PHASE TRANSFORMATIONS

Computational Methods for Determining Martensitic Transformation Characteristics in Binary and Multicomponent Functional Materials

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The theory of evolutionary algorithms for predicting crystal structures allows to calculate the maximum content of the second alloying component in binary materials, at which martensitic transformation can take place. As calculated, in the alloys of the Zr–Nb system the formation of the martensitic phase is possible up to 20 at.% Nb, while for the Hf–Nb system the maximum concentration of Nb is 35 at.%. A new physical parameter is proposed—the specific doping force, which determines the degree of influence of several alloying elements on the characteristic temperatures of martensitic transformation by estimating their corresponding electron concentration and its features.

Key words: Zr–Nb, Hf–Nb, martensitic transformation, program USPEX.

Теорія еволюційних алгоритмів для передбачення кристалічних структур дозволяє розрахувати максимальний вміст другого леґувального компонента в бінарних матеріялах, за якого може мати місце мартенситне перетворення. Розраховано, що в стопах системи Zr–Nb утворення мартенситної фази можливе до 20 ат.% Nb, у той час як для системи Hf–Nb максимальна концентрація Nb становить 35 ат.%. Запропоновано новий фізичний параметр — питому силу леґування, яка визначає ступінь впливу декількох леґувальних елементів на характеристичні температури мартенситного перетворення шляхом оцінки відповідної їм електронної концентрації та її особливостей (якщо такі є).

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The study of the martensitic transformation (MT) characteristics below the temperature of liquid nitrogen is technologically complicated. Therefore, to estimate the maximum concentration of niobium at which MT is possible ($M_s \rightarrow 0$ K), and to study all possible stable and metastable structures of the Zr–Nb and Hf–Nb systems, calculations using the USPEX program on the MIPT supercomputer cluster are carried out [1–5]. The calculations used a supercell consisting of a maximum of 50 atoms. The calculation is performed for a temperature of 0 K. In the first generation, 80 structures of any composition, from pure zirconium or hafnium to pure niobium, are randomly created. Each of the next 59 generations consisted of 50 structures created by 30%, 30%, 20% and 20% with the help of heredity operators, the algorithm for creating random structures, soft mutation and transmutation, respectively. The obtained structures are relaxed using the VASP package [6–8], using the generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof [9]. To regard the inner shell electrons used the Projector augmented-wave method (PAW) [10, 11]. The trimming energy is 700 eV. A grid with a resolution of $2\pi \cdot 0.05$ Å^{-1} in the centre of the first Brillouin zone is used. To determine the stability of the obtained structures a thermodynamic construction of a convex hull is used, a graph showing the thermodynamic stability. If the structure is on the convex hull, it is stable, if above it—metastable.

Figure 1 shows a calculated energy distribution graph of the formation of various structures that the program created during the simulation of the Zr–Nb system. It is obvious that most structures with a large enthalpy of formation are impossible under normal conditions in macrocrystals. In the framework of this task, we are interested in structures with a hexagonal syngony of minimum energy that can correspond to the martensitic phase in the alloys of the Zr–Nb system. Compositions with such hcp or distorted hcp structures in the simulated data are observed up to 20 at.% of Nb. In Figure 1 they are highlighted in dark grey colour.

To predict the properties of material during doping of Zr with niobium in an amount of less than 20 at.%, We consider a new physical parameter—the specific doping force, the essence of which will be presented below.

One of the most important characteristics of functional materials is the operating temperature of the demonstration of unusual properties. The main way to manage it is to change the chemical composition of the material. The choice of the required content of elements can be made

empirically, experimentally determining the dependence of the characteristic temperatures of martensitic transformation on the concentration (atomic or weight) of a particular element. Another way to control the transformation temperatures involves calculating the electron concentration of the material and comparing the results with data on the stability of a structure. Such studies are of particular interest in terms of the development of multicomponent and high entropy alloys.

One of the first researchers who drew attention to the relationship between the stability of different structures with the number of valence electrons per atom (e/a) is Pettifor [12], who calculated the difference in the energies of b.c.c., h.c.p., and f.c.c. structures depending on the parameter e/a for pure metals (Fig. 2). We are interested in the range of values of 4.2 el./at., where there is a phase instability between the bcc and hcp structures.

One of the parameters used to measure the effect of valence electrons on the transformation of martensitic phases is the ratio of the concentration of valence electrons to the total number of electrons in the alloy (c_v). This value is obtained by dividing the number of valence electrons of the atom (e_v) by the total number of electrons. In the case of an alloy, the expressions of these values are given in equations (1) and (2) [13], which represent the weighted average value of valence
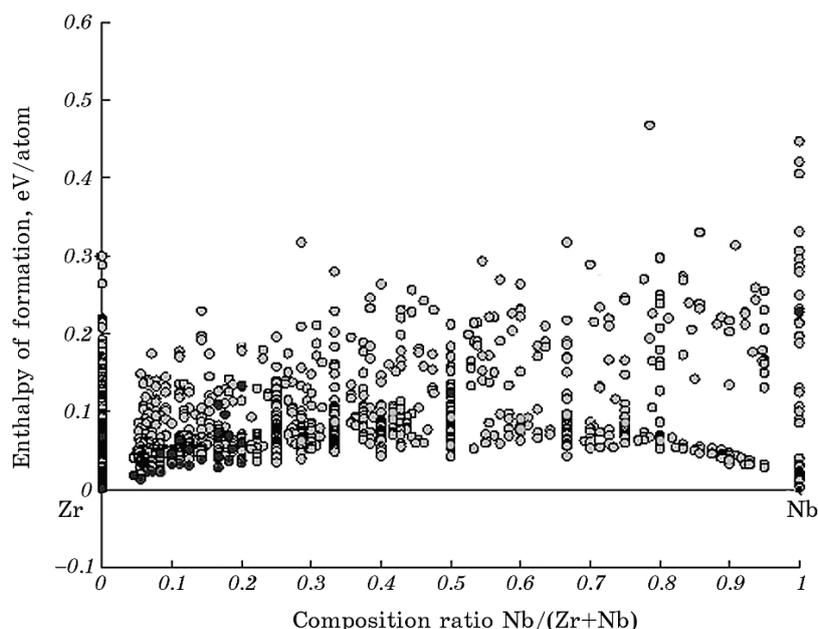

Fig. 1. Formation enthalpy of various structures for the Zr−Nb system depending on the concentration of elements. The h.c.p. structures are highlighted in dark grey colour.
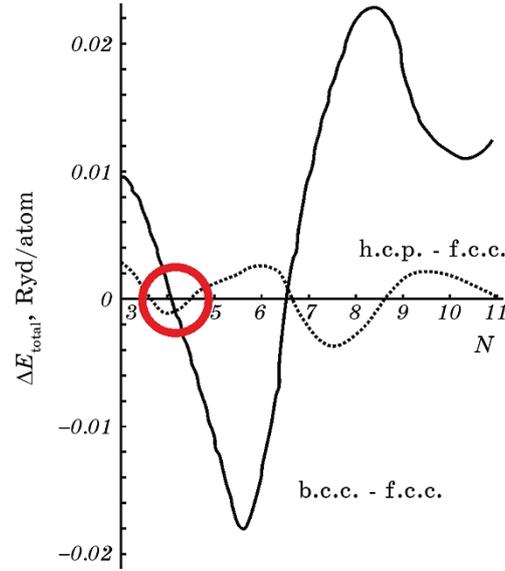
Fig. 2. The differences in total energy between the b.c.c., h.c.p., and f.c.c. structures [12].

electrons relative to the atomic fraction of each element in the alloy.

$$\frac{e_v}{\text{atom}} = f_{m1}e_v^{m1} + f_{m2}e_v^{m2} + f_{m3}e_v^{m3} + f_{m4}e_v^{m4} + \ldots + f_n e_v^n. \tag{1}$$

$$c_v = \frac{e_v}{e_t} = \frac{e_v}{f_{m1}Z^{m1} + f_{m2}Z^{m2} + f_{m3}Z^{m3} + f_{m4}Z^{m4} + \ldots + f_n Z^n}. \tag{2}$$

Alloys of Ti, Zr and Hf with niobium belong to the group of materials with 'low concentration of valence electrons' (<5 el./at.) [13]. Table 1 shows the data about Zr−Nb, Hf−Nb alloys and calculated their electron concentration at which martensitic transformation is possible.

Thus, the maximum concentration of niobium at which is possible the occurrence of MT in the alloys of the Zr−Nb system is 20 at.%. That is, the start temperature of the direct MT in Zr−Nb alloys in the

TABLE 1. Valence electrons concentration of Zr−Nb and Hf−Nb alloys.

Alloy	Range of e_v/at., where MT is possible	Range of c_v, where MT is possible	Range of possible MT temperatures, K	The structure of the martensitic phase
Zr−Nb	4−4.2	0.1−0.104	1130−0	h.c.p.
Hf−Nb	4−4.35	0.056−007	2010−0	h.c.p.

concentration range from pure zirconium to $Zr_{80}Nb_{20}$ will decrease to 0 K. In the first approximation, the change in MT temperature with increasing of valence electron concentration by 0.01 is '−57 K'. This parameter we will call the 'specific doping force'. It makes it possible to evaluate the effect of an individual element on the functional properties of the entire material system due to changes in the electron concentration. The obtained data correlate with our interpolated to low temperatures experimental results on the study of MT in Zr−Nb alloys. It should also be noted that the result of estimating the maximum concentration of niobium in 20 at.% coincides with the literature data [14], where similar simulations are performed, but by other methods using the program WIEN2k [15].

Figure 3 shows a calculated energy distribution graph of the formation of various structures, which the program USPEX created during the simulation of the Hf−Nb system. The nature of the behaviour of the martensitic phase formation for this system is similar to the Zr−Nb system. However, the presence of f-electrons in the Hf element makes its adjustments. For example, the temperature of the beginning of MT in pure hafnium is more than 1740°C. In the simulated structures, compositions with a potential hcp martensitic structure are observed at niobium concentrations up to 35 at.%.
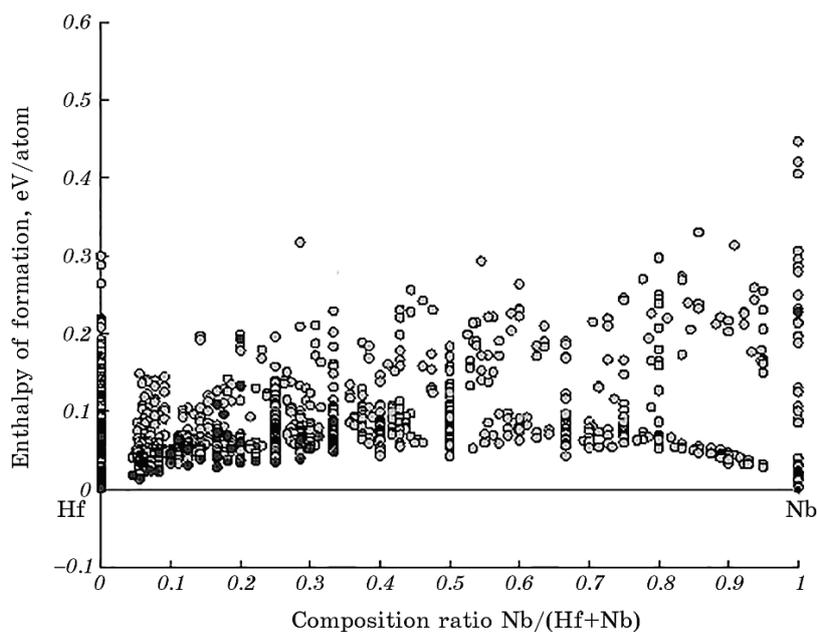

Fig. 3. Formation enthalpy of various structures for the Hf−Nb system depending on the concentration of elements. The h.c.p. structures are highlighted in dark grey colour.

Thus, the effect of niobium on the temperature of MT in the Hf−Nb system is '−57 K/at.%'.

The literature does not consider the issue of such modelling of MT in alloys of the Hf−Nb system. However, our experimental results indicate the presence of MT in the $Hf_{75}Nb_{25}$ alloy, and its absence in the alloy $Hf_{50}Nb_{50}$. Extrapolation of the dependence of experimentally determined MT characteristic temperatures on the concentration of niobium to 0 K does not contradict the data obtained in the USPEX program.

To predict the temperature range of MT in the manufacture of binary alloys of Zr−Nb and Hf−Nb systems, the following formulas can be used:

$$M_s(\text{Zr}) = 1130 - 57^* C_{\text{Nb}},$$

$$M_s(\text{Hf}) = 2010 - 57^* C_{\text{Nb}},$$

where M_s—direct MT start temperature, C_{Nb}—niobium concentration in at.%.

CONCLUSION

Using computer simulation methods of the USPEX program, the effect of niobium doping on the MT characteristic temperatures in alloys of Zr−Nb, Hf−Nb systems is evaluated and the maximum value of niobium concentration at which the MT can flow in these alloys is determined. For alloys of the Zr−Nb system, the formation of the martensitic phase is possible up to 20 at.% Nb, while for the Hf−Nb system, the maximum concentration of Nb is 35 at.%. A method for estimating the anticipated temperatures of MT in the manufacture of binary alloys of Zr−Nb and Hf−Nb systems is proposed.

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