



Crystal structures and elastic properties of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ phases

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Abstract: This paper focused on the crystal structures of two new ternary phases, $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$, which were studied by X-ray powder diffraction data using Rietveld method. Electron probe microanalysis was used for sample composition examination. Elastic properties of these phases were further measured by nano-indentation, and meanwhile calculated with first-principle (FP) calculations. It is found that the crystal structure of $\text{Ti}(\text{Cu,Pt})_2$ is of orthorhombic cell space group $Amm2$ (No. 38) with structural prototype of VAu_2 . The resolved structure of $\text{Ti}(\text{Cu,Pt})_3$ is of tetragonal AlPt_3 type, belonging to the space group $P4/mmm$ (No. 123). The nano-indentation measurement and FP calculations show that the elastic modulus of $\text{Ti}(\text{Cu,Pt})_2$ increases firstly then decreases with Pt content, whereas that of $\text{Ti}(\text{Cu,Pt})_3$ almost linearly increases with Pt content.

Key words: Ti–Cu–Pt phase; crystal structure; X-ray diffraction; first-principle calculations; elastic properties

1 Introduction

Ti–Cu intermetallic compounds have been used as implantable devices and dental prostheses because of their good biocompatibility [1], high hardness and strength, low melting temperature, and strong antibacterial ability [2–5]. The addition of other elements can improve their physical properties because of formation of solutions or new ternary compounds. For example, six ternary phases, $\tau_1\text{-Ti}(\text{Cu}_x\text{Ni}_{1-x})_2$, $\tau_2\text{-Ti}_2(\text{Cu}_x\text{Ni}_{1-x})_3\text{H}$, $\tau_3\text{-Ti}_2(\text{Cu}_x\text{Ni}_{1-x})_3\text{L}$, $\tau_4\text{-Ti}_5\text{CuNi}_{14}$, $\tau_5\text{-TiCuNi}_2$ (Cu_3Sb type), and $\tau_6\text{-TiCuNi}_2$ (TiAl_3 type) [6–10] were found in the Ti–Cu–Ni system, and $\text{TiCu}_{0.5}\text{Fe}_{0.5}$ [11], $\text{Ti}_6\text{CuCo}_{23}$ [12], TiCuZr [13], TiCu_2Zr [14], TiCuPd_6 [15] and Ti_4CuAg [16], were also reported in other systems. The hardness (H) and elastic modulus (E) of TiCu_2Zr can reach (7.5 ± 0.3) GPa and 128.4 GPa, respectively, which

are significantly higher than those of most binary Ti–Cu or Zr–Cu phases [14]. As a non-toxic element, Pt is commonly added to improve the physical property of cp-Ti, and Ti–Pt binary compounds are promising candidates for dental applications due to their grindability and mechanical compatibility with bone tissue than cp-Ti [17]. In light of alloying theory, it is expected that property of the binary Ti–Cu compounds may be improved and new compounds may be stabilized by adding Pt in Ti–Cu binary system.

Recently, two new ternary phases of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ have been reported by our research group [18]. The Pt contents for $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ are (4.0–47.6) at.% and (42.2–65.6) at.% at 1073 K, respectively. However, crystal structure and related properties of these two phases were not studied in detail. In this work, crystal structures and elastic properties of these two phases were investigated.

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2 Experimental

2.1 Materials and synthesis

Eight alloys of the $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0.05, 0.2, 0.35, 0.5$) and $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0.6, 0.7, 0.8, 0.9$) compounds with a mass of 2 g were arc-melted from high-purity metals, i.e. 99.99 Ti, 99.99 Cu and 99.99 Pt (wt.%), in a chamber filled with argon gas. These alloys were remelted four times to ensure complete fusion and composition homogeneity before being enclosed in an evacuated quartz tube and annealed at 1073 K for 60 d. The annealed alloys were then instantaneously quenched in water to room temperature.

2.2 Structure characterization and hardness measurement

The elemental compositions of the $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ compounds were obtained through wavelength-dispersive spectroscopy (WDS) on a JEOL JXA-8800R electron probe micro analyzer (EPMA).

Powder X-ray diffraction patterns of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ compounds were collected at room temperature using a Rigaku D/max 2550V powder diffractometer equipped with a Cu K_α radiation and a diffracted-beam graphite monochromator. The diffractometer was operated at 40 kV and 250 mA, the 2θ scan range was from 10° to 100° with a step size of 0.02° and a count time of 2 s per step. The Materials Data Inc. software Jade 5.0 [19] was used for phase identification. After data collection, the stability of both the X-ray source and the samples was checked by recording the diffraction lines again at low angles.

The H and E were measured on single phase or polycrystalline samples with nano-indentor (UNHT+MCT+MST, CSM, Switzerland). Test was repeated five times on each of the target phase. The surface of each sample was polished before the test.

3 First-principle calculations

Structural optimization and elastic constant calculations were performed with the VASP code [20,21], of which the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerh (PBE) functional [22] was used as the exchange-correlation potential. Integration over the

Brillouin zone was performed using the Monkhorst-Pack set [23] with 450 eV of energy cutoff. The structural parameters of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ were acquired from experimental values of lattice parameter, and the terminal phase models of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ were constructed from a unit cell in which the mixed sites are filled either with Cu or with Pt. The k -point meshes of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0, 1$) and $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0, 1$) were set as $15 \times 9 \times 15$ and $15 \times 15 \times 15$, respectively. The tolerances of total energy difference for geometry optimization were 10^{-5} eV/atom, the maximum force of 0.001 eV/Å, and the maximum displacement of 1.0×10^{-2} Å. Bulk modulus and volume dependence of the total energies were calculated by fitting the energy against volume data with Birche–Murnaghan equation of states.

4 Results and discussion

4.1 Crystal structure of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase

Electron probe microanalysis (EPMA) was employed to analyze whether the annealed alloys of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0.05, 0.2, 0.35, 0.5$) are single phase or not. Figure 1 shows the phases present in the annealed alloys. It is seen that only the $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0.35$) alloy is single phase (Fig. 1(c)), while other samples contain at least two phases. So the single-phase sample $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ was chosen to determine its crystal structure of $\text{Ti}(\text{Cu,Pt})_2$.

High-quality X-ray diffraction patterns of the $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ alloy powder were collected, as illustrated in Fig. 2. By using the Jade 5 program [19], the crystal structure of the $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase was successfully indexed and it has an orthorhombic unit cell with the following lattice parameters: $a=4.5688(2)$ Å, $b=8.1822(2)$ Å, $c=4.5603(3)$ Å. Reflection conditions (hkl : $k+l=2n$; $0kl$: $k+l=2n$; $h0l$: $l=2n$; $hk0$: $k=2n$; $h00$: no conditions; $0k0$: $k=2n$; $00l$: $l=2n$) indicated the possible space groups: $Cmcm$ (No. 63), $Amm2$ (No. 38), $Cmm2$ (No. 35), $C222$ (No. 21). By comparing the lattice parameters and PXRD pattern of the $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase with those presented in the structure-type database, it was found that $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ and VAu_2 [24] have the same structure type. So the space group $Amm2$ (No. 38) and the atomic position parameters of VAu_2 were taken as the starting values to refine the structural

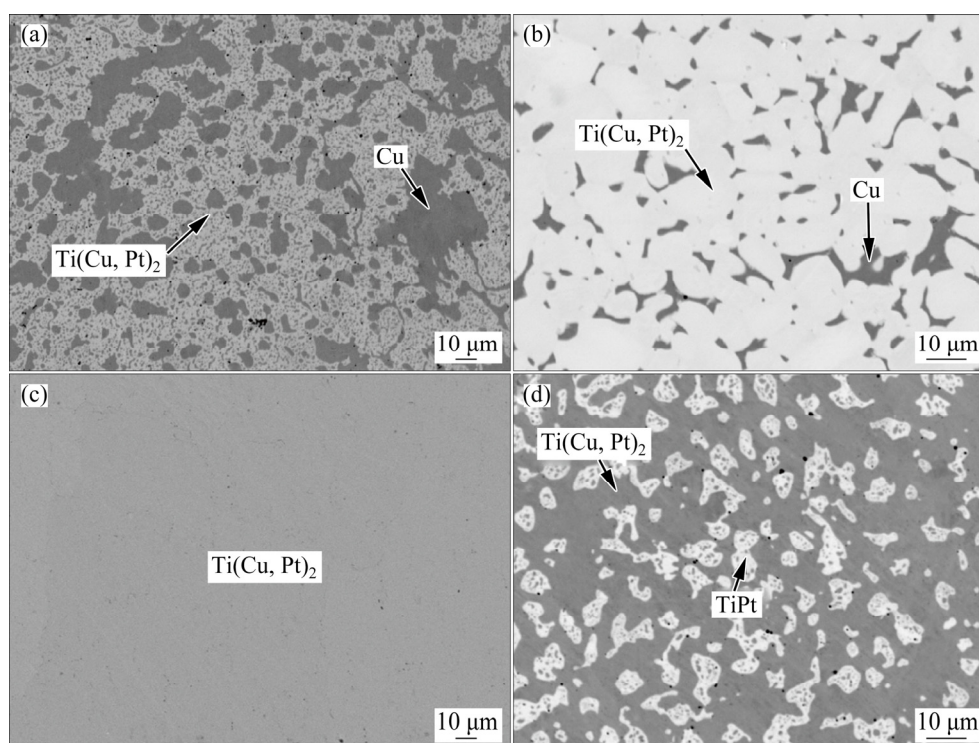


Fig. 1 Backscattered electron (BSE) images of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0.05\text{--}0.5$) alloys annealed at 1023 K for 60 d: (a) $\text{Ti}(\text{Cu}_{0.95}\text{Pt}_{0.05})_2$; (b) $\text{Ti}(\text{Cu}_{0.8}\text{Pt}_{0.2})_2$; (c) $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$; (d) $\text{Ti}(\text{Cu}_{0.5}\text{Pt}_{0.5})_2$

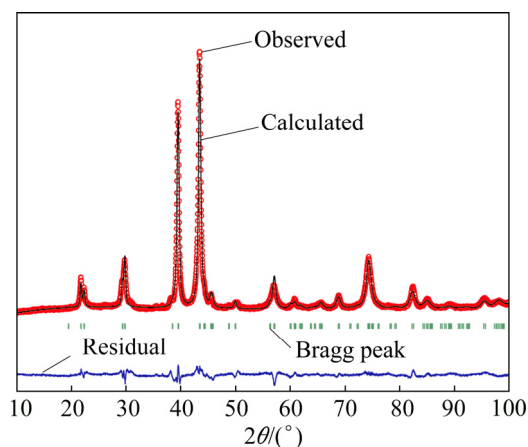


Fig. 2 Observed, calculated and residual powder XRD patterns and Bragg peak positions of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ alloy

parameters of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$. The structural refinement of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ was then performed using the Fullprof_suite program [25]. The pseudo-Voigt function was used for the simulation of the peak shapes. There are 27 refined parameters, including scale factor, cell parameters, atomic coordinates, full width at half maximum (FWHM), preferred orientation, and isotropic displacement parameters. Background correction used a 12-term polynomial. When Ti atoms occupy 2a and 2b

positions of V atoms, Cu and Pt atoms statistically occupy 4d and 4e positions, final refinement converged to rather good residual value (profile factor $R_p=5.07\%$, weighted profile factor $R_{wp}=6.83\%$, Bragg factor $R_B=7.85\%$, crystallographic R_F -factor $R_F=5.63\%$) and yielded a formula of $\text{Ti}_{33.33}\text{Cu}_{43.29}\text{Pt}_{23.38}$ which was in good agreement with the composition of a new phase of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ (32.95 at.% Ti, 43.20 at.% Cu, and 23.85 at.% Pt) by EPMA.

The crystal data, structural refinement, standardized atomic positions and isotropic atomic displacement parameters (B_{eq}) of the $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase are listed in Table 1.

A set of interatomic distances in $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ are given in Table 2. The shortest bond length in the structure is $d_{\text{Ti1-Cu2(Pt2)}}=2.6076 \text{ \AA}$, which corresponds to 95.6% of the sum of the atomic radii. The crystal structure of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ is shown in Fig. 3.

It should be pointed out that CENZUAL et al [26] also reported another structural type of Au_2V which crystallized in orthorhombic space group $Cmcm$ (No. 63). The unit cell has 12 atoms, 4 V atoms occupy 4c positions and 8 Au atoms occupy 8g positions. The results of structural

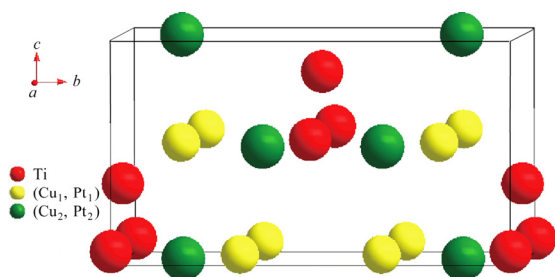
Table 1 Crystal data and structural refinement parameters for $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	$B_{\text{eq}}/\text{\AA}^2$
Ti ₁	2 <i>a</i>	0	0	0.0606(2)	1	1.3928(1)
Ti ₂	2 <i>b</i>	0.5	0	0.3355(9)	1	0.3355(9)
Cu ₁	4 <i>d</i>	0	0.1770(8)	0.5484(3)	0.6189(5)	1.2223(1)
Pt ₁	4 <i>d</i>	0	0.1770(8)	0.5484(3)	0.3810(5)	1.2223(1)
Cu ₂	4 <i>e</i>	0.5	0.1499(2)	0	0.6797(6)	0.8404(3)
Pt ₂	4 <i>e</i>	0.5	0.1499(2)	0	0.3202(4)	0.8404(3)

$\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$: Orthorhombic VAu_2 -type; $\text{Amm}2$ (No. 38); $a=4.5688(2)\text{\AA}$; $b=8.1822(2)\text{\AA}$; $c=4.5603(3)\text{\AA}$; $D_{\text{calc}}=10.789\text{ g/cm}^3$, $Z=4$; R -factors: $R_{\text{p}}=5.07\%$; $R_{\text{wp}}=6.83\%$; $R_{\text{f}}=5.63\%$; $R_{\text{B}}=7.85\%$

Table 2 Typical interatomic distance for $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ phase

Bond	Distance/ $\text{\AA}$	Multiplicity
Ti ₁ —Ti ₂	3.428(5)	$\times 2$
Ti ₁ —Cu ₁ (Pt ₁)	2.748(6)	$\times 2$
Ti ₁ —Cu ₂ (Pt ₂)	2.607(6)	$\times 4$
Ti ₂ —Cu ₁ (Pt ₁)	2.714(1)	$\times 4$
Ti ₂ —Cu ₂ (Pt ₂)	2.864(4)	$\times 2$
Cu ₁ (Pt ₁)—Cu ₁ (Pt ₁)	2.573(5)	$\times 2$
Cu ₁ (Pt ₁)—Cu ₂ (Pt ₂)	2.696(5)	$\times 2$
Cu ₂ (Pt ₂)—Cu ₂ (Pt ₂)	2.807(4)	$\times 2$

**Fig. 3** Schematic illustration of crystal structure of $\text{Ti}(\text{Cu,Pt})_2$ phase

refinement of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$ are $R_{\text{p}}=6.46\%$ and $R_{\text{wp}}=7.76\%$ which are not as good as the results obtained with $\text{Amm}2$. This may be related to the quenching in water of the samples at 1073 K.

4.2 Crystal structure of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$

Microstructures of the alloys with compositions of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0.6, 0.7, 0.8, 0.9$) are presented in Fig. 4. As can be seen, $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ alloy (Fig. 4(b)) is almost single phase. The elemental composition (25.08 at.% Ti, 22.52 at.% Cu, and 52.40 at.% Pt) of the compound was obtained from EPMA.

Powder XRD pattern of the alloy $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ was recollected by step-scanning mode with relatively high resolution as shown in Fig. 5. The indexing result of diffraction pattern indicated a tetragonal cell, with the lattice parameters $a=3.9097(2)\text{\AA}$ and $c=3.7227(3)\text{\AA}$. The analysis of systematic extinctions (no conditions) suggested that the possible space groups were $P4/mmm$, $P4m2$, $P42m$, $P4mm$ and $P422$. Among them, the $P4/mmm$ has a symmetric centre and high symmetry. We also chose trial-and-error and isostructural method to determine the crystal structure of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ phase. Finally, the best fit was found for AlPt_3 [27] structure with space group $P4/mmm$ (No. 123). The reliability R factors for the finally achieved parameter set were $R_{\text{p}}=8.41\%$, $R_{\text{wp}}=9.95\%$, $R_{\text{f}}=7.94\%$, $R_{\text{B}}=6.56\%$. The observed, calculated, and residuals X-ray powder diffraction patterns of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ are shown in Fig. 5.

In Refs. [28,29], AlPt_3 compound crystallizes not only the space group $P4/mmm$ (No. 123), but also $P4/mbm$ (No. 127) and $Pm\bar{3}m$ (No. 221). The results of structural refinement of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ for space group $P4/mbm$ are not acceptable.

The crystal structure data of the $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ phase are listed in Table 3. As can be seen that Ti atoms occupy 1*a* (0, 0, 0) site, while Cu and Pt atoms jointly occupy 1*c* (0.5, 0.5, 0) and 2*e* (0, 0.5, 0.5) sites. The interatomic distances of this phase are given in Table 4. All these bond lengths are reasonable with respect to atomic radii. The crystal structure of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ is a face tetragonal structure, as illustrated in Fig. 6.

4.3 Elastic properties

4.3.1 Nano-indentation measurement

The H of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ phases were measured through nano-indentation technique.

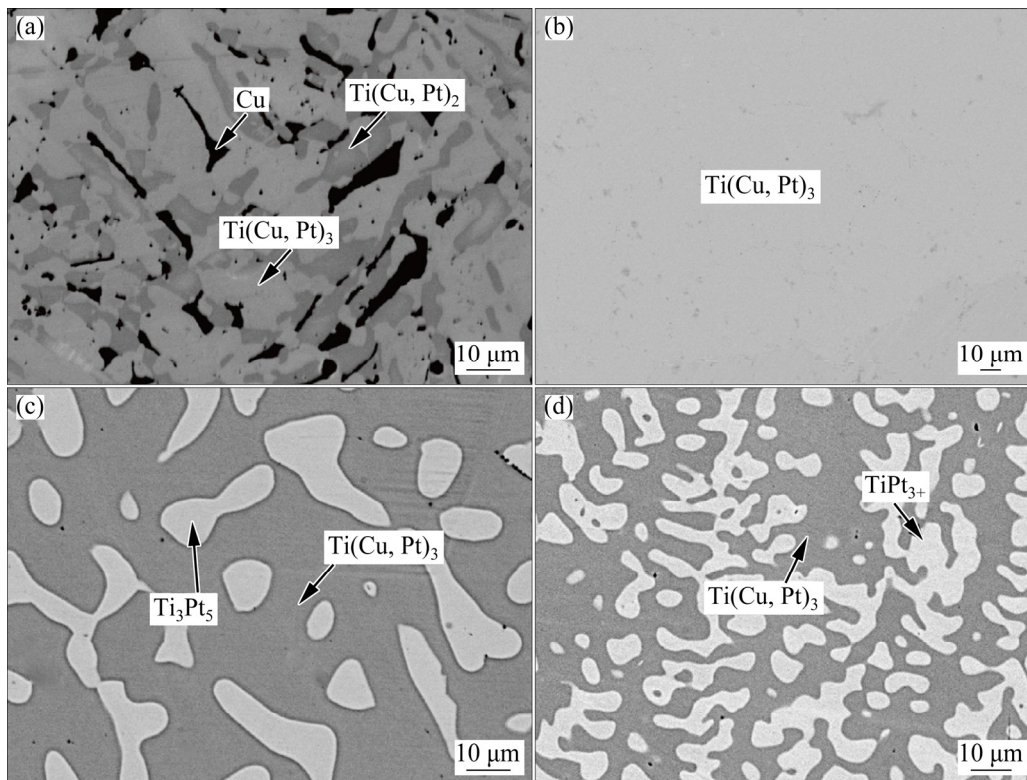


Fig. 4 Backscattered electron images (BSE) of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0.6\text{--}0.9$) alloys annealed at 1023 K for 60 d: (a) $\text{Ti}(\text{Cu}_{0.4}\text{Pt}_{0.6})_3$; (b) $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$; (c) $\text{Ti}(\text{Cu}_{0.2}\text{Pt}_{0.8})_3$; (d) $\text{Ti}(\text{Cu}_{0.1}\text{Pt}_{0.9})_3$

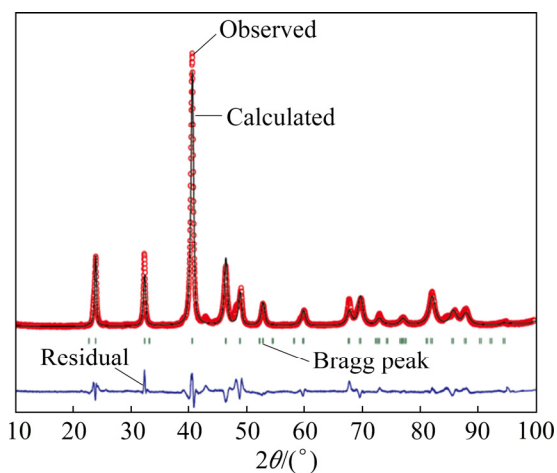


Fig. 5 Observed, calculated and residual powder XRD patterns and Bragg peak positions of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ alloy

For $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0.05, 0.2, 0.35, 0.5$) and $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0.6, 0.7, 0.8, 0.9$) alloys that contain multiple phases, indentation was performed on the target phase only, i.e. $\text{Ti}(\text{Cu,Pt})_2$ or $\text{Ti}(\text{Cu,Pt})_3$ phase.

A mathematical model was proposed to assess nano-hardness and modulus through indentation load–displacement data [30]. Usually, H is defined as the ratio of the maximum applied load (P_{max}) to

Table 3 Crystal data and refined parameters for $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ phase

Atom	Position	x	y	z	Occupancy	$B_{\text{eq}}/\text{\AA}^2$
Ti	1a	0	0	0	1	1.3928(1)
Cu ₁	1c	0.5	0.5	0	0.3021(4)	0.3355(9)
Pt ₁	1c	0.5	0.5	0	0.6978(6)	0.3355(9)
Cu ₂	2e	0	0.5	0.5	0.2977(2)	1.2223(1)
Pt ₂	2e	0	0.5	0.5	0.7022(8)	1.2223(1)

$\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$: Tetragonal AlPt_3 -type; $P4/mmm$ (No. 123); $a=3.9097(2)$ Å; $c=3.7227(3)$ Å; $D_{\text{calc}}=14.639$ g/cm³; $Z=1$; R -factors: $R_p=8.41\%$; $R_{wp}=9.95\%$; $R_f=7.94\%$; $R_B=6.56\%$

Table 4 Typical interatomic distance for $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ phase

Bond	Distance/Å	Multiplicity
Ti–Ti	3.909(7)	×4
Ti–Cu ₁ (Pt ₁)	2.764(6)	×4
Ti–Cu ₂ (Pt ₂)	2.699(2)	×8
Cu ₁ (Pt ₁)–Cu ₁ (Pt ₁)	3.722(7)	×2
Cu ₁ (Pt ₁)–Cu ₂ (Pt ₂)	2.699(2)	×8
Cu ₂ (Pt ₂)–Cu ₂ (Pt ₂)	3.909(7)	×4

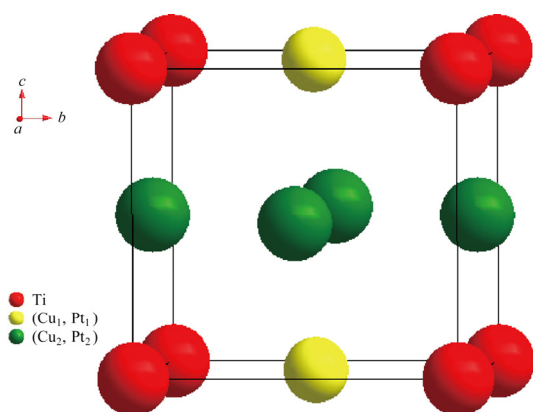


Fig. 6 Schematic illustration of crystal structure of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$ phase

the projected contact area of the indented impression (A):

$$H = \frac{P_{\max}}{A} \quad (1)$$

And the elastic modulus of the materials can be calculated as

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad (2)$$

where E_r is the reduced elastic modulus which takes into account the elastic contributions of the sample and the indenter tip; E and ν are respectively the elastic modulus and Poisson ratio of the tested material, while E_i and ν_i are those for the indenter.

Table 5 lists the H and E of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$. Both H and E of these two phases increase with increasing content of Pt. For $\text{Ti}(\text{Cu,Pt})_2$, whose composition formula is denoted as $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$, with x increasing from 0.08 to 0.48, E increases from 86.7 to 163.5 GPa and H increases from 4.5 to 6.1 GPa. It is worth noting that E of $\text{Ti}(\text{Cu}_{0.52}\text{Pt}_{0.48})_2$ phase reaches 163.5 GPa, higher than the highest E that has been reported for binary compound TiCu, 161.1 GPa [31]. For $\text{Ti}(\text{Cu,Pt})_3$, E increases from 218.4 to 262.2 GPa and H increases

from 9.4 to 13.6 GPa with x of $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ increasing from 0.62 to 0.88.

4.3.2 Elastic property calculation

First-principle calculations have been successfully used in disclosing the correlation between the crystal structure and the elastic properties [31–34]. Here, the elastic properties of the terminal members TiCu_2 and TiPt_2 of $\text{Ti}(\text{Cu,Pt})_2$, and TiCu_3 and TiPt_3 of $\text{Ti}(\text{Cu,Pt})_3$, were calculated using the same approach.

For the single-crystal material, elastic constant (C_{ij}) can be defined as means of a Taylor expansion of total energy, $E(V, \delta)$, in terms of the infinite small change of strain (δ) for the primitive cell volume (V) [35]:

$$E(V, \delta) = E(V_0, 0) + V_0 \left(\sum_i \tau_i \xi_i \delta_i + \frac{1}{2} \sum_{ij} C_{ij} \xi_i \delta_j \right) \quad (3)$$

where the indices i and j will run over 1, 2, 3, 4, 5 and 6, the volume of the unstrained system is denoted V_0 , $E(V_0, 0)$ is the corresponding total energy, τ_i is an element in the stress tensor and ξ_i is the factor which takes the value 1 if the Voigt numbers are 1, 2, or 3, and takes the value 2 if the Voigt numbers are 4, 5, or 6.

The bulk modulus B , shear modulus G , elastic modulus E and Poisson ratio ν for the polycrystalline materials can be found from the calculated elastic constants of single-crystal material by using the Voigt-Reuss-Hill (VRH) approximations [36–38]. In light of Ref. [36], for the orthorhombic and tetragonal structures, Voigt bulk modulus (B_V) and shear modulus (G_V) can be calculated as follows:

$$B_V = \frac{1}{9}(C_{11} + C_{22} + C_{33}) + \frac{2}{9}(C_{11} + C_{13} + C_{23}) \quad (4)$$

$$G_V = \frac{1}{15}[(C_{11} + C_{22} + C_{33} - (C_{12} + C_{13} + C_{23})) + \frac{3}{15}(C_{44} + C_{55} + C_{66})] \quad (5)$$

Table 5 Measured hardness (H) and elastic modulus (E) of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ phases

$\text{Ti}(\text{Cu,Pt})_2$					$\text{Ti}(\text{Cu,Pt})_3$				
Alloy No.	Nominal composition	Composition of target phase	E /GPa	H /GPa	Alloy No.	Nominal composition	Composition of target phase	E /GPa	H /GPa
A1	$\text{Ti}(\text{Cu}_{0.95}\text{Pt}_{0.05})_2$	$\text{Ti}(\text{Cu}_{0.92}\text{Pt}_{0.08})_2$	86.7	4.5	B1	$\text{Ti}(\text{Cu}_{0.4}\text{Pt}_{0.6})_3$	$\text{Ti}(\text{Cu}_{0.38}\text{Pt}_{0.62})_3$	218.4	9.4
A2	$\text{Ti}(\text{Cu}_{0.8}\text{Pt}_{0.2})_2$	$\text{Ti}(\text{Cu}_{0.78}\text{Pt}_{0.22})_2$	142.2	5.6	B2	$\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$	$\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$	225.7	10.3
A3	$\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$	$\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$	151.4	5.7	B3	$\text{Ti}(\text{Cu}_{0.2}\text{Pt}_{0.8})_3$	$\text{Ti}(\text{Cu}_{0.22}\text{Pt}_{0.78})_3$	259.3	12.5
A4	$\text{Ti}(\text{Cu}_{0.5}\text{Pt}_{0.5})_2$	$\text{Ti}(\text{Cu}_{0.52}\text{Pt}_{0.48})_2$	163.5	6.1	B4	$\text{Ti}(\text{Cu}_{0.1}\text{Pt}_{0.9})_3$	$\text{Ti}(\text{Cu}_{0.12}\text{Pt}_{0.88})_3$	262.2	13.6

while Reuss bulk modulus (B_R) and Reuss shear modulus (G_R) are defined as [39]

$$\frac{1}{B_R} = S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23}) \quad (6)$$

$$\frac{1}{G_R} = \frac{1}{15} [4(S_{11} + S_{22} + S_{33}) + 3(S_{44} + S_{55} + S_{66}) - 4(S_{12} + S_{13} + S_{23})] \quad (7)$$

where S is the compliance matrix and C is the elastic constant matrix related by $S=C^{-1}$.

HILL [38] considered that the average over Voigt and Reuss terms is considered to be the best approximation for finding the theoretical elastic modulus of polycrystalline materials:

$$B=(B_V+B_R)/2, \quad G=(G_V+G_R)/2 \quad (8)$$

For polycrystalline materials, E and ν can thus be obtained using the following relations:

$$E = \frac{9BG}{3B+G}, \quad \nu = \frac{3B-2G}{2(3B+G)} \quad (9)$$

The calculated equilibrium lattice parameters, volumes of terminal phases TiCu_2 and TiPt_2 of $\text{Ti}(\text{Cu,Pt})_2$ are listed in Table 6, together with the experimental data of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$. The calculated single-crystal elastic constants for terminal phases TiCu_2 and TiPt_2 of $\text{Ti}(\text{Cu,Pt})_2$ are listed in Table 7, and the B , G , E and ν are listed in Table 8. It is clear that these phases are elastically stable according to the mechanical stability criteria for orthorhombic structure, which are: $C_{11}>0$, $C_{22}>0$, $C_{33}>0$, $C_{44}>0$, $C_{55}>0$, $C_{66}>0$, $C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})>0$, $C_{11}+C_{22}-2C_{12}>0$, $C_{11}+C_{33}-2C_{13}>0$, and $C_{22}+C_{33}-2C_{23}>0$ [39].

Table 6 Calculated lattice parameters, unit-cell volumes of terminal phases TiCu_2 and TiPt_2 and experimental value of $\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2$

$\text{Ti}(\text{Cu,Pt})_2$	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
TiCu_2	4.4830	7.9798	4.5289	162.01
$\text{Ti}(\text{Cu}_{0.65}\text{Pt}_{0.35})_2(\text{exp.})$	4.5688	8.1822	4.5603	170.48
TiPt_2	4.6369	8.5491	4.8244	191.25

Table 7 Calculated elastic constants for $\text{Ti}(\text{Cu,Pt})_2$ phase

End-member	C_{11}	C_{12}	C_{13}	C_{22}	C_{23}	C_{33}	C_{44}	C_{55}	C_{66}
TiCu_2	229.9	55.2	29.6	184.0	45.3	139.3	69.9	66.5	6.0
TiPt_2	320.8	129.9	131.8	300.5	161.1	289.0	77.6	53.0	0.84

Table 8 Calculated bulk modulus B , shear modulus G , elastic modulus E and Poisson ratio ν for $\text{Ti}(\text{Cu,Pt})_2$ phase

End-member	B/GPa	G/GPa	E/GPa	ν	B/G
TiCu_2	90.7	29.3	79.3	0.35	3.10
TiPt_2	180.9	44.4	136.2	0.39	4.07

The ratio of B/G proposed by PUGH [40] can be used to predict the brittle or ductile behavior of a material. When B/G is larger than 1.75, the material is ductile, otherwise it is brittle. In Table 8, the B/G ratios of TiCu_2 and TiPt_2 are 3.10 and 4.07, respectively, implying that $\text{Ti}(\text{Cu,Pt})_2$ is a ductile phase.

LIU et al [41] proposed a method for modeling the effect of alloying elements on the elastic coefficients. As for the E of $\text{Ti}(\text{Cu,Pt})_2$, we have

$$E = E_{\text{TiCu}_2}(1-x) + E_{\text{TiPt}_2}x + E_{(\text{Ti,Cu,Pt})}x(1-x) \quad (10)$$

Figure 7 shows the E of $\text{Ti}(\text{Cu,Pt})_2$ as a function of Pt content. Dotted line means the changing trend between calculated and measured values, fitting result shows E a non-monotonic behavior with Pt content, i.e., it increases firstly then decreases. This nonlinearity fits well with Eq. (10): $E=136.22x+78.92(1-x)+235.77x(1-x)$.

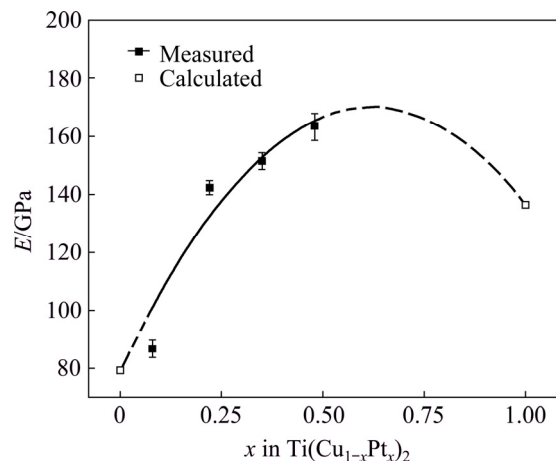


Fig. 7 Relationship between Pt content and elastic modulus for target phase $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_2$ ($x=0, 0.08, 0.22, 0.35, 0.48, 1$)

In the case of $\text{Ti}(\text{Cu,Pt})_3$, the calculated equilibrium lattice parameters, volumes of terminal phase TiCu_3 and TiPt_3 of $\text{Ti}(\text{Cu,Pt})_3$ are listed in Table 9, together with the experimental data of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$. The elastic constants and moduli of TiCu_3 and TiPt_3 are listed in Tables 10 and 11,

respectively. Similarly, the elastic constants also satisfy the mechanical stability criteria of tetragonal structure ($C_{11}>0$, $C_{33}>0$, $C_{44}>0$, $C_{66}>0$, $(C_{11}-C_{12})>0$, $(C_{11}+C_{33}-2C_{13})>0$ and $[2(C_{11}+C_{12})+C_{33}+4C_{13}]>0$) [42]. From Table 11, the B/G values of TiCu_3 and TiPt_3 are 5.74 and 2.12, respectively, both of which are larger than 1.75, indicating ductility of $\text{Ti}(\text{Cu,Pt})_3$ phase.

From Fig. 8, it is seen that E of $\text{Ti}(\text{Cu,Pt})_3$

Table 9 Calculated lattice parameters, unit-cell volumes of terminal phases TiCu_3 and TiPt_3 and experimental values of $\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3$

$\text{Ti}(\text{Cu,Pt})_3$	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
TiCu_3	3.7825	3.6668	52.46
$\text{Ti}(\text{Cu}_{0.3}\text{Pt}_{0.7})_3(\text{exp.})$	3.9097	3.7227	56.90
TiPt_3	3.9524	3.7626	58.77

Table 10 Calculated elastic constants for $\text{Ti}(\text{Cu,Pt})_3$ phase

End-member	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
TiCu_3	164.6	148.6	154.2	169.5	61.9	62.5
TiPt_3	343.5	180.9	180.7	343.3	135.9	136.0

Table 11 Calculated bulk modulus B , shear modulus G , elastic modulus E and Poisson ratio ν for $\text{Ti}(\text{Cu,Pt})_3$ phase

End-member	B/GPa	G/GPa	E/GPa	ν	B/G
TiCu_3	156.6	27.3	77.3	0.42	5.74
TiPt_3	235.0	110.6	286.9	0.30	2.12

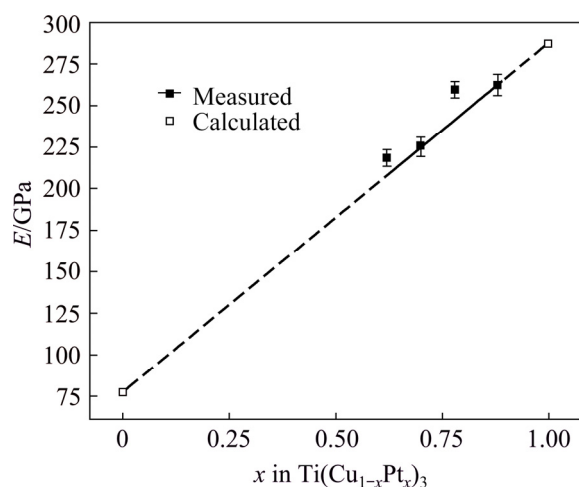


Fig. 8 Relationship between Pt content and elastic modulus for target phase $\text{Ti}(\text{Cu}_{1-x}\text{Pt}_x)_3$ ($x=0, 0.62, 0.70, 0.78, 0.88, 1$)

shows approximately linear relation with Pt content, which meets the linear function $E=210.23x+77.68$. In Fig. 8 dashed lines show the possible variation tendency among calculated and measured values of E . It is worth noting that this curve is constructed by combining the experimental and calculated values of E of $\text{Ti}(\text{Cu,Pt})_3$, further confirmation and discussion on the actual variation trend are still needed.

5 Conclusions

(1) The crystal structure and elastic properties of two new phases, $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$, were investigated. $\text{Ti}(\text{Cu,Pt})_2$ has VAu_2 -type structure, belonging to space group $\text{Amm}2$ (No. 38). Cu and Pt atoms share $4d$ and $4e$ sites, while Ti atoms occupy $2a$ and $2b$ sites. $\text{Ti}(\text{Cu,Pt})_3$ has tetragonal AlPt_3 -type structure of space group $P4/mmm$ (No. 123). Ti atoms occupy $1a$ site alone, and Cu and Pt occupy $1b$ and $2e$ sites.

(2) The elastic moduli of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ are in the range of 79.3–163.5 GPa and 77.3–286.9 GPa, respectively. The elastic modulus for $\text{Ti}(\text{Cu,Pt})_2$ phase exhibits a maximum value with increasing Pt content, while that for $\text{Ti}(\text{Cu,Pt})_3$ approximately increases linearly with content of Pt. Additionally, the B/G ratios of $\text{Ti}(\text{Cu,Pt})_2$ and $\text{Ti}(\text{Cu,Pt})_3$ are found in the range of 3.10–4.07 and 2.12–5.74, implying the good ductility of both phases.

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Ti(Cu,Pt)₂ 和 Ti(Cu,Pt)₃ 相的晶体结构和弹性性能

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摘 要: 利用 X 射线粉末衍射数据结合 Rietveld 结构精修方法研究并确定两个新三元相 Ti(Cu,Pt)₂ 和 Ti(Cu,Pt)₃ 的晶体结构。使用电子探针(EPMA)检测样品的成分, 同时结合纳米压痕技术和第一性原理计算对其弹性性能进行研究。研究发现, Ti(Cu,Pt)₂ 的空间群为 *Amm*2 (No. 38), 与 VAu₂ 有着相同的结构类型。Ti(Cu,Pt)₃ 的结构为四方晶系的 AlPt₃ 结构类型, 属于 *P4/mmm* 空间群 (No. 123)。纳米压痕测量和第一性原理计算表明, Ti(Cu,Pt)₂ 的弹性模量随 Pt 含量的增加先增大, 然后减小; 而 Ti(Cu,Pt)₃ 的弹性模量随 Pt 含量的增加几乎呈线性增加。

关键词: Ti–Cu–Pt 相; 晶体结构; X 射线衍射; 第一性原理计算; 弹性性能

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