of binary diagrams. A classification of division of state diagrams into three types is generally accepted [10]:

a) systems with absolute solubility of components in both liquid and solid states;

b) systems with limited solubility in a solid state without intermediate metallic compounds;

c) systems with limited solubility of components in a solid state accompanied by formation of one or more compounds.

Quite a lot of attention has been paid to a description of studies of phase and structural transformations in alloys based on V-Me1 and V-Me1-Me2 (Me1—the second element and Me2—the third element) in literature [13-16]. However, the search for correlation regularities in the interrelation between crystal-geometric and crystal-chemical parameters and the structure of state diagrams in binary systems based on V with neighboring elements of Mendeleev’s Periodic Table has been given very little attention [17].

Vanadium belongs to the VA group of transition elements and has properties typical for this group of elements: it has two external s-electrons and three electrons in the unfilled d-shell. Presence of one or two electrons in the outer s-shell characterizes the metallic bond type of atoms. At that, the total number of electrons in s- and d-shells is five (table 1). Such structure of d- and s-electron shells of vanadium atoms determines its mixed valence, which varies from two to five [18]. Such mixed valence leads to the change of atom sizes [19]. This phenomenon exerts a significant influence on the structure of phase diagrams in binary systems based on vanadium.

In combination with most elements, vanadium forms complex systems with a large number of chemical compounds [17, 18, 20]. The number of chemical compounds in binary systems of vanadium with metals from group IIIB is significant. For example, in the V-Ga system, the number of intermetallic compounds reaches five [20]. On the other hand, vanadium forms continuous solid solutions with metals of its group (Nb, Ta) and the VIA group (Cr, Mo, W) (figure 1). All these metals, as well as vanadium, have a body-centered cubic (BCC) structure (Table 1). At the same time, vanadium with elements of another neighboring group – IVA (Zr, Hf), which are part of V-Me1 systems, have bounded regions of solid solutions. In the Hf-V and V-Zr systems, elements Hf and Zr
have (BCC) and hexagonal closely packed (HCP) structures that transform into one another as a result of polymorphic transformation (βHf)→(αHf) and (βZr)→(αZr), correspondingly. This property of Hf and Zr elements leads to violation of one of the formation conditions of continuous series of solid solutions. As a result, peritectic reactions are observed in these systems (figure 1).

Table 1. Electronic structure and structure of alloy-forming elements in systems based on vanadium: V-Me (Me = Ti, Zr, Hf, Nb, Ta, Cr, Mo, W).

| Metal | Electronic structure | R, nm | Pearson symbol /spatial gr. | Structure type in Strukturbericht |
|-------|----------------------|-------|----------------------------|----------------------------------|
| Ti    | [Ar]3d^4s^2         | 0.1462| β-Ti cI/ Im3m               | A2                               |
| Zr    | [Kr]4d^5s^2         | 0.1602| β-Zr hP2/ P63/mmc           | A2                               |
| Hf    | [Xe]4f^45d^6s^2     | 0.1580| β-Hf cI2/ Im3m              | A2                               |
| V     | [Ar]3d^3s^2         | 0.1346| cI2/ Im3m                  | A2                               |
| Nb    | [Ar]4d^5s^1         | 0.1468| cI2/ Im3m                  | A2                               |
| Ta    | [Xe]4f^45d^6s^2     | 0.1467| cI2/ Im3m                  | A2                               |
| Cr    | [Ar]3d^3s^3         | 0.1360| cI2/ Im3m                  | A2                               |
| Mo    | [Kr]4d^5s^1         | 0.1400| cI2/ Im3m                  | A2                               |
| W     | [Xe]4f^45d^6s^2     | 0.1408| cI2/ Im3m                  | A2                               |
| Ni    | [Ar]3d^84s^2        | 0.1246| cF4/ Fm3m                  | A1                               |
| Ga    | [Ar]3d^{10}4s^24p^1 | 0.1411| oC8 /Cmca                 | A11                              |

For a number of elements that form systems with V (table 1), binary alloys correspond very well to the formation conditions of continuous series of solid solutions for metal compounds according to Hume-Rothery [21]:

- crystal lattices, forming an alloy of elements, are of the same type;
- there is atomic similarity among the components, forming compounds – similarity in sizes and electronic atomic structure;
- the type of the chemical bond in compounds is the same.

Under such conditions, calculation of the energy of mixing can be assessed using the following equation:

$$w = U_{AB} - \frac{U_{AA} + U_{BB}}{2}.$$  (1)

In this case, $U_{AB}$, $U_{AA}$ and $U_{BB}$ are potential energies of interaction between the atoms of different sorts A and B and in the atoms of the same sort A and B. Assessment of the energy of mixing under such conditions gives values close to zero, which according to [22] is a necessary condition for solid solutions formation. If the given value becomes substantially positive, then the mutual solubility of the elements, forming the alloy, decreases. If this value becomes substantially negative, then intermetallic compounds are formed either as a result of crystallization from the liquid state or in the course of formation of ordered structures during phase transitions “order–disorder” in the solid state. If the electronic factor predominates over the size one, then the violation of the above-mentioned regularities is possible [23].

Thus, according to the formation conditions of continuous series of solid solutions for metallic compounds according to Hume-Rothery [21], alloy-formation in Nb-V and Ta-V systems leads to formation of unbounded regions of continuous solid solutions (figure 1).

Vanadium also forms continuous solid solutions with other transition metals, with which it is isomorphic, has similar values of atomic radii and electrochemical properties. These are Ti-V, Cr-V, Mo-V, W-V systems.
Figure 1. Phase diagrams of binary compounds based on V [17, 20].

3. Binary phase diagrams in V-based systems with neighboring elements of Mendeleyev's Table

3.1. System Ti-V

In the Ti-V system, it was established that a solid solution (βTi,V) with a content of 30–50 at.% V was not stable. This phenomenon manifested itself during dissociation into two isomorphic solutions based
on (βTi) and (V) after annealing at 500 °C and long-term soakings for about 300 hours [20]. It was established that the solubility of V in (αTi) was of retrograde nature, reaching values of 3.7±3.8 at.% V at 500–600 °C and decreasing to 2.5 at.% V at 400 °C. In the Ti-V system, existence of monotectoid transformation in alloys of the Ti-V system was established at 675 °C. The temperature of the critical point of the bundle curve corresponded to 850 °C with a monotectoid point at 18 at.% The solid solution based on (αTi) was 2.7 at.% V. The monotectoid horizontal extended to 80 at.% V. A minimum in the range of 34 at.% V was observed on the fusibility curve.

3.2. System V-Zr
There are three different reactions in the Zr-V system. The first is eutectic (L↔ZrV₂+(βZr)); the second is a peritectic reaction (L+(V)↔ZrV₂); and the third is eutectoid decay ((βZr) ↔ (αZr) + ZrV₂). The solubility of V in (βZr) is significant and reaches values of 16.5 at.% V at eutectic temperature. The solubility of Zr in vanadium is less significant and reaches values of 5.2 at.% Zr at peritectic temperature. As a result of the peritectic reaction, a ZrV₂ compound with a narrow homogeneity region (1.5–2 at.%) is formed [20].

3.3. System Hf-V
The Hf-V system belongs to the eutectic systems with two eutectic transformations: L↔β(Hf)+HfV₂ and L↔HfV₂. The HfV₂ compound is formed congruently from the liquid state at a temperature of 1550 °C with a narrow homogeneity region. The HfV₂ phase has an insignificant homogeneity region [20].

3.4. Systems Ta-V and Nb-V
Vanadium and its group elements Nb and Ta have the same type of the crystal lattice, similar atomic radii and other similar metal and chemical properties (Table 1). This is reflected in the fact that in systems Ta-V and Nb-V, there is a continuous series of solid solutions among alloy-forming elements (figure 1). A peculiarity of the liquidus and solidus curves in systems Ta-V and Nb-V is the presence of a minimum on these curves at a concentration of 15 at.% Ta and a temperature of 1825 °C and at 22.8 at.%Nb and a temperature of 1810 °C, correspondingly [20]. At a temperature of 1310 °C, compound V₂Ta (β) with a homogeneity region in the concentration range of 32±39 at.% Ta is formed from the solid solution at 900 °C [13].

3.5. Systems Cr-V, Mo-V and W-V
The Cr-V, Mo-V and W-V systems (figure 1) are characterized by absolute solubility of components in
solid and liquid states. In the Cr-V system, on the liquidus curve there is a minimum at a concentration of 30 at. % V and a temperature of 1767 °C [20]. In the Mo-V and W-V systems, the solidus and liquidus curves rise monotonically from vanadium to molybdenum and tungsten; at that, in the Mo-V system, the solidus and liquidus curves have a “cigar-shaped” form. Such type of the fusibility curve indicates that the solid solution can be considered similar to ideal solid regular solutions [24]. The “cigar” is also possible with large positive values of the energy of mixing for a binary alloy in the approximation of nearest neighbors’ interaction (Equation 1).

3.6. System Ga-V
On the phase diagram of the Ga-V system (figure 2), five intermetallic compounds are represented by narrow homogeneity regions [20]. The GaV₃ phase is formed as a result of the congruent solid-phase decomposition of the solid solution (V) with a homogeneity region of 67±78 at. % in the temperature range of 950-1100 °C. The Ga₅V₆ compound is formed by the peritectoid reaction at high temperatures [20]. The Ga₇V₆ phase is formed by the peritectic reaction and decomposes eutectoidally at 1020 °C into Ga₃V₆ and Ga₅V₅ phases.

4. Deviation from Zen’s law and packing index in alloys of V-based systems with neighboring elements of Mendeleev’s Table
To search for general regularities, let us use an approach based on the analysis of a number of crystal-geometric factors: the size factor is \( \delta = R_A/R_B \) (where \( R_A \) and \( R_B \) – radii of atoms of A and B sort in binary alloys) [21, 23]; the concentration dependence of the deviation value on the linear dependence of the atomic volume is \( \Delta \Omega/\Omega_{exp} = (\Omega_{exp} - \Omega_2)/\Omega_{exp} \) (Zen’s law [23, 25]), etc. In this case, \( \Omega_{exp} \) – atomic volume (per atom in an elementary cell), determined from experimental data based on calculation of atomic diameters (obtained from the shortest distances between atoms in structures). \( \Omega_2 \) is atomic volume in Zen’s law. A parameter (packing parameter) that characterizes crystal structures is space fill factor \( \psi \) [23]. To analyze the density of filling the space with atoms of different crystal structures, let us use packing index \( \psi \) proposed by Laves-Partet [23]. A detailed description of application of these parameters is given in [25].

Figures 3 and 4 show the concentration dependences of the atomic volume and deviations from Zen’s law in solid solutions and in intermetallic compounds, accordingly. In the Mo-V system, there was practically full coincidence of the experimental concentration dependence of the atomic volume in solid solutions with Zen’s law. In the Nb-V and Ta-V systems, a positive deviation from Zen’s law was found. In the Ti-V and Cr-V systems, a negative deviation from Zen’s law was detected.

Among the systems under study, a maximum value of the positive deviation from Zen’s law in solid solutions is observed in the Ta-V system, which reaches a value of 0.037.

Figure 5 shows data obtained when determining packing coefficient \( \Psi \) in the system under consideration. It is obvious that in all other systems, values of packing coefficient are lower than \( \Psi \) values for structures with the BCC lattice, consisting of similar spheres. It is possible that this is due to mixed valence of the elements being alloy-forming in these systems [19, 23]. An exception is the Ti-V system. For the V-Zr and V-W systems, no experimental data on concentration dependences of parameters of the lattice in solid solutions, based on the BCC lattice, have been found in the literature.

In contrast to systems based on V with neighboring elements of Mendeleev’s Table, a significant negative deviation of the atomic volume from Zen’s law in intermetallic compounds was observed in the Ga-V system (figure 2 b, c). The maximum deviation reaches a very significant value of ~ 0.14. It should be noted that in this system, the region of solid solutions based on vanadium is very narrow at low temperatures (about 4±5 at.% Ga) (figure 2 a).
5. Deviation from Zen’s law and packing index in alloys of the Ga-V system

A phase diagram of the Ga-V system, which contains singular points determined by formation of a broad spectrum of compounds: GaV₃, Ga₃V₆, Ga₂V₆, Ga₅V₆ and Ga₅V₂, Ga₄V₈, is of particular interest [20] (Figure 2a). A number of things should be noted. In the Ga-V system, the largest deviation in the concentration dependence of the atomic volume from Zen’s law is observed in the region of the non-equiaxial Ga₅V₂ composition.

Calculated concentration dependences of the packing index (based on experimental values of lattice parameters [20]) in Ga₅V₆ compounds are in the region of higher values than dependences for the BCC structure made of atoms of one kind (Figure 2d). Among Ga₅V₆ compounds, compound
Ga$_3$V$_2$ (Pearson spatial group – $tP14$, Schoenflies one – $P4/mmb$, a prototype – Hg$_3$Mn$_2$) has the largest value.

This correlation between singular points on the phase diagram of the Ga-V system and high values of $\psi$ reflects an increase of interatomic interaction forces and a growth of covalent and ionic components of interaction among atoms relatively the metal one.

Thus, in the Ga-V system, five intermetallic compounds are formed directly from the liquid state. Singularities of liquidus curves on the state diagram correlate with significant deviations of atomic volumes by concentration dependences from the values of Zen’s law and in a significant increase of the packing index up to values $\psi \approx 0.7$ in intermetallic compounds.

![Diagrams showing deviation from Zen’s law in binary systems based on V](image)

**Figure 4.** Diagrams showing deviation from Zen’s law in binary systems based on V [17, 20, 26, 27].

6. **Crystal-geometric and thermodynamic factors and peculiarities of phase diagrams of vanadium-based systems**

To search for general regularities during analysis of binary state diagrams of the systems based on vanadium: V-Me (Me = Ti, Zr, Hf, Nb, Mo, Ta, Cr, W) and in the V-Ga system, let us use thermodynamic (entropy $n_S$ and temperature $n_T$ factors), dimensional (that of total volume $n_0$) and combined ($4n_T^2 + n_0^2$) factors [28].

The entropy factor is determined by the equation:

$$n_S = \frac{S_A}{S_B}$$  \hspace{1cm} (2)

where $S_A$ and $S_B$ are fusion entropies of elements A and B.

The temperature factor is:
where $T_A < T_B$—melting temperatures of elements A and B.

Total bulk factor $n_0$, according to V.M. Vozdvizhinskiy [28], represents a sum of three components:

$$n_0 = n_{\Omega} + b_{EF} = [(n_{\Omega})^3 - 1] + (n_{\Omega} - 1) + b_{EF},$$

(4)

$$b_{EF} = b_{MAX}[1 - n_{\Omega}],$$

(5)

$$b_{MAX} = 0.75 \times (U_{EF,A} - U_{EF,B}) = 0.75 \times \Delta U_{EF},$$

(6)

In this case, $U_{EF,A}$ and $U_{EF,B}$—effective ionization potentials of elements of A and B sorts, accordingly; $n_{\Omega}$—volumetric and $n_B$—size factors. Individual figures should normally be centred, but place two figures side-by-side if they fit comfortably like this as it saves space.

**Figure 5.** Concentration dependences of packing index in binary systems based on V.

In [28], an expression, determining threshold values of entropy factor $n_s$ during formation of unbounded solid solutions in binary systems, was established: $n_s \leq 1.10$. Calculation results of $n_s$ of binary systems based on vanadium V–Me (Me=Ti, Zr, Hf, Nb, Mo, Ta, Cr, W) are presented in Table 2. Analysis of $n_s$ values implies that in all the systems under consideration with $n_s \leq 1.10$, it is possible to form unbounded solid solutions.
Thus, in the systems under consideration, values of the entropy factor are within the limits determined by the threshold value of formation of unbounded solid solutions in binary systems (table 2 and figure 1). This statement is based on the fact that the use of entropy factor \( n_\text{S} \) is based on the established correlation between the fraction of the covalent (or metallic) bond and the value of fusion entropy. This is clearly manifested in the value of the entropy factor of the Ga–V system (table 2). In this system, \( n_\text{S}>1.10 \) and, correspondingly, the regions of solid solutions are very limited (figure 2 and table 2). Such value of the entropy factor reflects different values of contribution to interatomic interaction, depending on bond types. In this case, value \( n_\text{S}=1.95 \) of entropy factor is evidence of the predominant contribution of covalent and ionic bond types to interatomic interaction. At the same time, it is known that in distribution of electron density in transition metals when retaining predominantly a metallic bond, there is a tendency to form homeopolar bridges, which, correspondingly, leads to an increase of the entropy of fusion \( S_\text{f} \) [18]. It should be noted that among the systems under consideration, there are state diagrams that do not obey this regularity, established on the basis of statistical treatment of a large number of binary systems [18]. In our case, these are the V-Zr and V-Hf systems.

The temperature factor is used when searching for regularities in the structure of state diagrams since it reflects the influence of the interatomic interaction type and is also responsible for the view of separate fragments of the state diagram. The temperature factor influences the relative position of the liquidus and the solidus. With increasing temperature factor \( n_\text{T} \), the maximum distance between the liquidus and the solidus increases. In fact, in the Ti-V and Cr-V systems, the liquidus and solidus lines on the state diagrams are very similar, and the values of temperature factor \( n_\text{T} \) have low values of 0.1 and 0.01, accordingly (table 2). In the Nb-V, Ta-V, Mo-V and W-V systems, in which the liquidus and solidus lines on the state diagrams are far from each other, temperature factor \( n_\text{T} \) takes on higher values from 0.21 to 0.41 (table 2). In various variants, \( n_\text{T} \) is used when analyzing the regularities of the state diagram structure [28]. Analysis of the values of the temperature factor, given in Table 2, and the view of the state diagrams does not allow establishing regularities.

Table 3 shows crystal-chemical and crystal-geometric parameters for the state diagrams with bounded solid solutions. It is obvious that parameters values \( n_\text{S} \), \( n_\text{T} \), and \( 4n_\text{T}^2 + n_\text{0}^2 \), obtained for the Ga-V system, differ significantly from the values for all others in the systems under consideration. Such difference is due to the fact that contribution of metallic bonds decreases and that of the covalent increases [28]. The value of bulk factor \( n_\text{0} \) in the Ga-V system is in the range of average values given in tables 2 and 3.

It was shown in [28] that a promising approach for the analysis of state diagrams is the use of bulk factor \( n_\text{b} \), which includes two types of dimensional parameters \( n_\text{b} \) and \( n_\text{13} \). In the full bulk factor (expressions 4–6), there is information about a number of components. First of all, there is information about crystallographic dimensions of atoms (\( n_\text{b} \)) and atomic volume, in which atomic mass and density of components (\( \Omega = M_\Lambda / \rho_\Lambda \), \( M_\Lambda \) – atomic mass, \( \rho_\Lambda \) – density of the material from the element of A sort) are implicitly contained. In addition, there is information on the energy of electrons of a valence band and ion sizes (\( U_{\text{eff}} \)). Since all these data are reduced to one characteristic, it becomes possible to search for general regularities relatively other factors, for instance, a temperature one. For that, a statistical graph is used in coordinates \( n_\text{T}–n_\text{0} \) [28]. In Figure 6, each system is denoted by a corresponding point. The experimental points are located inside the region, limited by coordinate axes and the ellipse arc (curve II in figure 6), and correspond to systems, in which a continuous series of solid solutions is formed. The exception is the V-W system, which does not fall within a region, limited by a quarter of the ellipse. In the V-Hf and V-Zr systems, in which there are significant discontinuities in solubility, the points, corresponding to these systems, on the diagram in coordinates \( n_\text{T} \) and \( n_\text{0} \) are outside the region limited by a quarter of the ellipse (figure 6). The dashed line represents the regions, in which systems can fall due to inaccuracy in values of physical and chemical quantities. The ellipse equation in coordinates \( n_\text{T}–n_\text{0} \) can be represented in the form of [28]:

\[
\text{Equation for ellipse}
\]
This expression implies the necessary condition for formation of systems with continuous solid solutions. According to [27], this condition (equation 7) can be represented in the form of inequality:

$$4n_T^2 + n_0^2 \leq 1.$$  \hspace{1cm} (8)

The expression (equation 8) has a physical meaning, which consists in the fact that when the interatomic interaction values of the components differ substantially, which occurs under condition that $n_T > 0.5$; the components do not form a continuous solid solution, but tend to separate into isolated phases.

Parabolic dependence $n_T = n_0^2$ (curve I in figure 6) is the boundary between two types of shapes of solidus-liquidus lines. To the left of the parabola, there are the points of the diagrams, in which the “cigar-shaped” solidus-liquid lines are observed. This type of fusibility diagrams indicates that solid solutions in these systems can be considered close to ideal solid regular solutions [24, 28]. The “cigar-shaped” appearance of solidus-liquidus lines is possible also at large positive values of energy of mixing $w$ for a binary alloy in the approximation of the nearest neighbors’ interaction. For the considered V-based systems, two systems that are located near this line actually have a “cigar-shaped” appearance of solidus-liquidus lines. These are the Ta-V and Mo-V systems. At the same time, near curve I in Figure 6, there are points corresponding to the Ti-V and Cr-V diagrams.

**Table 2.** Entropy, temperature, bulk and combined factors for state diagrams with unbounded solid solutions

| Factors | Ti-V | Nb-V | Cr-V | Mo-V | Ta-V | W-V |
|---------|------|------|------|------|------|------|
| $n_S$   | 0.97 | 0.96 | 1.04 | 0.98 | 0.98 | 0.59 |
| $n_T$   | 0.015| 0.212| 0.014| 0.253| 0.339| 0.413|
| $n_0$   | 0.097| 0.906| 0.158| 0.628| 0.635| 1.08 |
| $4n_T^2 + n_0^2$ | 1.679| 1.892| 1.326| 1.527| 2.158| 2.545|

The parameter that distinguishes the Zr-V, Hf-V and Ga-V systems with bounded regions of continuous series of solid solutions from the systems with unbounded regions is combined parameter $4n_T^2 + n_0^2$. This parameter for the Zr-V, Hf-V and Ga-V systems has values over 2.5, which exceeds the corresponding values in the systems with unbounded regions of continuous series of solid solutions.

**Table 3.** Entropy, temperature, bulk and combined factors for state diagrams with bounded solid solutions

| Factors | Zr-V | Hf-V | Ga-V |
|---------|------|------|------|
| $n_S$   | 0.94 | 0.93 | 1.95 |
| $n_T$   | 0.016| 0.137| 0.86 |
| $n_0$   | 1.745| 1.541| 0.419|
| $4n_T^2 + n_0^2$ | 2.84 | 2.686| 3.453|

\[ \frac{n_T^2 + n_0^2}{0.5^2 + 1.0^2} = 1. \]  \hspace{1cm} (7)
Investigation of the relationship between the deviation of the atomic volume from Zen’s law and the space fill factor in the systems under study was carried out using a diagram in coordinates $\psi$ and $\Delta \Omega/\Omega_{\text{exp}}$ (figure 7). In this diagram, it is possible to identify three regions. The first region includes points of alloys in the Ta-V system. These points are obtained on the basis of the concentration dependence of the lattice parameter in the solid solution in the Ta-V system. In this system (figure 4), the deviations of the atomic volume relatively Zen’s law $\Delta \Omega/\Omega_{\text{exp}}$ have positive values. The second region (the most numerous one), in which the points in the diagram tend to locate in the form of linear dependence of parameter $\psi$ on $\Delta \Omega/\Omega_{\text{exp}}$ (Figure 7). In this region, the established line functional relation reflects the fact that for compounds and solid solutions of these systems, the size factor during formation plays an important role. And it is in these alloys that atoms can be represented as hard spheres. The third region is formed by points that are obtained from compounds with HCP structures and to which higher values of packing indices than those in solid solutions based on the BCC lattice correspond. There are few such compounds and they occupy a small region, which is in the space of positive values of deviations of atomic volume relatively Zen’s law.

Figure 6. Statistical graph for V-based systems with neighboring elements of Mendeleev’s Table and systems Ga-Me (V-Me (Me=Ti, Zr, Hf, V, Nb, Mo, Ta, Cr, W))
Figure 7. Dependence of packing index on deviation of atomic volume from Zen’s law

In compounds with the HCP structure, violation of line dependence $\psi$ on $\Delta \Omega / \Omega_{\text{exp}}$ manifests itself (figure 7). This is evidence of the fact that in these compounds, it is not allowed using a representation of atoms in the form of rigid spheres to describe their properties. Thus, the study of the interrelation between the values of deviations of the atomic volume relatively Zen's law and the space fill factor in compounds and solid solutions allows identifying such alloys and compounds in which atoms are represented in the form of rigid spheres.

7. Conclusion

The search for correlations between the structure of state diagrams of binary systems based on V-Me (Me = Ti, Zr, Hf, Nb, Ta, Cr, Mo, W) and crystal-geometric and crystal-chemical parameters was presented. The manifestation of both positive and negative deviations in the experimental concentration dependences of the atomic volume in solid solutions in systems V-Me (Me = Ti, Nb, Ta, Cr, Mo) from Zen’s law was established. It was found that in systems with unbounded regions of solid solutions, the deviation from Zen's law was insignificant. A correlation between the types of state diagrams and the difference among atomic volumes of alloy-forming elements in systems V-Me (Me = Ti, Nb, Ta, Cr, Mo) was revealed.

The performed calculation of concentration dependences of atomic volumes allowed establishing the manifestation of both positive and negative deviations in the experimental concentration dependences of the atomic volume in solid solutions in systems V-Me (Me = Ti, Nb, Ta, Cr, Mo) from Zen’s law.

The conducted analysis allowed establishing a number of regularities. In binary systems based on vanadium, in which state diagrams have bounded regions of solid solutions, total bulk factor $n_0$ has values greater than two ($n_0>2$). In vanadium-based systems with unbounded regions of solid solutions, it is $n_0<2$ and the entropy factor is $n_s<1$. The exception is the V-W system. In this system, $n_0>1$ and $n_s<1$. Such atypical combination of values of the total bulk and entropy factors may be evidence of the presence of unique physical and mechanical properties in alloys based on V-W.

The presented results of the search for correlations between the crystal-geometric parameters and peculiarities of structural and phase states in alloys based on V-Me (Me= Ti, Zr, Hf, Nb, Ta, Cr, Mo, W, Ga) showed that it was most advisable to use total bulk factor $n_0$, representing a sum of three components: effective ionization potentials of alloy able elements, bulk and size factors. Threshold values of total bulk factor $n_0$ during formation of unbounded solid solutions in binary systems were $n_s \leq 1.10$. 
Based on the analysis of crystal-geometric and crystal-chemical parameters of solid solutions and intermetallic compounds in systems made from elements of the IVA-VIA group of Mendeleev’s Table, a characteristic combination of values of packing indices, temperature, entropy and total bulk factors was revealed.

It is advisable to use a number of factors (entropy ($n_3$), temperature ($n_1$), total bulk ($n_0$), combined ($4n_1^2 + n_0^2$) factors), deviations of the concentration dependence from Zen’s law $\Delta\Omega/\Omega_{exp}$ and packing index ($\psi$) as crystal-geometric and thermodynamic parameters to search for general regularities of the structure of binary vanadium-based systems. Such approach to analysis of relations of these parameters and the structure of state diagrams of binary vanadium-based systems is promising for identifying characteristic features of their behavior under different types of influence (during deformation, heating, under irradiation).

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