Structure feature of ternary state diagrams of Cr-Ti-V and Cr-Mn-V systems

Anatoliy Klopotov^{1,2*}, Irina Kurzina¹, Alexander Potekaev¹, Artem Ustinov^{1,2}, Taras Dement^{1,2},
Ludmila Kazantseva¹, Ekaterina Marchenko¹, and Natalia Karakchieva^{1,3}

¹National Research Tomsk State University, 634050, Tomsk, Russia

²Tomsk State University of Architecture and Building, 634003, Tomsk, Russia

³Siberian Research Institute of Agriculture and Peat – branch of the Siberian Federal Scientific Center of Agro Bio Technologies of the Russian Academy of Sciences, 634050, Tomsk, Russia

Abstract. This paper presents the research results of features of structural and phase states in Cr-Ti-V and Cr-Mn-V systems based on analysis of crystal-geometric and crystal-chemical factors. The diagrams of isothermal sections of state diagrams of Cr-Ti-V and Cr-Mn-V systems were built in coordinates of the electron number ($s+d$) per atom with homogeneity regions of solid solutions and intermetallic compounds. It was shown that in the Cr-Ti-V system, addition of Mn atoms leads to substantial extension of the existence domain of the disordered solid solution based on the BCC lattice.

1 Introduction

At present, approaches aimed at creation of materials resistant to radiation embrittlement are being developed in metalphysics. This is related to the fact that in reactor construction, a strategy in creation of materials for the operation of reactor plants of VVEP type throughout 60 years was developed [1]. Solution of this task is connected to creation of structural materials resistant to radiation exposure. This class of materials includes Cr-Ti-V-based alloys [2-5]. Therefore, research on the study of peculiarities of structural and phase states based on analysis of crystal-geometric parameters in solid solutions and intermetallic compounds in the Cr-Ti-V system is of importance. Creation of metallic multicomponent high-entropic alloys (HEAs) based on Cr-Ti-V alloys is of interest from the standpoint of creation of radiation-resistant materials. This is related to the fact that high-entropic alloys possess delayed diffusion of element atoms, which is accompanied by their cooperative transition. This phenomenon impedes the decomposition of substitutional solid solutions and prevents from creation of new phases [6-8]. The composition of alloys of this class includes heterogeneous atoms of elements with a different electronic structure, sizes and thermodynamic properties. The number of elements, included in high-entropic alloys, is usually about 5-10. At the same time, in the burdening composition, they are usually in the equiatomic ratio. Such chemical composition contributes to substantial distortion of the crystal lattice of alloys [7, 8]. In these alloys, high entropy of mixing of elements is considered as a measure of probability of

preserving their structural and phase state in [9-11]. In high-entropic alloys, the presence of a set of mentioned factors contributes to increased thermal stability of structural and phase states and, as a consequence, of high mechanical, physical and chemical properties [9-11]. The composition of multicomponent high-entropic alloys usually includes elements which are within the 4th and 5th periods of the Periodic system of elements (Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zr, Nb and Mo) with valence (sd)-electrons. Therefore, in the framework of the approach, transformation of alloys in the Cr-Ti-V system in high-entropic alloys, it is of interest to research what influence additional Mn alloying can exert on structural-phase states of one-phase alloys (Cr, Mn, Ti, V.) in a disordered state based on the BCC lattice. Earlier to search for regularities when studying peculiarities of structural and phase states in binary and ternary systems, the authors used an approach based on analysis of crystal-geometric and crystal-chemical characteristics of metallic compounds and solid solutions [12-15]. The purpose of this paper is to present the results of researching the features of structural and phase states in ternary Cr-Ti-V and Cr-Mn-V systems based on the analysis of binary state diagrams, forming them, and crystal-geometric and crystal-chemical factors.

2 Methods and Materials

To search of the regularities of structural and phase states in binary and ternary systems, the authors used an approach based on analysis of crystal-geometric and crystal-chemical characteristics of metallic compounds and solid solutions [12-15]. It was investigated the state

*Corresponding author: klopotovaa@tsuab.ru

diagram of Cr-Ti, Cr-V, Ti-Cr, Cr-Mn, Cr-V, Mn-V, Cr-Ti-V and Cr-Mn-V systems.

3 Results and Discussion

3.1 State diagram of Cr-Ti, Cr-V, Ti-Cr, Cr-Mn, Cr-V, Mn-V, Cr-Ti-V and Cr-Mn-V systems

A peculiarity of the binary and ternary systems under consideration is conditioned by the electronic structure of alloy-forming elements and a dimensional factor. The electronic structure and the structure of alloy-forming elements and their crystal structures in these systems are given in the Table 1.

Table 1. The electronic structure and the structure of alloy-forming elements in Cr-Ti-V and Cr-Mn-V systems.

Metal	Electronic structure	Valency	R, nm	Phase, Pearson symbol /spatial group	Structure type in Strukturbericht
Ti	[Ar]3d ² 4s ²	4	0.1462	β -Ti, <i>cI2/Im3m</i> α -Ti, <i>hP2/P6₃/mmc</i>	A2 A3
V	[Ar]3d ³ 4s ²	5	0.1346	<i>cI2/ cI2/Im3m</i>	A2
Cr	[Ar]3d ⁵ 4s ¹	3 6	0.1360 0.1282	<i>cI2/ Im3m</i>	A2
Mn	[Ar]3d ⁵ 4s ²	4 6	0.1360 0.1264	α Mn, <i>I43m/ cI58</i> β Mn, <i>P4₁32/ cP20</i> γ Mn, <i>Fm3m/ cF4</i> δ Mn, <i>cI2/ Im3m</i>	A12 A13 A1 A2

Ti-V system

In the Ti-V system, it was established that the solid solution (β Ti, V) with the content of 30–50 at.% V is unstable. This phenomenon manifests itself during decay into two isomorphous solutions based on (β Ti) and (V) after annealing at 500 °C and long-term soakings for about 300 hours [16]. It was established that solubility of V in (α Ti) is of retrograde nature, reaching the 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, the existence of monotectoid transformation in the alloys of the Ti-V system at 675 °C was established. The temperature of the critical point of layering curve corresponds to 850 °C with a monotectoid point at 18 at.%. The (α Ti)-based solid solution amounts to 2.7 at.% V. The monotectoid horizontal extends to 80 at.% V. The minimum within 34 at.% V is observed on the meltability curve.

Cr-V system

The Cr-V system (Figure 1) is characterised by unlimited solubility of components in solid and liquid states. In the Cr-V system, on the liquidus curve there is a minimum within 30 at. % V and the temperature of 1767 °C [16].

Fig. 1. Binary state diagrams of Cr-Ti, Cr-V, Ti-V systems [17] and isothermal sections of the ternary Cr– Ti–V system at the temperature of 500°C. Figures denote two-phase and three-phase regions in isothermal triangle Cr-Ti-V: 1 – $\lambda_2 + \beta$ -(Cr,Ti,V); 2 – $\lambda_2 + \alpha + \beta$ -(Cr,Ti,V); 3 – $\alpha + \beta$ -(Cr,Ti,V); 4 – $\lambda_2 + \alpha$ [18].

Cr-Ti system

On the phase diagram of the Ti-Cr system, there is a continuous dissolution of titanium and chromium in the liquid state accompanied by formation of solid solutions (β -Ti, Cr) in the wide homogeneity region. The main transformations in the Ti-Cr system occur in a solid state. In the region of the TiCr_2 composition, intermediate phases are formed with a structure of Laves phases C14 (prototype - MgZn_2), C15 (MgCu_2) and C36 (MgNi_2). The high-temperature modification of Laves phases C36 (λ_1) forms congruently from the solid solution (β -Ti, Cr) at a temperature of 1370 °C.

With the temperature decrease below 1270 °C, high-temperature phase C36 (λ_1) transforms into medium-temperature Laves phase C14 (λ_2). The low-temperature modification of Laves phase C15 (λ_3) forms according to a peritectoid reaction from Laves phase C14 (λ_2) and from (β -Ti, Cr) at a temperature of ~1220 °C. In the Ti-Cr system, there are two eutectoid reactions of decay of the solid solution (β -Ti, Cr) and Laves phase C14 [16, 17].

Cr-Mn system

In the Cr-Mn system, manganese allotropy complicates the state diagram on the part of manganese. Existence of different polymorphic forms of crystal structures based on Mn (α Mn), (β Mn), (γ Mn) and (δ Mn)), a wide homogeneity region of the solid solution based on Cr

and two intermediate phases $\alpha(\text{CrMn}_2)$ and $\sigma(\text{CrMn}_3)$ were revealed [16].

Cr-Ti-V system

Figure 1 presents an isothermal section of the Cr-Ti-V system at 500 °C [18]. On the isothermal triangle in this system, one vast region of a three-component solid solution, based on the disordered BCC lattice, can be easily revealed: $\beta(\text{Cr,Ti,V})$. In the base of formation of this region, there is a binary system, the components of which are miscible in all proportions in each other. The size of the region of the three-component solid solution (Cr,Ti,V) is limited by the extent of corresponding regions of solid solutions in binary systems Cr-Ti and Ti-V. Along the Ti-V side of the isothermal triangle, this region is limited by the concentration to ~40 at.% V. On the Cr-Ti side of the isothermal triangle, there is a bounded region of ternary compounds based on Laves phases. Also inside the isothermal triangle, there is vast two-phase region from Laves phase λ_2 and solid solution $\beta(\text{Cr,Ti,V})$.

In [19], it is shown that one of the main factors influencing the stability of the structural and phase state of alloys is their electronic structure. A parameter that characterises the electronic structure of alloys is electronic concentration. At the same time, according to [19], the electronic concentration of the alloy depends on the electronic structure of alloy-forming elements. Therefore, to analyse it, the authors use isothermal sections of state diagrams of ternary systems in coordinates of the number of electrons ($s+d$) per atom (Figure 2). The value of electronic concentration ($s+d$) of alloy electrons was calculated as an arithmetic mean value of valence electrons of all individual alloy-forming elements.

Fig. 2. Isothermal sections of state diagrams of Cr-Ti-V (a) and Mn-Ti-V (b) systems in coordinates of the number of ($s+d$) electrons per atom with homogeneity regions of solid solutions and intermetallic compounds. Classification of structures in the diagram is given according to Strukturbericht.

In the Cr-Ti-V system, in the vast region of values of electronic concentration from 4.4 to 6 electron/atom, there is a bounded region of the unbounded three-

component solid solution (Cr, Ti, V) based on the disordered BCC lattice with the A2 structure (Figure 2).

In Figure 2, the diagram shows that in the Ti-Cr system in the concentration region of 5.3 electron/atom, Laves phases form in different temperature ranges (Figure 1). At the same time, addition of V atoms suppresses Laves phases' formation.

Cr-Mn-V system

The isothermal section of the ternary Cr-Mn-V system is given in Figure 3 at a temperature of 25 °C [20].

Fig. 3. Binary state diagrams of Cr-Mn, Cr-V, Mn-V systems [16] and isothermal section of the ternary Cr-Mn-V system at the temperature of 25 °C [20].

In this system, two regions with well-defined regions of homogeneity manifest themselves vividly. This is a region of the three-component solid solution (Cr, Mn, V) based on the disordered BCC lattice, which occupies a significant part of the isothermal triangle and leans on the Cr-V side of the isothermal triangle. Another region belongs to the three-component compound with a σ -phase structure ($tP30$, $P42/mnm$, prototype σCrFe). The three-component intermetallic compound of the σ -phase has a narrow homogeneity region and forms based on binary compounds on two sides Cr-Mn and Mn-V of the isothermal triangle based on binary compounds CrMn_3 and CrV_3 (Figure 3).

The diagram in Figure 2 shows that in the Cr-Mn-V system in the concentration region from 5 electron/atom to 6.2 electron/atom, there is a disordered solid solution (Cr, Mn, V).

Replacement of Ti atoms by Mn atoms during transition from the Cr-Ti-V system to the Cr-Mn-V system extends substantially the region of existence of the disordered solid solution based on the BCC lattice in the (Cr,V) Mn_3 alloys. In (Cr, V) Mn_3 alloys the electronic concentration of 6.6–6.8 electron/atom, leads to formation of the three-component region of existence of the σ -phase with the $D8_b$ structure (Figure 2, b).

In the Cr-Mn-V systems with electronic concentration values from 4.4 to 6 electron/atom, there is a region of the unbounded three-component solid solution (Cr, Mn, V) based on the disordered BCC lattice with the A2 structure (Figure 2). A three-component compound with the σ -phase structure in the form of a narrow homogeneity region forms on two sides Cr-Mn and Cr-V of the isothermal triangle with the electronic concentration of 6.6÷6.8 electron/atom.

Compounds with the σ -phase possess wide and narrow regions of homogeneity [21]. The uniqueness of the σ -phase consists in the fact that this phase has no strict stoichiometric composition and this manifests itself by the presence of different stoichiometric compositions in this phase: AB (FeV), A₂B (Mn₂Mo), A₃B (Mn₃Cr) and A₄B (Mn₄V). The formation processes and stability of compounds with the σ -phase are influenced by dimensional and electronic factors. On the one hand, the decisive role belongs to the dimensional factor, on the other – to the electronic factor [22]. With the change in the electronic concentration, the composition of this phase changes from AB₃ to A₂B. The σ -phase formation is also significantly influenced by the electronic configuration of forming components [23].

3.2 Crystal-geometric and thermodynamic factors and features of state diagrams of Cr-Ti-V and Cr-Mn-Ti systems

To search for common regularities when analysing the state diagrams of the systems, dimensional (δ) and entropic (nS) factors were used [13-14, 24].

The dimensional factor was determined by the formula by means of the expression:

$$\delta = 1 - R_B/R_A, \quad (1)$$

where R_A and R_B – atom radii of grade A and B.

The role of the relative sizes of atoms when forming structural and phase states in ternary systems Cr-Ti-V and Cr-Mn-Ti was determined by means of diagrams shown in Figure 4. According to Hume-Rothery [25, 26], formation of unbounded solid solutions is possible with dimensional factor $\delta < 0.15$. The dimensional factor was determined by the formula using expression $\delta = 1 - R_B/R_A$ (R_A and R_B – atom radii of grade A and B). These diagrams show that the dimensional factor is favourable for formation of unbounded solid solutions in the systems under consideration. Nevertheless, in the Cr-Ti, Cr-Mn and Mn-V systems, there is formation of compounds from disordered solid solutions, and decay is observed in the Ti-V system.

Of the two ternary systems Cr-Ti-V and Cr-Mn-Ti, the Cr-Mn-Ti system is the most favourable for formation of unbounded solid solutions. This is reflected in more extensive regions of unbounded solid solutions in isothermal triangles (Figure 1-3). Therefore, additional alloying of alloys of the Cr-Ti-V system by Mn atoms in the vanadium angle of the isothermal triangle enables extension of the region of four-component unbounded solid solutions (Cr, Mn, Ti, V).

Fig. 4. Diagrams, reflecting contributions of the dimensional factor in binary systems into the sizes of the homogeneity regions of solid solutions in ternary Cr-Ti-V (a) and Cr-Mn-V (b) systems.

As per the data given in the table 1 and conditions of formation of continuous series of solid solutions for metallic compounds, according to Hume-Rothery [25, 26], alloy formation in the considered systems leads to formation of unbounded regions of continuous solid solutions and this finds confirmation in the state diagrams (Figure 1).

The parameter that reflects the change in the bond type is the entropy of melting S_{mel} [24]. Since the entropy of component melting reflects the destruction degree of the long-range order during a phase transition from solid solution to liquid, the elements and compounds with a valency bond have greater entropy of melting than the elements and compounds with a metallic bond. This parameter is applicable for the analysis of state diagrams of ternary systems Cr-Ti-V and Cr-Mn-Ti.

The entropy factor was determined using the expression:

$$nS = S_A/S_B, \quad (2)$$

where S_A and S_B are entropies of melting of A and B elements.

Specific threshold values n_s , determining the opportunity of a certain type of interaction were defined in [24]. For ternary state diagrams, the condition of formation of unbounded solid solutions can be written in the form of the following inequalities:

$$\begin{aligned} n_{S1} &= S_A/S_B \leq 1.10, \\ n_{S2} &= S_A/S_C \leq 1.10, \\ n_{S3} &= S_B/S_C \leq 1.10. \end{aligned} \quad (3)$$

In this case S_A , S_B and S_C are entropies of elements A, B and C accordingly.

The values of the entropy factor when forming structural-phase states in ternary systems Cr-Ti-V and Cr-Mn-Ti were determined by means of the diagrams shown in Figure 5.

The mentioned diagrams demonstrate that the entropic factor for the elements, forming the analysed systems, is less than the threshold value of 1.10. Thus, in the ternary Cr-Ti-V and Cr-Mn-Ti systems, the values of the entropy factor are within the limits that are favourable for formation of unbounded solid solutions in binary systems. But, nevertheless, intermediate phases form in the Cr-Ti, Cr-Mn, Mn-V systems, and in the Ti-V system there is a decay into two isomorphous solutions. All this is evidence of significant influence of the

electronic factor on stability of structural-phase states in these systems.

Fig. 5. Diagrams characterising the entropic factor in binary Cr-V, Ti-V, Cr-Ti (a) and Cr-Mn, Cr-V, Mn-V (b) systems.

The presence of intermediate phases in the Cr-Ti, Cr-Mn, Mn-V systems and the presence of decay into two isomorphous solutions in the Ti-V system are evidence of a significant influence of the electronic factor on the structural and phase states in alloys of these systems.

Conclusion

A search for correlations among the structure of state diagrams of binary systems, based on V-Me (Me=Cr, Mn, Ti), and ternary state diagrams Cr-Ti-V and Cr-Mn-V, and crystal-geometric and crystal-chemical parameters was carried out. It was established that only in the binary Cr-V system, the main parameters exerting a dominating influence on the formation of unbounded regions of solid solutions, based on the disordered BCC lattice, are the dimensional and entropic parameters. In binary Cr-Ti, Cr-Mn, Ti-Mn systems and ternary Cr-Ti-V, Cr-Mn-V systems, the influence of the electronic factor on the sizes of regions of unbounded solid solutions, based on the disordered BCC lattice, increases.

In one-phase alloys in the Cr-Ti-V system, it is possible to obtain increased thermal stability of the structural-phase composition by additional Mn alloying. It is necessary to note that transfer of meaning of disordered alloys (Cr, Mn, Ti, V), based on the BCC lattice, to the class of multicomponent high-entropic alloys is possible owing to additional introduction of Mn, as well as elements from IV, V and VI groups of Mendeleev's periodic system, into their composition.

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