Calculation of the $P–T$ phase diagram and tendency toward decomposition in equiatomic TiZr alloy

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Abstract

Electronic, structural and thermodynamic properties of the equiatomic alloy TiZr are calculated within the electron density functional theory and the Debye–Grüneisen model. The calculated values of the lattice parameters $a$ and $c/a$ agree well with the experimental data for the $α$, $ω$ and $β$ phases. The $ω$ phase is shown to be stable at atmospheric pressure and low temperatures; it remains energetically preferable up to $T = 600$ K. The $α$ phase of the TiZr alloy becomes stable in the range $600$ K $< T < 900$ K, and the $β$ phase at temperatures above $900$ K. The constructed phase diagram qualitatively agrees with the experimental data available. The tendency toward decomposition in the equiatomic alloy $ω$-TiZr is studied. It is shown that in the ground state the $ω$ phase of the ordered equiatomic alloy TiZr exhibits a tendency toward ordering, rather than decomposition.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Technologies of fabrication of up-to-date devices based on the use of promising materials require a deep insight into the physical processes occurring on the atomic level. This is of particular importance when using new materials designed to operate in conditions of extremely high temperatures and pressures. The use of first-principles methods for theoretical study and prediction of the physical properties of a substance under different external conditions is a promising approach to optimizing the process of fabrication of materials with desired properties.

The sequence of structural transformations in crystals experimentally observed under pressure at low temperatures may be determined by analyzing the variation with pressure of the ground-state energy calculated from first principles within the density functional theory (DFT) for different crystalline structures. For theoretical description of high-temperature phase transitions, the energy of lattice vibrations and the system entropy should be additionally taken into account. In harmonic crystals the phonon spectra can be calculated in the DFT linear response approximation [1]. In such systems the problem of determining the structural stability and constructing the $P–T$ phase diagrams may be solved entirely from first principles, while in the presence of strongly anharmonic vibrations simple ab initio methods for calculating the lattice energy are lacking. A number of DFT-based techniques have been recently developed for theoretical description of the structural $P–T$ phase diagrams in strongly anharmonic monatomic metals [2–5]. In the case of polyatomic systems the DFT calculation of the lattice vibration contribution to the free energy is a complicated task, and the study of structural stability of such systems is based, as a rule, only on a comparison of the total energies without regard for the lattice vibrations.

In multicomponent systems, in addition to ordinary structural transformations due to the change in the lattice, there may occur processes of decomposition or ordering with no change of the lattice type. As a result, on the $P–T$ phase diagram areas appear in which decomposition processes are observed. Such systems may be exemplified by the equiatomic alloy TiZr. Experimentally, the structural stability of the TiZr alloy was investigated in [6–8]. From the theoretical standpoint the equiatomic TiZr alloy is of interest because its elemental
constituents Ti and Zr are similar in electron structure. The TiZr phase diagram resembles to a great extent the phase diagrams of pure Ti and Zr. The distinctive feature of Ti and Zr is that in these metals the high-temperature lattice vibrations are of evidently strongly anharmonic character which substantially determines the $P$–$T$ diagram and the mechanism of structural transformations. The presence of a strongly anharmonicity can be hypothesized with a high probability in the TiZr alloy too. Theoretical studies of the TiZr properties may prove useful for a better understanding of the role of strongly anharmonic vibrations in structural phase transitions.

It has been experimentally found that the TiZr system is characterized by full solubility of its constituents. As in pure titanium and zirconium, three phases ($\alpha$, $\beta$ and $\omega$) are observed in the TiZr alloy [6–8]. The structural $\alpha$–$\beta$ transformations of the equiatomic TiZr alloy were extensively studied in [6] by differential thermal analysis (DTA) at temperatures up to 1023 K, and pressures up to 7 GPa. It was found that the $\beta$–$\alpha$ transition temperature, being equal to 852 K at atmospheric pressure, decreases with pressure down to the triple $\alpha$–$\beta$–$\omega$ equilibrium point ($P_e = 4.9 \pm 0.3$ GPa, $T_e = 733 \pm 30$ K). At pressures above the triple point the $\beta$ phase transforms immediately to the $\omega$ phase with a slight positive slope of the equilibrium line. If a sample is cooled to room temperature at a pressure of 6 GPa, and then unloaded, one can obtain at atmospheric pressure a metastable $\omega$ phase which on heating transforms into an $\alpha$ phase in the temperature interval from 698 to 743 K. Cooling of the $\beta$ phase in the pressure range 2.8–4.8 GPa results in the formation of a two-phase mixture of a stable $\alpha$ and a metastable $\omega$ phase. The structural $\alpha$ – $\omega$ transformations in the TiZr alloy were studied in detail in [8]. Investigating TiZr samples under shear-strain conditions at pressures up to 9 GPa, and temperatures of 300 and 77 K, the authors arrived at the conclusion that in equiatomic TiZr the equilibrium $\alpha$–$\omega$ boundary is situated on the $P$–$T$ diagram at 6.6 GPa. In the same paper the phase diagram of TiZr was constructed in the regular-solution approximation, and the triple point parameters were calculated ($P = 8.5$ GPa, $T = 693$ K). As may be seen, these values differ substantially from those obtained in [6].

Detailed studies performed in [9] have shown that in the region of high pressures and temperatures two $\omega$ phases exist that differ in atomic volume by about 14%. The authors suggested the existence of an isostructural transformation connected with changes in the electron structure of the alloy. They supposed that the large difference in the atomic volume between the two phases points to the existence of an s–d electronic transition in $\omega$-TiZr. Later, phase separation of a hexagonal TiZr $\omega$ phase was experimentally detected in [10]. The $\omega \rightarrow \omega_1 + \omega_2$ decomposition was revealed after a prolonged heat treatment at $P = 5.5 \pm 0.6$ GPa and $T = 440 \pm 30$°C. It was supposed that in a wide concentration range at pressures above the triple equilibrium point, the $\omega$ phase may exist in the Ti$_2$Zr$_{1-x}$ alloy only as a metastable one that persists due to low diffusive mobility of its constituents. The decomposition of the $\omega$-TiZr solid solution into two $\omega$ phases of different structure was used as an alternative explanation for the experimental results obtained in [9].

### Table 1. Equilibrium values of the TiZr lattice parameters in atomic units.

| Phase | $a_{\text{calc}}$ | $(c/a)_{\text{calc}}$ | $a_{\text{exp}}$ | $(c/a)_{\text{exp}}$ |
|-------|------------------|---------------------|-----------------|---------------------|
| $\beta$ | 6.457 ± 0.001 | 1.00 ± 0.001 | 6.457 ± 0.001 | 1.00 ± 0.001 |
| $\alpha$ | 5.860 ± 0.001 | 1.583 ± 0.001 | 5.866 ± 0.001 | 1.583 ± 0.001 |
| $\omega$ | 9.122 ± 0.001 | 0.617 ± 0.001 | 9.152 ± 0.001 | 0.617 ± 0.001 |

Up to now the electron structure and structural transformations of the equiatomic alloy TiZr have never been calculated. Below we present the results of our theoretical calculations of electronic, structural and thermodynamic properties of the equiatomic alloy TiZr performed within the framework of the electron density functional theory and the Debye–Gruneisen model. The tendency of the ordered equiatomic alloy $\omega$-TiZr to decompose is also investigated.

### 1.1. Calculation technique

The electron structure and total energy were calculated by the scalar relativistic full-potential linearized augmented-plane-wave (FPLAPW) method, using the WIEN2K package [11] with a GGA exchange–correlation potential [12]. In a paper [2] we have shown that the choice of an LDA or a GGA representation for the exchange–correlation potential has a considerable effect on the Zr phase diagram. The calculations performed in [2, 13] demonstrated that the GGA potential approximation allows one to construct the phase diagrams of pure titanium and zirconium in good agreement with experiment. To ensure the desired accuracy of the total energy calculation, the number of plane waves was defined by the condition $Rk_{\text{max}} = 7$, the total number of $k$-points in the Brillouin zone was equal to 3000, 3000 and 600 for the $\beta$, $\alpha$ and $\omega$ phases, respectively. The total and partial densities of states were obtained by a modified tetrahedron method [14]. The atomic radii were the same for all phases and pressures: 2.42 au for Zr, and 2.26 au for Ti.

In figure 1 the crystal structures of the $\beta$, $\alpha$, and $\omega$ phases of the equiatomic alloy TiZr used in the calculation are shown. It is seen that the $\beta$ phase was represented by a structure of the CsCl type with Zr atoms at the cube sites and a Ti atom at the center. The $\alpha$ phase had a hexagonal close-packed lattice in which one atom was Zr, the other Ti. Finally, to describe the $\omega$ phase we used a hexagonal lattice with six atoms per cell (an $\omega$ lattice doubled along the $z$ axis). The atomic arrangement and species in this case were chosen as follows: (0, 0, 0)-Zr, $(1 \frac{1}{2}, 1 \frac{1}{2}, 1 \frac{1}{2})$-Ti, $(1 \frac{1}{2}, 1 \frac{1}{2}, 1 \frac{1}{2})$-Zr, (0, 0, $\frac{1}{2}$)-Ti, $(1 \frac{1}{2}, 1 \frac{1}{2}, \frac{3}{2})$-Zr, $(\frac{1}{2}, \frac{3}{2}, \frac{3}{2})$-Zr. Thus, the $\beta$ and $\alpha$ phases were represented by layers of Ti and Zr alternating along the $z$ axis, and in the $\omega$ phase layers of Ti and Zr were separated by mixed Ti–Zr layers.

In the hexagonal structures the ratio $c/a$ was optimized for the experimental volume values. In the following, when calculating the volume dependence of the total energy, the $c/a$ ratio was considered to be constant. The calculated and experimental equilibrium values of the TiZr lattice parameters are listed in table 1.

It is seen from the table that the lattice parameters $a$ and $c/a$ obtained in our calculation agree well with the
Figure 1. Crystal structure of the $\beta$, $\alpha$ and $\omega$ phases of equiatomic TiZr alloy. The Zr atoms are shown as gray, the Ti atoms are shown dark.

Figure 2. Volume dependence of the total energy of equiatomic TiZr alloy for the $\beta$, $\alpha$ and $\omega$ phases.

Experimental data. The greatest discrepancy is observed for the lattice constant of the $\omega$ phase. It should be noted, however, that in [6] the lattice parameters were calculated for a metastable $\omega$ structure at atmospheric pressure, and in [8] for pressure-strained samples.

The total energy of each structure was calculated for seven values of the cell volume $V$. The data obtained were then interpolated using the technique proposed by Moruzzi [15]. Such an interpolation scheme, together with the Debye–Grüneisen model, makes it possible to include anharmonic effects implicitly. The curves obtained for the volume dependence of the electron subsystem total energy are shown in figure 2 where the energy zero corresponds to $-8906.0$ Ryd.

As seen from the figure, the energy minimum in the ground state falls on the $\omega$ phase, and only at the volume value $V = 15.8 \text{ Å}^3$ does the $\beta$ phase become energetically preferable. A similar situation was also observed in pure Ti and Zr. However the difference in energy between the $\alpha$ and $\omega$ phases in TiZr is $\Delta E_{\alpha-\omega} = 6$ mRyd, while in pure Ti and Zr it amounts to only 0.8 mRyd and 1 mRyd, respectively. Hence it follows that in the equiatomic alloy TiZr the stability region of the $\omega$ phase should be much higher in temperature than in the pure metals Ti and Zr. The equilibrium values of the volume are $V_{\alpha} = 20.47 \text{ Å}^3$, $20.52 \text{ Å}^3$, and $19.97 \text{ Å}^3$ for the $\alpha$, $\omega$ and $\beta$ phases, respectively.

Figure 3 presents the volume dependence of the free energy at different temperatures and zero pressure. The free energy of the TiZr alloy was calculated in the Debye–Grüneisen model with allowance made for the contributions from the electron entropy. The technique for calculating the latter has been described in detail in [16].

The free energy $F(V, T)$ was calculated, for a given value of temperature $T$ and volume $V$, in the adiabatic approximation of noninteracting electrons and phonons:

$$F(V, T) = E_e(V) - T S_e(V, T) + E_D(V, T) - T S_D(V, T).$$

(1)

Here $E_e(V)$ is the total energy of the electron subsystem in the ground state, $E_D$ and $S_D$ are the lattice energy and entropy in the Debye model. The electron entropy $S_e$ was calculated from the density of electron states and the Fermi–Dirac distribution function.
The Debye temperature $\Theta_D(T, V)$ was defined as follows [15]:

$$\Theta_D = K \frac{h}{k_B} \left( \frac{48\pi^5}{5} \right)^{1/6} \sqrt{\frac{r_0 B}{M}},$$

where $r_0$ is the Wigner–Seitz equilibrium radius, $M$ is the atomic mass of the element. The energy derivatives necessary for calculating the bulk modulus $B = -V \partial P/\partial V$ and pressure $P = -\partial E(V)/\partial V$ were found using the analytical expressions obtained from an interpolating four-parameter exponential Morse function [15] constructed on a discrete set of $E(V)$ values.

As seen from figure 3, the relationship between the energies of different structures changes with temperature. So, at 300 K the energy minimum falls, as in the ground state, on the $\omega$ phase which remains energetically preferable up to $T = 600$ K. In the temperature range $600$ K $< T < 900$ K it is the $\alpha$ phase of TiZr which becomes stable, while above 900 K it is the $\beta$ phase.

2. Phase diagram

The phase diagram of TiZr based on the analysis of the Gibbs potentials ($G = F + PV$) for different modifications of the TiZr alloy is presented in figure 4. The calculation results are shown by the solid line. The dotted line denotes the experimental equilibrium boundaries for the $\alpha$, $\beta$ and $\omega$ phases of TiZr obtained in [6]. The experimental values for the $\alpha \rightarrow \omega$ transition at room temperature are taken from [7, 8], and for the $\omega \rightarrow \beta$ transition from [7].

On the whole, a good agreement of the calculated triple point ($P_{\text{theor}} = 4.2$ GPa, $T_{\text{theor}} = 720$ K) with the experimental values $P_{\text{exp}} = 4.9 \pm 0.3$ GPa, $T_{\text{exp}} = 733 \pm 30$ K [6] is observed. At zero pressure the calculated temperature of the
\( \beta \rightarrow \alpha \) transition is \( T_{\beta \rightarrow \alpha}^{\text{theor}} = 943 \) K. This value is higher than the experimental one, \( T_{\beta \rightarrow \alpha}^{\exp} = 852 \) K, defined in [6] as the average of the temperatures of the transition onset on heating and cooling. It should be noted that a significant hysteresis is observed upon the \( \omega \rightarrow \beta \) transformation in TiZr. At atmospheric pressure the maxima of thermal peaks in the DTA curves fall on \( T \sim 912 \) K on heating and \( T \sim 810 \) K on cooling, the typical peak width being \( \Delta T \sim 40 \) K. With this in mind, one can consider the calculation results of the \( \omega \rightarrow \beta \) equilibrium boundary in the Debye–Grüneisen model as quite satisfactory.

The greatest discrepancy between the theoretical calculation and the experimental evidence available is observed for the \( \alpha \rightarrow \omega \) transition. In [8] the pressure at which this transition occurs at room temperature was estimated to be \( P_{\alpha \rightarrow \omega} = 6.6 \) GPa. Note that the equilibrium point of the \( \alpha \) and \( \omega \) phases was determined under shear-strain conditions at pressures up to 9 GPa, although the shearing strain is known to lower the pressure at which the phase transition begins. In [7] it was shown by the x-ray diffraction method that the \( \alpha \) phase of TiZr remains the sole stable phase under quasi-hydrostatic pressure up to 12.2 GPa. Only from 15.5 GPa on, does the \( \omega \) phase which remains stable up to 56.9 GPa become dominant. At pressures above 56.9 GPa a high-pressure phase forms with a bcc lattice.

As seen from figure 4, in the calculation at atmospheric pressure and moderate (up to 610 K) temperatures the \( \omega \) phase is stable, and hence no \( \alpha \rightarrow \omega \) transition occurs at room temperature. Note that in our calculations of pure Ti [13] and Zr [2], in complete agreement with the experimental data, the \( \alpha \) phase is stable at atmospheric pressure and room temperature, and the \( \omega \) phase is stable only under pressure. That the \( \omega \) phase in TiZr at normal conditions is energetically preferable immediately follows from a comparison of the calculated free energies (see figure 3). Recall that the difference in energy between the \( \alpha \) and \( \omega \) structures in the equiatomic TiZr alloy is almost five times greater than in pure titanium and zirconium.

The discrepancy between experiment and theory may be due to the fact that the calculation was performed for ideal crystalline structures (see figure 1), whereas the experimental samples were imperfect crystals with defects. In particular, the \( \omega \) phase in the TiZr alloy shear-strained under pressure was shown [8] to be represented by aggregations of oblong particles with characteristic size of 3–5 nm, and 15–30 nm long. If \( \omega \)-phase particles are situated in a coarse grain of \( \alpha \) phase, they are mainly located at its boundaries. It was also noted [6] that the different state of imperfect structure in samples pre-treated in different ways has a noticeable effect on the course of structural transformations. Evidently, we could not model a real imperfect structure with first-principles calculations.

The correctness of our results may be supported by the following experimental evidence [6]: firstly, the metastable \( \omega \) phase was obtained at atmospheric pressure as a result of cooling of the \( \beta \) phase under a pressure of 6 GPa with subsequent unloading at room temperature. Secondly, between 2.2 and 4.8 GPa, on cooling of the \( \beta \) phase a two-phase mixture of a stable \( \alpha \) and a metastable \( \omega \) phase formed. And lastly, it was found that at atmospheric pressure the \( \omega \) phase in the TiZr alloy, when heated above 698 K, transforms into an \( \alpha \) phase [6]. In [8] the temperature of this transformation was defined as \( T = 623 \) K at \( P = 0.1 \) MPa. This value differs only by 13 K from the temperature \( T_{\omega \rightarrow \alpha}^{\exp} = 610 \) K we have calculated for the \( \omega \rightarrow \alpha \) transition.

It should also be noted that at room temperature the pressure calculated for the \( \omega \rightarrow \beta \) transition is nearly half as large as the experimental value. Since, however, the temperatures considered are not high, we do not believe this discrepancy to be connected with the choice of the Debye model for describing the thermodynamic properties. It is rather due to the deviation of real alloys from the ideal periodic structures used in calculating the total energy in the ground state. The above evidence suggests, in our opinion, that in the TiZr alloy with ideal crystal lattice the phase diagram should look as it is depicted in figure 4.

3. Calculation of the tendency toward decomposition

To estimate the tendency toward decomposition in \( \omega \)-TiZr in the ground state, the total energy was calculated for four structure types (see figure 5). Structure I was represented by layers of pure titanium and pure zirconium alternating along the \( z \) axis and separated by intermediate mixed Ti–Zr layers. In structure II two layers of pure titanium alternated along the \( z \) axis with two layers of pure zirconium with no intermediate Ti–Zr layer. For structure III six Ti layers alternating with six Zr layers were chosen also without intermediate layer. And lastly, in variant IV five Ti layers were separated by an intermediate Ti–Zr layer from five Zr layers.

The free energy was calculated by the scalar relativistic full-potential linearized augmented-plane-wave (FPLAPW) method, using the WIEN2K package [11]. In the first two variants the number of atoms per unit cell was six (three Ti atoms and three Zr atoms). In variants III and IV the number of atoms in the cell amounted to 18 (nine atoms of each species). For variants I and II structural optimization of the \( c/a \) ratio was
performed, and the equilibrium atom positions were defined by the procedure of minimizing the forces acting on atoms (relaxation).

In figure 6 the lattice energy change after relaxation $\Delta E = E_{\text{relax}} - E_0$ is shown as a function of the unit cell volume for structures I and II. Here $E_0$ is the total energy of the system with atomic arrangement corresponding to the ideal $\omega$ lattice; $E_{\text{relax}}$ is the system energy after minimization of the forces acting on atoms for a given volume. As seen from the figure, with decreasing volume the atoms become displaced from the positions corresponding to the ideal $\omega$ lattice, the displacement magnitude depending on the volume and the structure type. For the structure of type I, corresponding to the most uniform distribution of Ti and Zr atoms, at $V < 15 \, \text{Å}^3$ a sharp decrease of $\Delta E$ occurs due to significant atomic rearrangement. For the two-layer system (II) such a rearrangement is not observed in the considered interval of volume change.

In figure 7 the (110) planes are depicted for the lattices of type I (a) and II (b) at $V = 13 \, \text{Å}^3$. The arrows indicate the direction of atomic displacements on relaxation (the $z$ axis is pointing upwards). It is seen that in both cases the atomic displacements are directed only along the $z$ axis. In the two-layer system (II) the atoms of titanium and zirconium are displaced in opposite directions, whereas in system I the atomic chain displacement occurs without strain. The displacements shown in figure 7(a) correspond to those characteristic of the $\omega \rightarrow \beta$ transition. The volume value $V \approx 15 \, \text{Å}^3$ at which a sharp decrease in $\Delta E$ begins agrees well with the result of phase stability calculation ($V = 15.8 \, \text{Å}^3$) obtained from a comparison of the total energies of the $\omega$ and $\beta$ phases of TiZr (see figure 2). Based on the data presented, we can draw an important conclusion that the pressure value at which the $\omega \rightarrow \beta$ transition occurs depends substantially on the ordering type in the equiatomic TiZr alloy. This also indirectly confirms our statement that the disagreement with the experiment concerning the $\omega$–$\beta$ equilibrium boundary position on the phase diagram calculated in the Debye model (figure 4) is caused by the presence of inhomogeneities in the actual TiZr alloys used in experiments in [6–8].

The volume dependence of the total energy is plotted in figure 8 for the relaxed and non-relaxed structures of type I, relaxed structure II, and non-relaxed structures III, IV. As seen from a comparison of the curves I (relax) and I (non-relax), relaxation does not result in considerable energy changes. That is why the relaxation procedure was not performed for large systems (III, IV). It may be seen that in the whole range of volume change the energy minimum is for the structure of type I with the most uniform distribution of Ti and Zr atoms. As decomposition grows (structure III), the system energy increases. This tendency persists on further decomposition. In the structure of type IV, five Ti layers are separated from five Zr layers by a mixed intermediate layer, while in structure III...
there are six layers of each metal with no intermediate layer. As the thickness of pure metal layers increases (from one to five layers), the system energy significantly increases. The presence of an intermediate layer reduces the total energy of the system. This follows from a comparison of the energy values at $V \approx 18.5$ Å$^3$ for the structures of type III and IV (structure III is presented in the figure by a single point).

4. Conclusion

To summarize, the calculations performed show that in the ground state the $\omega$ phase of TiZr exhibits a tendency toward ordering and not toward decomposition, as was suggested in [10]. The analysis of the total energy curves has shown that the allowance for temperature effects in the Debye–Grüneisen model will not change the relationship between the energies of structures with different types of decomposition, and cannot explain the experimentally observed formation of two $\omega$ structures. Besides, we have not found any peculiarities connected with the s–d electron transition in the total energy curves. Thus, also the suggestion advanced in [9] that an isostructural transition exists due to the pressure-induced changes in the electron structure is not confirmed by the calculation. In our opinion, the high-temperature decomposition of the $\omega$ phase in equiatomic TiZr alloy is connected not with changes in the electron structure under pressure, but with peculiarities of the lattice dynamics, in particular, with the presence of strongly anharmonic vibrational modes which are of crucial importance in stabilization of the $\omega$ lattice in pure titanium and zirconium [4].

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