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

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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 $\omega-$TiZr is studied. It is shown that in the ground state the ω phase of the ordered equiatomic alloy TiZr has a tendency toward ordering, rather than decomposition.

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Introduction

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 (α, β and ω) are observed in the TiZr alloy[1–3]. The structural $\alpha \rightarrow \beta$ transformations of the equiatomic alloy were extensively studied in Ref.[1] by the differential thermal analysis (DTA) at temperatures up to 1023 K, and pressures up to 7 GPa. It was found that the $\beta \rightarrow \alpha$ transition temperature, being equal to 852 K at atmospheric pressure, decreases with pressure down to the triple equilibrium point of the α, β and ω phases ($P_{tr} = 4.9 \pm 0.3$ GPa, $T_{tr} = 733 \pm 30$ K). At pressures above the triple point the β phase transforms immediately to the ω phase with a light 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 ω phase which on heating transforms into an α phase in the temperature interval from 698 K to 743 K. Cooling of the β phase in the pressure range 2.8 - 4.8 GPa results in the formation of a two-phase mixture of a stable α and a metastable ω phase. The structural $\alpha \rightarrow \omega$ transformations in the TiZr alloy were studied in detail in Ref.[3]. Investigating TiZr samples under shear-strain conditions at pressures up to 9 GPa at temperatures 300 and 77 K, the authors arrived at the conclusion that in equiatomic TiZr the equilibrium $\alpha \rightarrow \omega$ 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 of Ref.[1].

Detailed studies performed in Ref.[4] have shown that in the region of high pressures and temperatures there exist two ω phases (ω and ω_1) that differ in atomic volume by about 14%. The authors suggested the existence of a isostructural phase transition $\omega - \omega_1$ 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 ω phase was experimentally detected in Ref.[5]. The $\omega \rightarrow \omega_1 + \omega_2$ decomposition was revealed after a prolonged heat treatment at $P = 5.5 \pm 0.6$ GPa and $T = 440 \pm 30^0$ C. It was supposed that in a wide concentration range at pressures above the triple equilibrium point, the ω phase may exist in the Ti_xZr_{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 ω phases of different structure was used as an alternative explanation for the experimental results obtained in Ref.[4].

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-Grüneisen model. The tendency of the ordered equiatomic alloy $\omega-$TiZr to decompose is also investigated.

I. 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[7]. To ensure the desired accuracy of the total energy calculation, the number of plane waves was defined by the condition $RK_{max} = 7$, the total number of k-points in the Brillouin zone was equal to 3000, 3000, 600 for the β, α and ω phase, respectively. The total and partial densities of states were obtained by a modified tetrahedron method[6]. The atomic radii were the same for all phases and pressures: 2.42 a.u. for Zr,