ISSN 0031-918X, Physics of Metals and Metallography, 2020, Vol. 121, No. 12, pp. 1188–1192. © Pleiades Publishing, Ltd., 2020.
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STRUCTURE, PHASE TRANSFORMATIONS, AND DIFFUSION

Estimation of Enthalpy of Formation of TiCu by Density-Functional Method

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Received February 12, 2020; revised September 1, 2020; accepted September 3, 2020

Abstract—The enthalpies of formation of γ- and δ-phases of the TiCu alloy were estimated using the density-functional method. The enthalpies of formation are −22 and −12.8 kJ/mol for the γ- and δ-TiCu, respectively. The comparison of X-ray data and quantum-chemical calculations demonstrates that the discrepancy in the experimental values of enthalpy of formation of the TiCu crystals correlates with different content of the γ and δ modifications in the TiCu alloy.

Keywords: intermetallic TiCu, enthalpy of formation, density-functional method

DOI: 10.1134/S0031918X20120078

INTRODUCTION

The TiCu alloys have special electronic and magnetic properties, high corrosion and oxidation resistances, as well as high hardness and thermal stability [1–5]. According to the diagram, these alloys compose a series of intermetallics [6] and the TiCu alloy with equimolar composition is the most interesting of these. Due to a low melting temperature ($T_m = 982$°C) and vitrification ability upon fast cooling of the alloy, amorphous TiCu is applied as highly plastic and chemically homogeneous solder for electrodes in hydrogen production, and is considered to be a prospective material for hydrogen-storage facilities.

Upon fast cooling, the TiCu alloy with equiatomic composition forms amorphous alloys, i.e., metallic glasses. Upon heating, in amorphous $Ti_{50}Cu_{50}$, the self-spreading waves of crystallization, which occur upon heating to the temperatures 250–350°C [7], can be observed. It was shown that the crystallization proceeds without melting of TiCu and is accompanied by an exothermic effect which is caused by the phase transition from an amorphous to a crystalline state. Two modifications of TiCu crystals are known [6], i.e., γ- and δ-phases of the tetragonal syngony, which differ in space group and lattice parameters (Table 1). It was shown in [6] that the TiCu γ-phase forms at 900°C; and the δ phase, at 800°C. Both modifications were prepared by melting a mixture of Ti and Cu powders in a high-frequency vacuum induction furnace. When TiCu crystalizes upon heating of the so-called metallic glass, there is a high probability that the low-temperature δ-phase will develop. The question of which modification, i.e., γ- or δ-TiCu, is formed upon crystallization was not considered in [7]. The possibility of preferably crystalizing into one of the TiCu modifications can be estimated with the enthalpy of formation. However, there are no data in the literature on

Table 1. Structural data of the γ- and δ-TiCu crystals [6]

Lattice parameter	γ-TiCu	δ-TiCu
a, Å	3.108	4.440
c, Å	5.887	2.856
V, Å^3	56.9	28.2
Space group	*P*4/*nmm* (no. 129)	*P*4/*mmm* (no. 123)
Cu coordinates [8]	0 0 0 (1*c*)	0 0 0 (1*a*)
Ti coordinates [8]	0.5 0.5 0.5 (2*c*)	0.5 0.5 0.5 (1*d*)

correspondence between the TiCu enthalpies and the modifications. The review of experimental $\Delta H°$ data on TiCu [9–13] has showed error in the enthalpy within 20% (Table 2).

The aim of this work is to calculate the enthalpy of formation and structure parameters of the γ- and δ-TiCu crystals by the density-functional theory (DFT) and to compare the results with data of x-ray structural analysis of TiCu obtained in the course of heating of the amorphous alloy.

Table 2. The enthalpy of formation of TiCu

Reference	$-\Delta H°$, kJ/mol
[9]	18.8
[10]	19.2
[11]	18.8
[12]	22.2
[13]	17.5

EXPERIMENTAL AND CALCULATION METHODS

The powder obtained after heating the amorphous TiCu was used as an initial material for x-ray analysis [7]. Diffraction patterns were taken in a step-by-step mode in the Cu $K\alpha$-radiation in the range of $2\theta = 20°–80°$ with a step of 0.02° and exposure of 2 s with a DRON-3M diffractometer. The profile analysis was carried out by the Rietveld refinement method using Full Prof software [14]. The calculations fitted parameters of profiles of reflections, background, and lattice parameters. Theoretical x-ray-diffraction patterns and figures of structures were calculated using Mercury 3.3 software [15]. Data on experimental and theoretical diffraction patterns (Fig. 1) are listed in Table 3.

Quantum-chemical calculations (QCC) were performed by the DFT method realized in the "VASP 5.0" code [16, 17] with a Blohin supercomputer at the International Smart Materials Research Institute at the Southern Federal University. The exchange-correlation potential was used in the GGA approximation within the Perdew–Burke–Ernzerhof scheme. The basis was constructed of plane waves with kinetic energy of less than 220 eV. For the Brillouin zone, the $11 \times 11 \times 11$ k-mesh was employed. The lattice parameters for enthalpy calculations were used after geometry optimization. The calculations took into account the spin polarization and Van der Waals interaction by the DFT-D3 method [18, 19].

RESULTS

Figure 1a demonstrates the experimental powder-diffraction pattern of the alloy obtained after heating amorphous TiCu. The analysis of patterns using structural models *P*4/*nmm* and *P*4/*mmm* does not unambiguously identify space group of TiCu. A structure model which yields minimal *R*-factors of the profile analysis is usually selected. The minimal R_{wp} value is obtained for the δ-TiCu (*P*4/*mmm*). However, quality

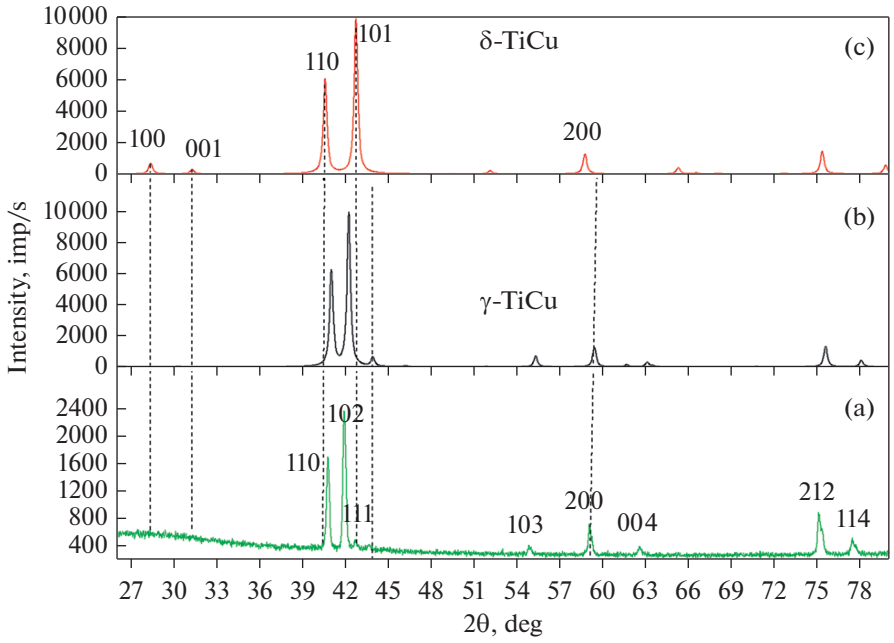

Fig. 1. Experimental (a) and theoretical (b,c) diffraction patterns of γ and δ TiCu.

Table 3. Results of structural analysis of TiCu

@Параметр	δ-TiCu [6]	δ-TiCu*	γ-TiCu [6]	γ-TiCu*
a, Å	3.14	3.1202(1)	3.108	3.1213(1)
c, Å	2.856	2.9629(2)	5.887	5.9275(2)
V, Å^3	28.16	28.85(2)	56.9	57.75(2)
Z	1	1	2	2
R_w(%)	–	7.8	–	8.4
R_p(%)	–	9.1	–	9.9
R_b(%)	–	5.9		6.2
R_e(%)	–	5.3	–	5.3
GofF	–	1.5	–	1.6

* This work.

indices of experiments for the γ-TiCu and δ-TiCu crystals are close (Table 3).

The pattern does not have weak reflections 100 (2θ ≈ 28.7°) and 001 (2θ ≈ 31.4°) which are characteristic of the δ-TiCu crystals. Therefore, the comparison of the calculated and experimental patterns of the γ- and δ-TiCu (Fig. 1) shows that the amorphous alloy crystallizes only into the γ-TiCu crystals.

The crystal structure of the δ-TiCu is layered (Fig. 2). This structure is characterized by monoatomic Ti and Cu layers being parallel to the 0*bc* plane of the unit cell and alternate with each other in the *a*- and *b*-axes direction. The spacing between the layers is ≈1.57 Å. Cu atoms occupy site 1a; Ti atoms, 1d.

The γ-TiCu structure is characterized by heteroatomic layers, i.e., they consist of both Ti and Cu atoms. The layers alternate along the 110 direction of the unit cell (Fig. 3). The interplanar spacing is 2.20 Å. The difference in the spacing values is explained by the position of atoms one above the other in γ-TiCu (Fig. 3), whereas with a 1/2 *a* and *b* shift in the δ-TiCu (Fig. 2). Cu and Ti atoms in the γ-TiCu crystals occupy sites 2*c* with various coordinates

Experimental $\Delta H°$ values of TiCu crystals are different (Table 2). The discrepancy in data on thermodynamic properties obtained by different researchers is likely caused by the presence of two modifications of the TiCu alloy. The enthalpies of formation of crystals with different packing patterns vary.

Quantum-chemical calculations of enthalpy of formation, $\Delta H°$, of intermetallic crystals were carried out according to [18–20], as follows:

$$\Delta H° \approx \Delta\varepsilon = \varepsilon_{total}/Z - (\varepsilon_1/Z_1 + \varepsilon_2/Z_2),$$

where Z, $Z_{1,2}$ are numbers of formular units in the unit cells of the intermetallics (TiCu) and initial reagents (Ti, Cu); ε_{total}, $\varepsilon_{1,2}$, energies of the unit cells of intermetallics (TiCu) and initial reagents (Ti, Cu).

To estimate the reliability of the calculations, five titanium containing intermetallic alloys (TiFe, TiAl, TiNi, TiCo and TiPd) with known experimental values of enthalpy of formation were considered [19–21]. As a result, the satisfactory agreement of 12% accuracy of experimental $\left(\Delta H^{\circ}_{exp}\right)$ and theoretical $\left(\Delta H^{\circ}_{theor}\right)$ values of the enthalpies of formation of Ti-containing intermetallics were obtained (Table 4).

The analysis of data of Table 4 demonstrates that the γ-phase of TiCu is more energetically advantageous compared with the δ-phase. This is likely the reason for the formation of the stable γ-phase crystals upon heating of the amorphous TiCu alloy. It could also be that the discrepancy in the experimental results of $\Delta H°$ of TiCu correlates with the presence of differ-

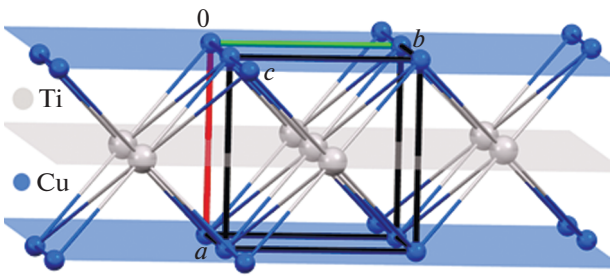

Fig. 2. Crystal structure of δ TiCu.

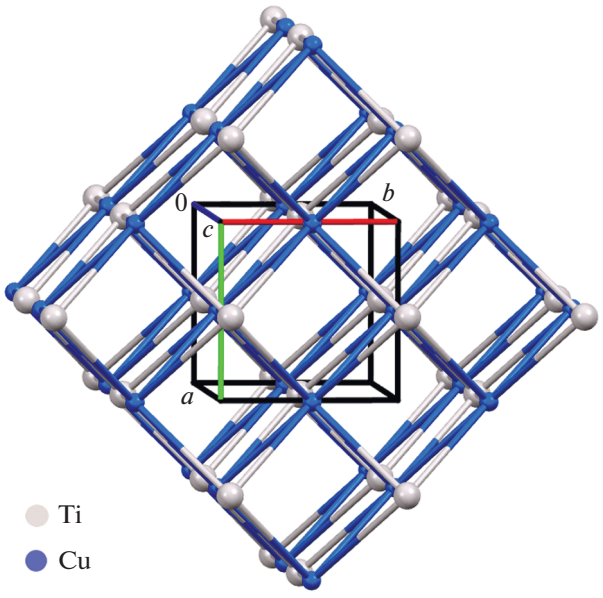

Fig. 3. Crystal structure of γ TiCu.

Table 4. Results of structural analysis, the ΔH° measurements and QCC of Ti-containing intermetallic alloys

Lattice parameter	TiFe [18]	TiAl [18]	TiNi [21]	TiCo [22]	TiPd [23]	γ-TiCu [6, 9–13]*	δ-TiCu [6]
a_{exp}, Å	2.979	2.832	3.015	2.995	3.180	3.118	3.14
a_{calc}, Å	2.949	2.812	3.007	2.975	3.167	3.111	3.350
c_{exp}, Å	–	4.070	–	–	–	5.921	2.856
c_{calc}, Å	–	4.084	–	–	–	5.919	2.529
V_{exp}, Å^3	26.4	32.6	27.4	26.9	32.2	57.56	28.16
V_{calc}, Å^3	25.6	32.3	27.3	26.4	31.8	57.3	28.38
Space group	*Pm*-3*m*	*P*4/*mmm*	*Pm*-3*m*	*Pm*-3*m*	*Pm*-3*m*	*P*4/*nmm*	*P*4/*mmm*
Z	1	1	1	1	1	2	1
ΔH°_{exp}, kJ/mol	−22	−84	−66	−21	−110	−17…−22	–
ΔH°_{calc}, kJ/mol	−19	−85	−75	−25	−96	−22	−13

* References to works with experimentally determined ΔH° values.

ent modifications of crystals in the samples under investigation.

CONCLUSIONS

The enthalpies of formation of the γ- and δ-phases of the intermetallic TiCu alloy were estimated by the density-functional method. The calculated enthalpy of formation of the γ-TiCu (*P*4/*nmm*) is −22 kJ/mol and falls into the range of the experimental values of enthalpy of TiCu. It was shown that the δ-phase of TiCu (*P*4/*mmm*) with the calculated enthalpy of formation −12.8 kJ/mol is less thermodynamically stable. The x-ray structural analysis of the alloy obtained by heating the metallic TiCu glass demonstrated that the phase transition from the amorphous to crystalline state results in the formation of the γ-TiCu crystals.

FUNDING

The work is performed within the state assignment ISMAN (theme 44 No. 0091-2018-0001). S.A. Guda acknowledges the financial support of The Southern Federal University (VnGr-07/2017-08).

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Translated by O. A. Golovnya

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