Decomposition of the \(\omega\)-phase in the equiatomic TiZr alloy under high pressure

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Abstract. The phase decomposition phenomenon is found in the hexagonal \(\omega\)-phase of the Ti–Zr system under high pressure. The \(\omega \rightarrow \omega_1 + \omega_2\) decomposition of the equiatomic TiZr alloy occurred due to long thermobaric treatment at \(P = 5.5 \pm 0.6\) GPa and \(T = 710 \pm 30\) K. The chemical compositions of the \(\omega_1\) - and \(\omega_2\)-phases recovered to ambient conditions were estimated from the X-ray data to be around Ti\(_{20}\)Zr\(_{80}\) and Ti\(_{83}\)Zr\(_{17}\). The experimental data were used to calculate the mixing energy and the top of the decomposition curve in the isobaric \(T\)-\(C\) diagram of this system.

We find that the equilibrium \(T\)-\(C\) phase diagram of the Ti–Zr system at pressures above \(\sim 8\) GPa is of the eutectoid type with the high-temperature \(\beta\)-phase and the low-temperature \(\omega_1\)- and \(\omega_2\)-phases.

1. Introduction

Two modifications are known for titanium and zirconium at atmospheric pressure, the low-temperature hexagonal close-packed (\(hcp\)) \(\alpha\)-phase and the high-temperature body-centered cubic (\(bcc\)) \(\beta\)-phase. Both phases of the Ti–Zr system form continuous solid solutions, and characteristic of the \(T\)-\(C\) phase diagram is the monotectic point located at 52 at.% Zr [1] and 852 K [2]. Applied pressure induces a transition of the \(\alpha\)-phase to the hexagonal \(\omega\)-phase both in elemental Ti and Zr [3-5] and in the binary Ti–Zr alloys [2,6]. The \(\omega\)-phase recovered from the high-pressure experiments at room and moderate temperatures has also been reported to form continuous solid solutions [2,6]. The \(\alpha\)-phase solid solutions showed the concentration dependence of the specific volume close to the Vegard’s law, and the reported values of the specific volumes were by less than 1 % above the straight line drawn between the volumes of pure elements.

Earlier, the pressure effect on the phase diagram has been studied by means of the differential thermal analysis (DTA) carried out on the equiatomic TiZr alloy up to 7 GPa [2]. There were plotted the lines of the isoconcentrational \(\alpha\leftrightarrow\beta\) and \(\beta\leftrightarrow\omega\) transformations. The \(\alpha\rightarrow\beta\) transformation had a hysteresis of 70 K whereas the hysteresis of the \(\beta\rightarrow\omega\) transformation was close to zero, and the parameters of the \(\alpha\rightarrow\beta\rightarrow\omega\) triple point determined by DTA were as low as \(P = 4.9\) GPa and \(T = 733\) K. In contrast, the hysteresis of the...
The thermodynamic calculation of the $T$–$P$–$C$ phase diagram of the Ti–Zr system has been attempted under the assumption of the isoconcentrational $\alpha$–$\beta$, $\alpha$–$\omega$ and $\beta$–$\omega$ phase transformations [6]. The estimated value of the mixing energy of the $\omega$-phase solid solutions was positive and rather high, $W_m = 11.3$ kJ/mole. This estimate as well as the positive deviation from the Vegard’s law indicates that the $\omega$-phase solid solutions tend to decompose under pressure. Therefore, one should assume that some $\omega_1 + \omega_2$ two-phase region is the case in the equilibrium $T$–$P$–$C$ phase diagram. This work was aimed at the experimental search of the $\omega \to \omega_1 + \omega_2$ decomposition reaction in the TiZr alloy at pressures above its triple point.

2. Experimental

The TiZr alloy was prepared from the metallic elements with the total impurity contents 0.04 at.% or less using multiple electron-arc melting in vacuum. The chemical composition of the final alloy, 49.6 at.% Ti and 50.4 at.% Zr, was measured with the electron microprobe, JXA-5. The composition was uniform over the ingot within ±0.4 at.%. This same alloy (the hcp $\alpha$-phase with the lattice parameters $a = 3.104$ Å and $c = 4.923$ Å) was used previously for the study of the $T$–$P$ diagram [2] and the structural high-pressure measurements [7]. To refine the grain structure and to minimize the sample texture in this work, a piece of the alloy was hydrogenated to the atomic ratio of H/Me $\approx 1.5$, ground in a mortar to a characteristic powder size of 0.1 mm, and then hydrogen was evacuated by vacuum annealing at $T \leq 1020$ K so that to avoid sintering of the powder. The experimental samples compacted of the TiZr powder at $P = 0.7$ GPa were shaped as pellets of 6 mm diameter and 1.5 mm high.

High pressure was generated using the quasi-hydrostatic toroid-type device with the operation range to 7 GPa. The device was calibrated against the high-pressure transitions in Bi and Tl and provided the accuracy of the pressure determination of ±5 %. To avoid the reaction of the TiZr alloy with the materials of the high-pressure cell, the sample was encapsulated into the NaCl medium, annealed in air to 500 K, and then the capsule with the sample was mounted into the operation zone of the cell.

The X-ray diffraction was measured at room temperature using the CuK$_{a1}$ irradiation at the Siemens D500 diffractometer provided with the SiO$_2$ monochromator of the incident beam and the Ni filter at the position-sensitive detector. The data were registered with a step of 0.02° typically at a rate of 0.15°/min.

3. Thermobaric treatment

The $\omega \to \omega_1 + \omega_2$ decomposition reaction should occur in the $T$–$P$ region where the $\omega$-TiZr phase becomes stable with respect to the $\alpha$- and $\beta$-phases. From the kinetic reasons, the temperature of the thermobaric treatment had to be close, but below the $\omega$–$\beta$ transition temperature. There were carried out several experiments where the sample was mounted in the high-pressure cell together with the Bi reference (cf. the BiIV–VI transition line in Ref. [3]). This allowed estimation of the long-term behavior of the cell during the thermobaric treatment. The $T$–$P$ parameters of the present thermobaric treatment are plotted in the earlier $T$–$P$ diagram of the isoconcentrational equilibria in the TiZr alloy [2] (figure 1). In this diagram, the dashed line shows an assumptive position of the $\alpha$–$\omega$ transition line whereas the actual transition line may be between the dashed line and the dotted line connecting the $\alpha$–$\beta$–$\omega$ triple point and the onset of the $\omega$–$\alpha$ transition observed by calorimetry [2]. With this choice of the $T$–$P$ parameters, we could deliberately compensate their variation due to relaxation of the high-pressure cell during long high-pressure annealing.
We noted also in the preliminary experiments that the transformation to the $\omega_1 + \omega_2$ two-phase state was more complete when the initial sample state was the $\omega$-phase rather than the $\alpha$-phase. For this reason, the present TiZr sample was brought first to the $\omega$-phase by means of cycling the sample over the $\omega-\beta$ transition line, that is, between $T = 670$ and 820 K. In the following experiment, the $\omega$-TiZr sample was maintained at $P = 5.5 \pm 0.6$ GPa and $T = 710 \pm 30$ K for 100 h, cooled and recovered to ambient conditions. The X-ray diffraction patterns of the sample states obtained in these experiments are compared in the next section.

4. X-ray characterization

Figure 2 represents the diffraction patterns of the TiZr alloy after the $\omega \leftrightarrow \beta$ thermal cycling at $P \approx 6$ GPa (at the top) and after the 100-hour thermodbaric treatment (at the bottom). The first pattern is well described within the $\omega$-phase structure (sp. gr. $P6/mm$) with the lattice parameters $a = 4.844$ Å, $c = 2.996$ Å and $c/a = 0.618$, in good correspondence with the earlier data [2]. In addition to the $\omega$-phase reflections, the pattern includes several very weak reflections that may be related to the residual $\alpha$-phase with a rather distorted hcp lattice ($a = 3.088$ Å, $c = 5.006$ Å and $c/a = 1.621$).

The bottom pattern in figure 2 is more complex. A comparison of the low-angle peaks shows that the pattern represents a superposition of two sets of reflections with the intensities correlated within each set like those in the $\omega$-phase. The peaks in the set with the lower 2$\theta$ values are not symmetric therefore the Rietveld refinement of the pattern is still in progress. A fit using the POWDERCELL program gives indexing of the main features within two $\omega$-phases with the lattice parameters for the $\omega_1$-phase equal to $a = 4.921$ Å, $c = 3.060$ Å and $c/a = 0.622$ and those for the $\omega_2$-phase $a = 4.680$ Å, $c = 2.864$ Å and $c/a = 0.612$. In addition to the main reflections, a few broad low-intensity features are quite discernible in this pattern at $2\theta < 40^\circ$. These features may be interpreted as an admixture of the $\alpha$-phase with the lattice parameters of $a = 3.049$ Å, $c = 4.873$ Å and $c/a = 1.598$.

It seems that the asymmetry of the $\omega_1$-phase reflections as well as the admixture of the $\alpha$-phase are of a kinetic nature and result from the incomplete decomposition reaction. A longer thermodbaric treatment is expected to give a larger degree of the transformation.
Figure 2. X-ray diffraction patterns measured on the $\omega$-TiZr alloy (top) and on the ($\omega_1 + \omega_2$)-TiZr alloy (bottom). Bar diagrams show the calculated peak positions for the phases involved.

5. Simulation of the high-pressure $T$–$C$ phase diagram
The above lattice parameters of the $\omega_1$- and $\omega_2$-phases were used to calculate their specific volumes and to estimate their compositions using the Vegard’s law. The obtained compositions were Ti$_{20.5}$Zr$_{79.5}$ for the $\omega_1$-phase and Ti$_{83.1}$Zr$_{16.9}$ for the $\omega_2$-phase. These values are rather symmetric with respect to the equiatomic composition therefore we applied the model of the regular solid solutions in order to calculate the curve of the $\omega \leftrightarrow (\omega_1 + \omega_2)$ equilibrium in the Ti–Zr system under pressure.

According to the model of the regular solid solutions,
\[ W_m = T_0 \cdot R \cdot \ln \frac{1 - C_1}{C_1} \frac{C_1}{1 - 2C_1} \]

where \( W_m \) is the mixing energy, \( T_0 \) is the temperature of the phase equilibrium, \( C_1 = 1 - C_2 \) is the concentration of one of the phases in equilibrium, and \( R \) is the gas constant. This equation describes a symmetric curve with a maximum, and \( C_1 = 0.5 \) in the critical point at the top of the curve therefore the critical temperature is \( T_{cr} = 0.5 W_m/R \).

If we accept \( T_0 = 710 \text{ K}, \ C_1 = 0.19 \) for the present experiment, the equation returns \( W_m = 13.8 \text{ kJ/mole} \). The change of the \( W_m \) value is less than \( \pm 0.2 \text{ kJ/mole} \) when the \( C_1 \) value is changed by \( \pm 0.01 \) (compare with the difference in the \( \omega_1 \) and \( \omega_2 \) compositions). The critical temperature is estimated then as \( T_{cr} = 830 \text{ K} \). The calculated \( \omega \leftrightarrow (\omega_1 + \omega_2) \) equilibrium curve is represented in figure 3 in thick solid line with a dotted segment showing a part of the line that enters into the stability region of the \( \beta \)-phase. For simplicity, other elements of the isobaric \( T-C \) section of the phase diagram are related to \( 8 \text{ GPa} \), the pressure of the \( \alpha-\beta-\omega \) triple point in Ti [5]. Thus we eliminated the \( \alpha \)-phase from consideration. The \( \beta-\omega \) transition temperature in Zr at 8 GPa is estimated from the graphic data in Ref. [4]. The line of equal Gibbs potentials of the \( \beta \)- and \( \omega \)-phases (dashed) is drawn through the end points for pure Ti and Zr and the temperature of the isoconcentrational \( \beta-\omega \) transition in the TiZr alloy [2]. The choice of the equilibrium eutectoid temperature and the shape of the \( (\beta+\omega_1) \) and \( (\beta+\omega_2) \) two-phase boundaries is arbitrary; these curves are drawn in thin solid lines.

![Figure 3](image-url)  
**Figure 3.** An outline of the equilibrium \( T-C \) phase diagram of the Ti–Zr system at \( P \geq 8 \text{ GPa} \). Thick solid lines show the calculated boundaries of the \( \omega \rightarrow \omega_1 + \omega_2 \) decomposition reaction; the end-capping high-temperature segment of the calculated curve is in the \( \beta \)-phase stability region (dotted line). The dashed curve represents the line of equal Gibbs potentials for the \( \beta \)- and \( \omega \)-phases. Thin solid lines are drawn through the end points in compliance with the available experimental data. Squares show the experimental data.
So, the equilibrium \( T-C \) phase diagrams in some pressure range above the Ti and Zr triple points are of the eutectoid type, the \( \alpha \)-phase stability regions should be taken into consideration at lower pressures.

### 6. Conclusion

The present experimental data clearly demonstrate that the equilibrium \( T-P-C \) phase diagram of the Ti–Zr system includes the \( \omega_1 + \omega_2 \) two-phase region where \( \omega \)-TiZr may persist only as a metastable phase due to slow diffusion kinetics of the components. The \( \omega \rightarrow \omega_1 + \omega_2 \) decomposition reaction occurs even at pressures just above the triple point of the alloy.

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