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REINVESTIGATION OF THE SYSTEM Ti–Cu–Al AT 800°C

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The isothermal section of the phase diagram of the ternary system Ti–Cu–Al at the temperature of 800°C was investigated using X-ray powder diffraction, microstructural analysis and energy-dispersive X-ray spectroscopy. The homogeneity ranges at 800°C of three purely ternary compounds were determined: $TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3) (structure type Cu_3Au), $TiCu_{2+x}Al_{1-x}$, x=0–0.52(2) (structure type $MnCu_2Al$) and $TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3) (structure type $MgZn_2$). The crystal structure of an additional compound near the composition $TiAl_3$ was refined on X-ray powder diffraction data ($Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$, structure type $ZrAl_3$; Pearson symbol *tI*16, space group *I*4/*mmm*, a=3.9159(3), c=16.556(2) Å). This ternary compound, observed at 800°C, is probably an extension of the solid solution of the binary high-temperature phase reported as Ti_5Al_{11} with the same structure type. The microhardness of the ternary compounds was measured.

Keywords: aluminum, copper, titanium, X-ray powder diffraction, phase diagram, ternary compound, microstructure, hardness.

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Introduction

Literature data on the Ti–Cu–Al system has been summarized by Ran and Stadelmaier [1]. The existence of a ternary aluminide with equiatomic composition in the system Ti–Cu–Al was established already in 1935 and a cell corresponding to the hexagonal Laves type $MgZn_2$ was reported; thirty years later $TiCu_2Al$ with CsCl-type structure was reported, and cell parameters for the same phase were published [2,3]. Three compounds, $TiCu_{0.08}Al_{2.92}$, $TiCu_{0.12}Al_{2.88}$ and $TiCu_{0.16}Al_{2.84}$, with different variants of cubic close-packing (structure types $TiAl_3$, Cu_3Au and $ZrAl_3$, respectively), were reported close to the boundary system Ti–Al, and the structure of the compound $TiCu_{2.25}Al_{0.75}$ was assigned the type $MnCu_2Al$, commonly referred to as Heusler phase [4]. The latter appears to be the same as the compound earlier reported as $TiCu_2Al$, the $MnCu_2Al$ type being an ordered derivative of the CsCl type.

The interaction of the components in the system Ti–Cu–Al at 500°C [5], 540°C [6] and 800°C [5] has been investigated in almost the whole concentration range (Figs. 1–3). The authors confirmed the existence of three ternary compounds with idealized compositions Ti_2CuAl_5 ($TiCu_{0.5}Al_{2.5}$, structure type Cu_3Au), $TiCu_2Al$ ($MnCu_2Al$), and TiCuAl ($MgZn_2$) and determined their homogeneity ranges. According to Virdis and Zwicker [6], at 540°C all three compounds can have variable Ti content, from 5 at.% (Ti_2CuAl_5 and TiCuAl) to 9 at.% ($TiCu_2Al$), whereas according to Markiv et al. [5] only one of the compounds, $TiCu_2Al$, can contain more or less Ti (4 at.%). The compound TiCuAl was reported to have a homogeneity range along the isoconcentrate 40 at.% Ti from 30 to 40 at.% Al at 540°C [6], but according to Markiv et al. [5], at 500°C this compound is located along the isoconcentrate 33.3 at.% Ti and extends from 35 to 44 at.% Al. In both works, the cubic close-packed phase Ti_2CuAl_5 and the Heusler phase $TiCu_2Al$ are located along the isoconcentrate 25 at.% Ti, but slightly different homogeneity ranges were found: 57–65 at.% Al (540°C) and 55–6 3 at.% Al (500°C) for the former, and 5–25 at.% Al (540°C) and 13–25 at.% Al (500°C) for the latter. For these three compounds the homogeneity ranges at 800°C are the same as at 500°C, while the phase equilibria differ slightly.

Information about hardness measurements is available for some compounds in the system Ti–Cu [7]. The hardness of the pure metals is as follows:

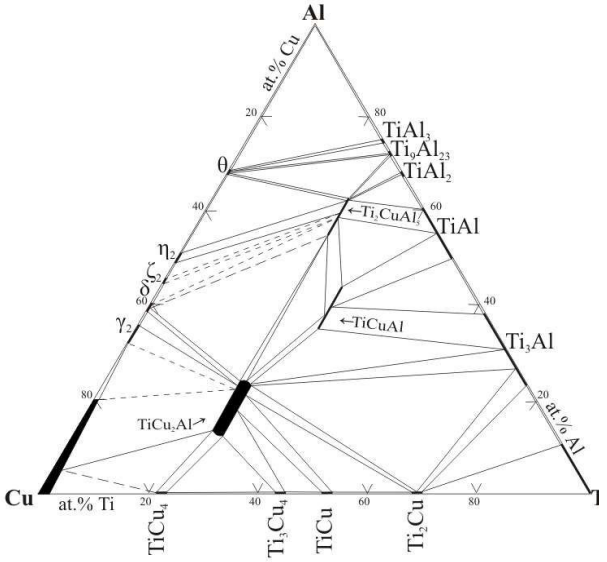


Fig. 1. Isothermal section of the phase diagram of the system Ti–Cu–Al at 500°C according to Markiv et al. [5]

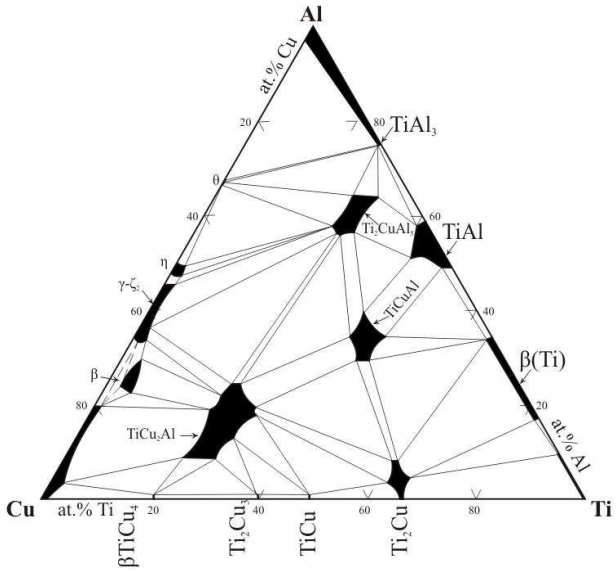


Fig. 2. Isothermal section of the phase diagram of the system Ti–Cu–Al at 540°C according to Virdis and Zwicker [6]

0.970 GPa, 0.369 GPa and 0.167 GPa for titanium, copper and aluminum, respectively. According to ref. [7], the hardness of the compound TiCu is 0.370 GPa, i.e. lower than for titanium, but similar to the value for copper.

Experimental

Alloys of the system Ti–Cu–Al were synthesized from the metals (purity for Ti ≥99.99 wt.%, Cu ≥99.99 wt.%, Al ≥99.998 wt.%) by arc melting under a purified argon atmosphere. The ingots were annealed at 800°C under vacuum in quartz ampoules for 1 week and subsequently quenched in cold water. Phase and structural analyses were performed on X-ray powder diffraction data (diffractometers DRON 2.0M, FeK_α radiation, and STOE Stadi P, $CuK_{\alpha 1}$ radiation, angular range $6^0 \le 2\theta \le 108^0$, step 0.015^0, scan time 230 s per step). The profile and structural parameters were refined by the Rietveld method, using the program DBWS [8].

The microstructure of the samples was studied by scanning electron microscopy (SEM, JEOL JSM-7600F equipped with an energy dispersive X-ray (EDX) analyzer Oxford Instruments, X-max 50 mm^2). The parameters of the microscope for sample observation in COMPO mode and EDX chemical analysis were set at 15 kV.

The hardness was measured with a Microhardness Tester (FM-100, Future-Tech Corp.). A square-based pyramidal diamond was pressed using a force of 5 N for a loading time of 10 s; at least eight areas across each joint were analyzed to obtain an average value.

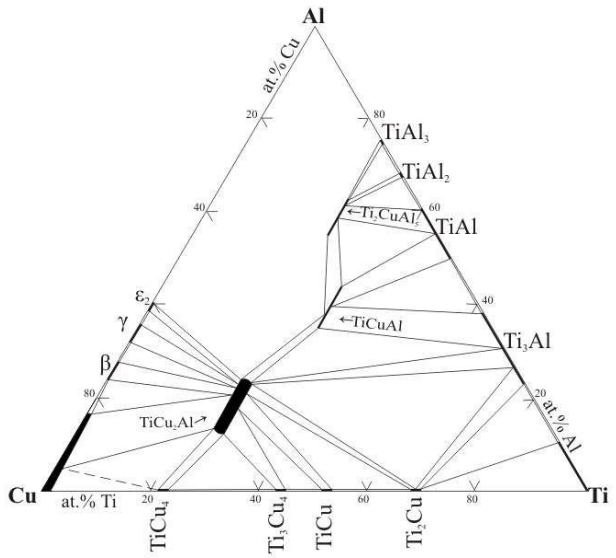


Fig. 3. Isothermal section of the phase diagram of the system Ti–Cu–Al at 800°C according to Markiv et al. [5]

Results and discussion

X-ray phase analysis

Table 1 presents the results of the phase analysis by X-ray diffraction of 2 binary and 33 ternary samples annealed at 800°C. The unit-cell parameters of some of the binary compounds in the systems Ti–Cu, Ti–Al, and Cu–Al (TiCu, Ti_2Cu, TiAl, Ti_3Al, $Cu_{1.7}Al$, and Cu_9Al_4) and the compositions and unit-cell parameters of the four ternary compounds in the system Ti–Cu–Al ($Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$,

Table 1

Phase composition of the samples investigated in the ternary system Ti–Cu–Al

Nominal composition of the sample	Phases [a]	Structure type, space group, unit-cell parameters
1	2	3
$Cu_{62.96}Al_{37.04}$	$Cu_{1.7}Al$	$Co_{1.75}Ge$, $P6_3/mmc$, a=4.108(1), c=5.014(1) Å
$Cu_{69.23}Al_{30.77}$	Cu_9Al_4	Cu_9Al_4, P-43m, a=8.694(1) Å
$Ti_{10}Cu_{50}Al_{40}$	Cu_9Al_4 $TiCu_{0.5}Al_{2.5}$	Cu_9Al_4, P-43m, a=8.7056(9) Å Cu_3Au, Pm-3m, a=3.9075(7) Å
$Ti_{10}Cu_{60}Al_{30}$	Cu_9Al_4 $TiCu_2Al$	Cu_9Al_4, P-43m, a=8.704(1) Å $MnCu_2Al$, Fm-3m, a=6.0163(8) Å
$Ti_{17}Cu_{33}Al_{50}$	$TiCu_{0.5}Al_{2.5}$ Cu_9Al_4	Cu_3Au, Pm-3m, a=3.9138(5) Å Cu_9Al_4, P-43m, a=8.720(1) Å
$Ti_{20}Cu_{20}Al_{60}$	$TiCu_{0.5}Al_{2.5}$ $Cu_{1.7}Al$	Cu_3Au, Pm-3m, a=3.9138(5) Å $Co_{1.75}Ge$, $P6_3/mmc$, a=4.1022(1), c=5.008(2) Å
$Ti_{20}Cu_{60}Al_{20}$	TiCuAl $TiCu_2Al$ $TiCu_{0.5}Al_{2.5}$	$MgZn_2$, $P6_3/mmc$, a=5.0402(8), c=8.1073(1) Å $MnCu_2Al$, Fm-3m, a=6.0212(1) Å Cu_3Au, Pm-3m, a=3.9077(7) Å
$Ti_{25}Cu_{6.25}Al_{68.75}$	$TiCu_{0.5}Al_{2.5}$ $Ti_{1.15}Cu_{0.09}Al_{2.76}$	Cu_3Au, Pm-3m, a=3.9416(2) Å $ZrAl_3$, $I4/mmm$, a=3.8935(3), c=16.6423(2) Å
$Ti_{25}Cu_{7.5}Al_{67.5}$	$TiCu_{0.5}Al_{2.5}$ $Ti_{1.15}Cu_{0.09}Al_{2.76}$	Cu_3Au, Pm-3m, a=3.9384(6) Å $ZrAl_3$, $I4/mmm$, a=3.8903(1), c=16.625(7) Å
$Ti_{25}Cu_{10}Al_{65}$	$TiCu_{0.5}Al_{2.5}$	Cu_3Au, Pm-3m, a=3.9386(6) Å
$Ti_{25}Cu_{15}Al_{60}$	$TiCu_{0.5}Al_{2.5}$	Cu_3Au, Pm-3m, a=3.9193(5) Å
$Ti_{25}Cu_{50}Al_{25}$	$TiCu_2Al$ Cu_9Al_4 $TiCu_{0.5}Al_{2.5}$	$MnCu_2Al$, Fm-3m, a=6.016(1) Å Cu_9Al_4, P-43m, a=8.708(2) Å Cu_3Au, Pm-3m, a=3.907(1) Å
$Ti_{25}Cu_{55}Al_{20}$	$TiCu_2Al$	$MnCu_2Al$, Fm-3m, a=6.003(2) Å
$Ti_{25}Cu_{60}Al_{15}$	$TiCu_2Al$	$MnCu_2Al$, Fm-3m, a=5.986(1) Å
$Ti_{25}Cu_{63}Al_{12}$	$TiCu_2Al$	$MnCu_2Al$, Fm-3m, a=5.976(3) Å
$Ti_{27}Cu_2Al_{71}$	$Ti_{1.15}Cu_{0.09}Al_{2.76}$	$ZrAl_3$, $I4/mmm$, a=3.9159(3), c=16.556(2) Å
$Ti_{29}Cu_2Al_{69}$	$Ti_{1.15}Cu_{0.09}Al_{2.76}$	$ZrAl_3$, $I4/mmm$, a=3.9150(1), c=16.554(7) Å
$Ti_{28}Cu_{34}Al_{38}$	$TiCu_2Al$	$MnCu_2Al$, Fm-3m, a=6.0111(4) Å
$Ti_{30}Cu_{40}Al_{30}$	TiCuAl $TiCu_2Al$	$MgZn_2$, $P6_3/mmc$, a=5.0303(7), c=8.098(1) Å $MnCu_2Al$, Fm-3m, a=6.0212(9) Å
$Ti_{30}Cu_{50}Al_{20}$	$TiCu_2Al$ Ti_2Cu	$MnCu_2Al$, Fm-3m, a=6.005(1) Å Zr_2Cu, $I4/mmm$, a=2.978(2), c=10.57(1) Å
$Ti_{30}Cu_{60}Al_{10}$	$TiCu_2Al$ TiCu	$MnCu_2Al$, Fm-3m, a=5.971(2) Å TiCu, $P4/mmm$, a=3.137(2), c=2.847(5) Å
$Ti_{31}Cu_2Al_{67}$	$Ti_{1.15}Cu_{0.09}Al_{2.76}$	$ZrAl_3$, $I4/mmm$, a=3.9155(1), c=16.559(7) Å
$Ti_{33.3}Cu_{16}Al_{50.7}$	TiCuAl TiAl $TiCu_{0.5}Al_{2.5}$	$MgZn_2$, $P6_3/mmc$, a=5.0303(7), c=8.098(1) Å CuAu, $P4/mmm$, a=2.8117(6), c=4.050(1) Å Cu_3Au, Pm-3m, a=3.9265(6) Å
$Ti_{33.3}Cu_{18}Al_{48.7}$	TiCuAl $TiCu_{0.5}Al_{2.5}$	$MgZn_2$, $P6_3/mmc$, a=5.0615(5), c=8.1789(9) Å Cu_3Au, Pm-3m, a=3.9213(5) Å
$Ti_{33.3}Cu_{23}Al_{43.7}$	TiCuAl	$MgZn_2$, $P6_3/mmc$, a=5.0553(4), c=8.1361(7) Å
$Ti_{33.3}Cu_{28}Al_{38.7}$	TiCuAl	$MgZn_2$, $P6_3/mmc$, a=5.0364(6), c=8.1065(9) Å
$Ti_{33.3}Cu_{33.3}Al_{33.3}$	TiCuAl $TiCu_{0.5}Al_{2.5}$	$MgZn_2$, $P6_3/mmc$, a=5.0165(5), c=8.0920(1) Å Cu_3Au, Pm-3m, a=3.9101(5) Å
$Ti_{33.3}Cu_{38}Al_{28.7}$	TiCuAl	$MgZn_2$, $P6_3/mmc$, a=5.0053(5), c=8.0906(8) Å
$Ti_{35}Cu_5Al_{60}$	$TiCu_{0.5}Al_{2.5}$ TiAl	Cu_3Au, Pm-3m, a=3.928(2) Å CuAu, $P4/mmm$, a=2.815(2), c=4.045(3) Å
$Ti_{40}Cu_{40}Al_{20}$	$TiCu_2Al$ $TiCu_{0.5}Al_{2.5}$	$MnCu_2Al$, Pm-3m, a=5.993(3) Å Cu_3Au, Pm-3m, a=3.920(2) Å

(continued on next page)

Table 1 (continued)

1	2	3
$Ti_{40}Cu_{50}Al_{10}$	$TiCu_2Al$ TiCu Ti_2Cu	$MnCu_2Al$, *Fm*-3*m*, a=6.061(5) Å TiCu, *P*4/*mmm*, a=3.131(3), c=2.9110(2) Å Zr_2Cu, *I*4/*mmm*, a=2.999(7), c=10.69(4) Å
$Ti_{45}Cu_{10}Al_{45}$	TiCuAl TiAl	$MgZn_2$, $P6_3/mmc$, a=5.034(2), c=8.107(3) Å CuAu, *P*4/*mmm*, a=2.820(1), c=4.049(2) Å
$Ti_{45}Cu_{20}Al_{35}$	TiCuAl Ti_3Al	$MgZn_2$, $P6_3/mmc$, a=5.026(2), c=8.104(3) Å Mg_3Cd, $P6_3/mmc$, a=5.767(3), c=4.633(2) Å
$Ti_{50}Cu_{40}Al_{10}$	Ti_2Cu TiCuAl $TiCu_2Al$	Zr_2Cu, *I*4/*mmm*, a=3.039(2), c=10.693(9) Å $MgZn_2$, $P6_3/mmc$, a=5.013(3), c=8.179(9) Å $MnCu_2Al$, *Fm*-3*m*, a=6.112(4) Å
$Ti_{60}Cu_{10}Al_{30}$	Ti_3Al Ti_2Cu	Mg_3Cd, $P6_3/mmc$, a=5.766(6), c=4.620(3) Å Zr_2Cu, *I*4/*mmm*, a=2.981(4), c=10.82(2) Å

Note: [a] – $TiCu_{0.5}Al_{2.5}$: $TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3); $TiCu_2Al$: $TiCu_{2+x}Al_{1-x}$, x=0–0.52(2); TiCuAl: $TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3).

Table 2

Crystallographic parameters of the binary and ternary compounds observed in the system Ti–Cu–Al at 800°C

Compound	Structure type	Pearson symbol	Space group	a, Å	c, Å	Reference
$TiCu_{0.12}Al_{2.88}$	Cu_3Au	*cP*4	*Pm*-3*m*	3.927	–	[4]
$TiCu_{0.30(3)}Al_{2.70(3)}$-$TiCu_{0.60(3)}Al_{2.40(3)}$				3.9384(6)–3.9193(5)	–	[a]
$TiCu_{0.16}Al_{2.84}$	$ZrAl_3$	*tI*16	*I*4/*mmm*	3.901	16.60	[4]
$Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$				3.9159(3)	16.556(2)	[a]
$TiCu_{2.25}Al_{0.75}$	$MnCu_2Al$	*cF*16	*Fm*-3*m*	5.93	–	[4]
$TiCu_2Al$-$TiCu_{2.52(2)}Al_{0.48(2)}$				6.016(1)–5.976(3)	–	[a]
TiCuAl	$MgZn_2$	*hP*12	$P6_3/mmc$	5.00	8.165	[4]
$TiCu_{0.54(3)}Al_{1.46(3)}$-$TiCu_{1.14(3)}Al_{0.86(3)}$				5.0615(5)–5.0053(5)	8.1789(9)–8.0906(8)	[a]
TiCu	TiCu	*tP*2	*P*4/*mmm*	3.140	2.856	[2]
				3.131(3)	2.9110(2)	[a]
Ti_2Cu	Zr_2Cu	*tI*6	*I*4/*mmm*	2.935	10.772	[9]
				3.039(2)	10.693(9)	[a]
TiAl	CuAu	*tP*2	*P*4/*mmm*	2.8284	4.075	[10]
				2.815(2)	4.045(3)	[a]
Ti_3Al	Mg_3Cd	*hP*8	$P6_3/mmc$	5.764	4.664	[11]
				5.766(6)	4.620(3)	[a]
$Cu_{1.7}Al$	$Co_{1.75}Ge$	*hP*6	$P6_3/mmc$	4.146	5.063	[2]
				4.108(1)	5.014(1)	[a]
Cu_9Al_4	Cu_9Al_4	*cP*52	*P*-43*m*	8.707	–	[2]
				8.694(1)		[a]

Note: [a] – this work.

$TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3), $TiCu_{2+x}Al_{1-x}$, x=0–0.52(2), and $TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3)) were determined and are listed in Table 2. It should be mentioned that the high-temperature phase with W-type structure (β phase), reported to form at 70–80 at.% Cu above 567°C in the Cu–Al system, was not observed in this work, presumably because of not efficient quenching.

Three ternary compounds with variable composition at 800°C exhibit the following

Table 3

Unit-cell parameters of ternary compounds with extended homogeneity ranges in the system Ti–Cu–Al at 800°C

Nominal composition of the sample	x	a, Å	c, Å	V, Å^3
$TiCu_xAl_{3-x}$, x=0.30(3) –0.60(3) (structure type Cu_3Au)				
$Ti_{25}Cu_{7.5}Al_{67.5}$	0.30	3.9384(6)	–	61.09(2)
$Ti_{25}Cu_{10}Al_{65}$	0.40	3.9386(6)	–	61.10(2)
$Ti_{25}Cu_{15}Al_{60}$	0.60	3.9193(5)	–	60.20(1)
$TiCu_{2+x}Al_{1-x}$, x=0–0.52(2) (structure type $MnCu_2Al$)				
$Ti_{25}Cu_{50}Al_{25}$	0	6.016(1)	–	217.7(1)
$Ti_{25}Cu_{55}Al_{20}$	0.20	6.003(2)	–	216.3(1)
$Ti_{25}Cu_{60}Al_{15}$	0.40	5.986(1)	–	214.5(1)
$Ti_{25}Cu_{63}Al_{12}$	0.52	5.976(3)	–	213.4(2)
$TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3) (structure type $MgZn_2$)				
$Ti_{33.3}Cu_{18}Al_{48.7}$	0.54	5.0615(5)	8.1789(9)	181.4(3)
$Ti_{33.3}Cu_{23}Al_{43.7}$	0.69	5.0553(4)	8.1361(7)	180.1(3)
$Ti_{33.3}Cu_{28}Al_{38.7}$	0.84	5.0364(6)	8.1065(9)	178.1(4)
$Ti_{33.3}Cu_{33.3}Al_{33.3}$	1	5.0165(5)	8.0920(1)	176.4(3)
$Ti_{33.3}Cu_{38}Al_{28.7}$	1.14	5.0053(5)	8.0906(8)	175.5(3)

homogeneity ranges: 7.5 at.% Al (Cu) along the isoconcentrate 25 at.% Ti ($TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3)), 13 at.% Al (Cu) along 25 at.% Ti ($TiCu_{2+x}Al_{1-x}$, x=0–0.52(2)), and 20 at.% Al (Cu) along 33.3 at.% Ti ($TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3)). Table 3 shows the unit-cell parameters as a function of the Cu content. In the three cases the unit-cell parameters decrease with increasing Cu content and decreasing Al content, in agreement with the difference between the atomic radii of Al (r_{Al}=1.43 Å) and Cu (r_{Cu}=1.28 Å).

Microstructure analysis

Figures 4–6 show the microstructure of three investigated samples. The compositions of the phases that exist in these samples are given in Table 4. It appears that the Ti content is in general slightly lower than expected (approx. 5 at.%) and the Ti content in the proposed chemical formulas was normalized to 25 at.% for the Cu_3Au-type and Heusler phases and 33.3 at.% for the Laves phase. According to the X-ray diffraction diagram, the sample $Ti_{25}Cu_{6.25}Al_{68.75}$ contains two phases. The composition of the majority phase (grey phase in Fig. 4) with Cu_3Au-type structure was found to be $Ti_{23.8}Cu_{11.5}Al_{64.7}$ from EDX analysis, normalized to $TiCu_{0.45(4)}Al_{2.55(4)}$, which is well within the homogeneity range determined by X-ray diffraction (Table 3). The dark phase with $ZrAl_3$-type structure (see below) was found to contain slightly more than 25 at.% Ti, in agreement with earlier reports. Assuming the same underestimation of the Ti content as in the other cases, we propose the approximate composition $Ti_{1.06}Cu_{0.08}Al_{2.86}$.

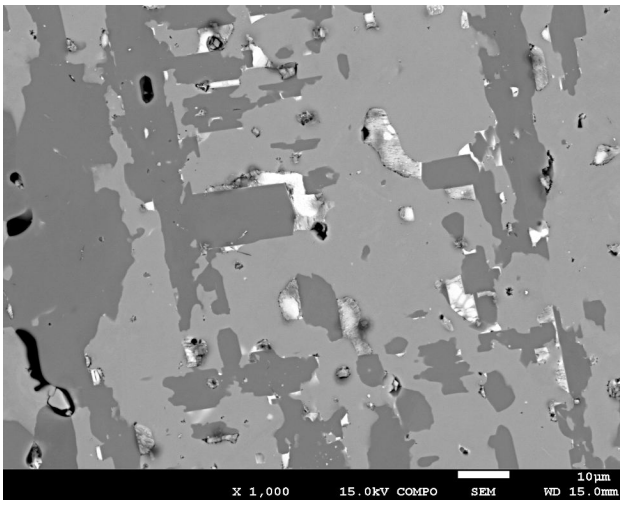


Fig. 4. EDX maps of the sample $Ti_{25}Cu_{6.25}Al_{68.75}$ (grey phase – $TiCu_{0.45(4)}Al_{2.55(4)}$, dark phase – $Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$)

Table 4

EDX analysis of three samples in the Ti–Cu–Al system

Nominal composition of the sample	Composition from EDX, at.%	Proposed chemical formula
$Ti_{25}Cu_{6.25}Al_{68.75}$	$Ti_{23.81}Cu_{11.45}Al_{64.74}$ $Ti_{25.25}Cu_{1.90}Al_{72.85}$	$TiCu_{0.45}Al_{2.55}$ $Ti_{1.15}Cu_{0.09}Al_{2.76}$
$Ti_{25}Cu_{50}Al_{25}$ [a]	$Ti_{23.67}Cu_{53.65}Al_{22.68}$	$TiCu_{2.11}Al_{0.89}$
$Ti_{33.3}Cu_{23}Al_{43.7}$	$Ti_{31.68}Cu_{24.69}Al_{43.63}$ $Ti_{46.63}Al_{53.37}$	$TiCu_{0.72}Al_{1.28}$ $Ti_{0.93}Al_{1.07}$

Note: [a] – the sample contains small amounts of Cu_9Al_4 and $TiCu_{0.5}Al_{2.5}$.

The dominating phase in the $Ti_{25}Cu_{50}Al_{25}$

sample (Fig. 5) is the Heusler compound with $MnCu_2Al$-type structure, accompanied by trace amounts of the ternary Cu_3Au-type phase and binary gamma-brass Cu_9Al_4. The chemical formula of the Cu_3Au-type phase was normalized to $TiCu_{2.11(4)}Al_{0.89(4)}$. Here too the composition from EDX analysis is in good agreement with the homogeneity range from X-ray diffraction in Table 3.

The photograph of the sample $Ti_{33.3}Cu_{23}Al_{43.7}$ in Fig. 6 shows two phases. The light phase is the Laves phase with $MgZn_2$-type structure. The normalized composition from the EDX analysis is $TiCu_{0.72(3)}Al_{1.28(3)}$, i.e. well inside the homogeneity range $TiCu_xAl_{2-x}$, x=0.54(3)−1.14(3). The second phase has the composition $Ti_{0.93(2)}Al_{1.07(2)}$ and CuAu-type structure.

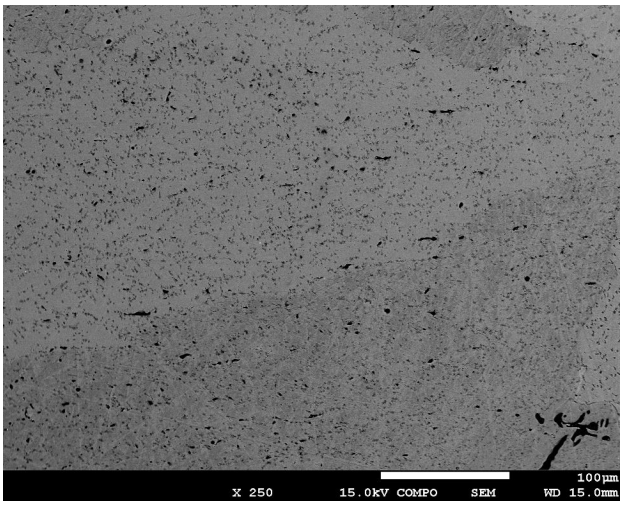


Fig. 5. EDX maps of the sample $Ti_{25}Cu_{50}Al_{25}$ (grey phase − $TiCu_{2.11(4)}Al_{0.89(4)}$)

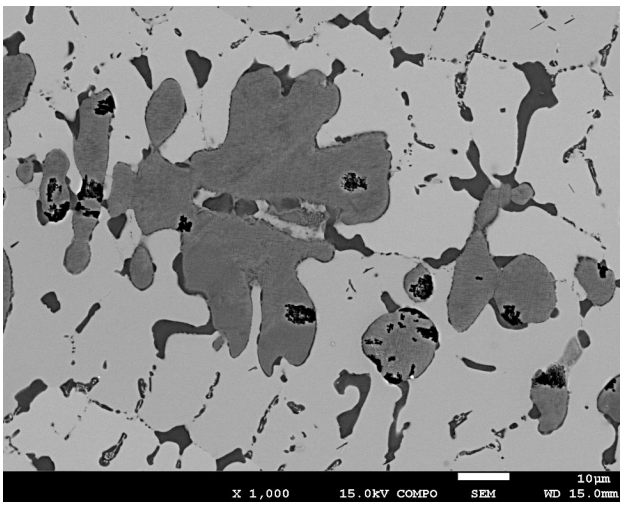


Fig. 6. EDX maps of the sample $Ti_{33.3}Cu_{23}Al_{43.7}$ (light phase − $TiCu_{0.72(3)}Al_{1.28(3)}$, dark phase − $Ti_{0.93(2)}Al_{1.07(2)}$)

Differential thermal analysis

The DTA curve of the sample $Ti_{25}Cu_{6.25}Al_{68.75}$ (Fig. 7,a) shows two thermal effects, at 941.5°C/1326.1°C and 936.7°C/1354.2°C in the heating and cooling regimes, respectively. The thermal effects recorded during heating of the sample correspond to the melting temperature of the two ternary compounds: $Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$ ($ZrAl_3$-type structure) and $TiCu_{0.45(4)}Al_{2.55(4)}$ (Cu_3Au). The peaks on the cooling curve show the temperatures of crystallization of these compounds. According to ref. [12], the ternary compound Ti_2CuAl_5 forms at 1350°C, in agreement with our DTA results.

The DTA curve for the sample $Ti_{25}Cu_{50}Al_{25}$ (Fig. 7,b) contains several peaks. On the heating curve, the first one at 953.7°C is in agreement with the temperature of peritectoid formation of the room-temperature modification of the binary compound Cu_9Al_4 (873°C in ref. [13]). The peak at 1012°C corresponds to the structural transition Cu_9Al_4 rt − Cu_9Al_4 ht (1022°C in ref. [13]), whereas the third peak, at 1067°C, shows the melting temperature of the ternary compound $TiCu_{2.11(4)}Al_{0.89(4)}$ with $MnCu_2Al$-type structure, in slight disagreement with ref. [12] (1125°C).

The DTA curve of the sample $Ti_{33.3}Cu_{23}Al_{43.7}$ contains two peaks (Fig. 7,c): the thermal effect on the heating curve at 1240.1°C corresponds to the melting temperature of the ternary compound $TiCu_{0.72(3)}Al_{1.28(3)}$ ($MgZn_2$) and the peak on the cooling curve at 1241.8°C to the crystallization of this compound. The results obtained here are in agreement with refs. [5,6] (1200°C).

Isothermal section of the system Ti−Cu−Al at 800°C

The isothermal section of the system Ti−Cu−Al at 800°C presented in Fig. 8 was constructed based on literature data available for the binary boundary systems and own ternary alloys. Aluminum being liquid at 800°C, the equilibria in the Al-rich corner are tentative, and those of the Cu-rich corner were assigned in agreement with earlier study [5]. The section contains 18 single-phase regions, 35 two-phase and 19 three-phase regions.

According to ref. [13], the solid solubility of Cu in Ti is limited to 1.5 at.% Cu at 800°C, while the solubility of Ti in Cu exceeds 5 at.% Ti. Al dissolves very little Ti, but Cu dissolves more than 5 at.% Ti. The solid solubility of Al in Cu is almost 18 at.% Al. Based on the cell parameters of the binary compounds in ternary samples, we deduce that the binary compounds of the systems Ti−Cu and Ti−Al dissolve less than 2 at.% of the third component.

As shown above, the existence of three purely

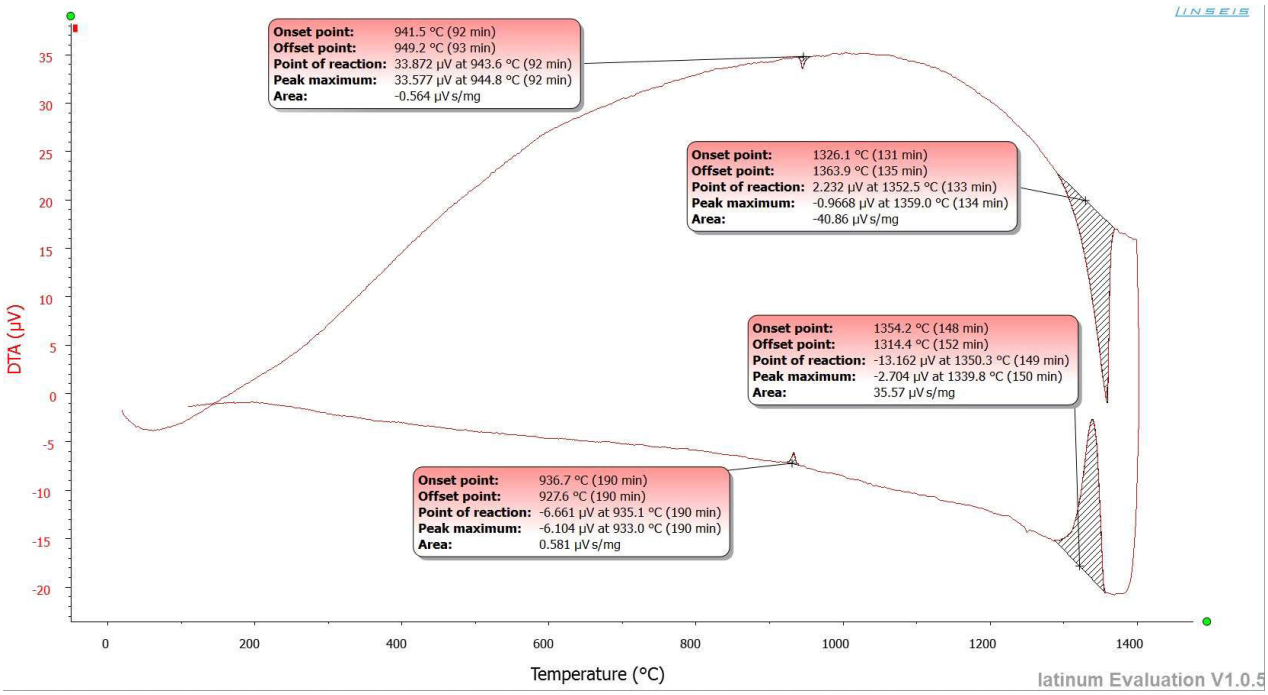

Onset point: 941.5 °C (92 min)
Offset point: 949.2 °C (93 min)
Point of reaction: 33.872 µV at 943.6 °C (92 min)
Peak maximum: 33.577 µV at 944.8 °C (92 min)
Area: -0.564 µV s/mg
Onset point: 1326.1 °C (131 min)
Offset point: 1363.9 °C (135 min)
Point of reaction: 2.232 µV at 1352.5 °C (133 min)
Peak maximum: -0.9668 µV at 1359.0 °C (134 min)
Area: -40.86 µV s/mg
Onset point: 1354.2 °C (148 min)
Offset point: 1314.4 °C (152 min)
Point of reaction: -13.162 µV at 1350.3 °C (149 min)
Peak maximum: -2.704 µV at 1339.8 °C (150 min)
Area: 35.57 µV s/mg
Onset point: 936.7 °C (190 min)
Offset point: 927.6 °C (190 min)
Point of reaction: -6.661 µV at 935.1 °C (190 min)
Peak maximum: -6.104 µV at 933.0 °C (190 min)
Area: 0.581 µV s/mg
DTA (µV)
Temperature (°C)
latinum Evaluation V1.0.5

Fig. 7,a

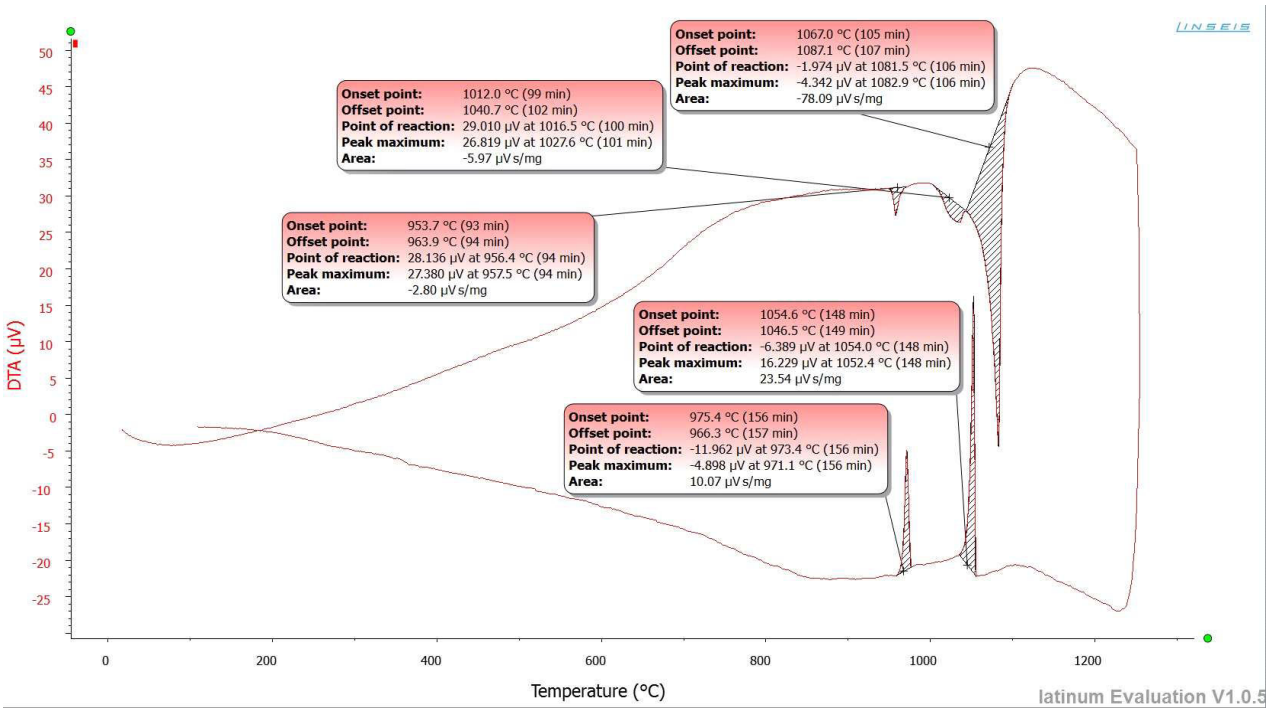
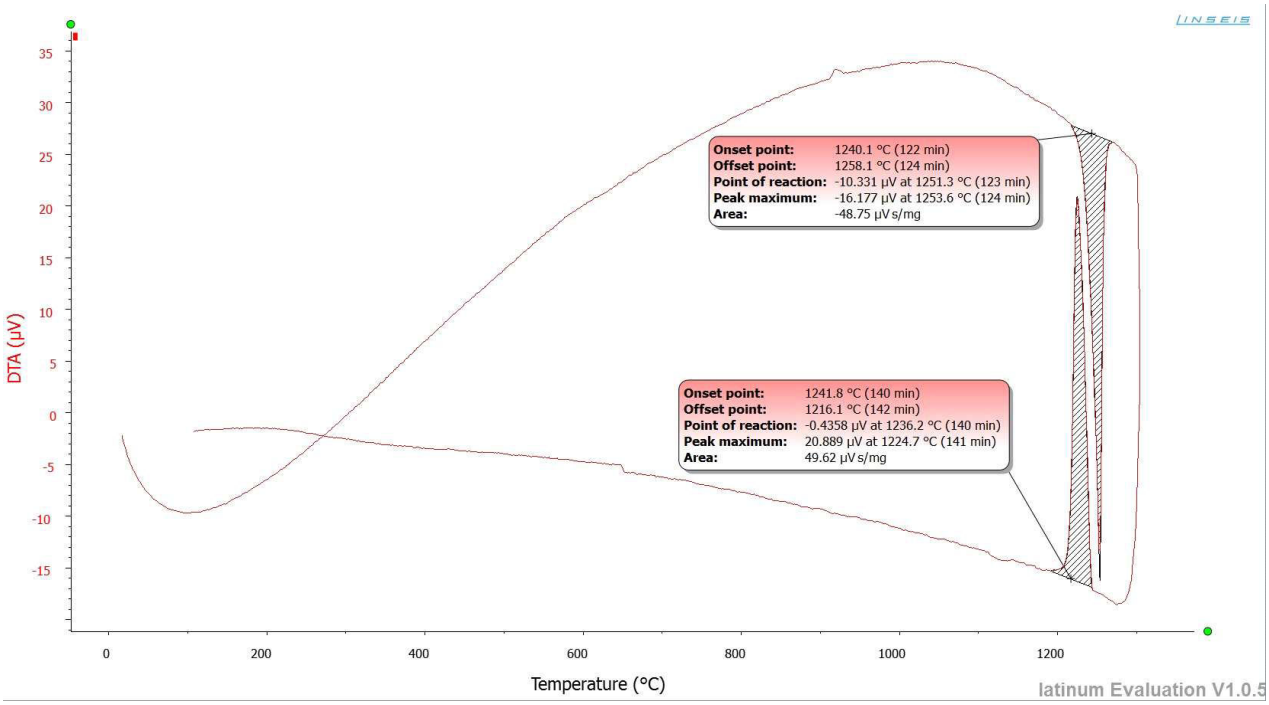

Onset point: 1067.0 °C (105 min)
Offset point: 1087.1 °C (107 min)
Point of reaction: -1.974 µV at 1081.5 °C (106 min)
Peak maximum: -4.342 µV at 1082.9 °C (106 min)
Area: -78.09 µV s/mg
Onset point: 1012.0 °C (99 min)
Offset point: 1040.7 °C (102 min)
Point of reaction: 29.010 µV at 1016.5 °C (100 min)
Peak maximum: 26.819 µV at 1027.6 °C (101 min)
Area: -5.97 µV s/mg
Onset point: 953.7 °C (93 min)
Offset point: 963.9 °C (94 min)
Point of reaction: 28.136 µV at 956.4 °C (94 min)
Peak maximum: 27.380 µV at 957.5 °C (94 min)
Area: -2.80 µV s/mg
Onset point: 1054.6 °C (148 min)
Offset point: 1046.5 °C (149 min)
Point of reaction: -6.389 µV at 1054.0 °C (148 min)
Peak maximum: 16.229 µV at 1052.4 °C (148 min)
Area: 23.54 µV s/mg
Onset point: 975.4 °C (156 min)
Offset point: 966.3 °C (157 min)
Point of reaction: -11.962 µV at 973.4 °C (156 min)
Peak maximum: -4.898 µV at 971.1 °C (156 min)
Area: 10.07 µV s/mg
DTA (µV)
Temperature (°C)
latinum Evaluation V1.0.5

Fig. 7,b



c

Fig. 7. DTA curves for the samples a – $Ti_{25}Cu_{6.25}Al_{68.75}$, b – $Ti_{25}Cu_{50}Al_{25}$ and c – $Ti_{33.3}Cu_{23}Al_{43.7}$

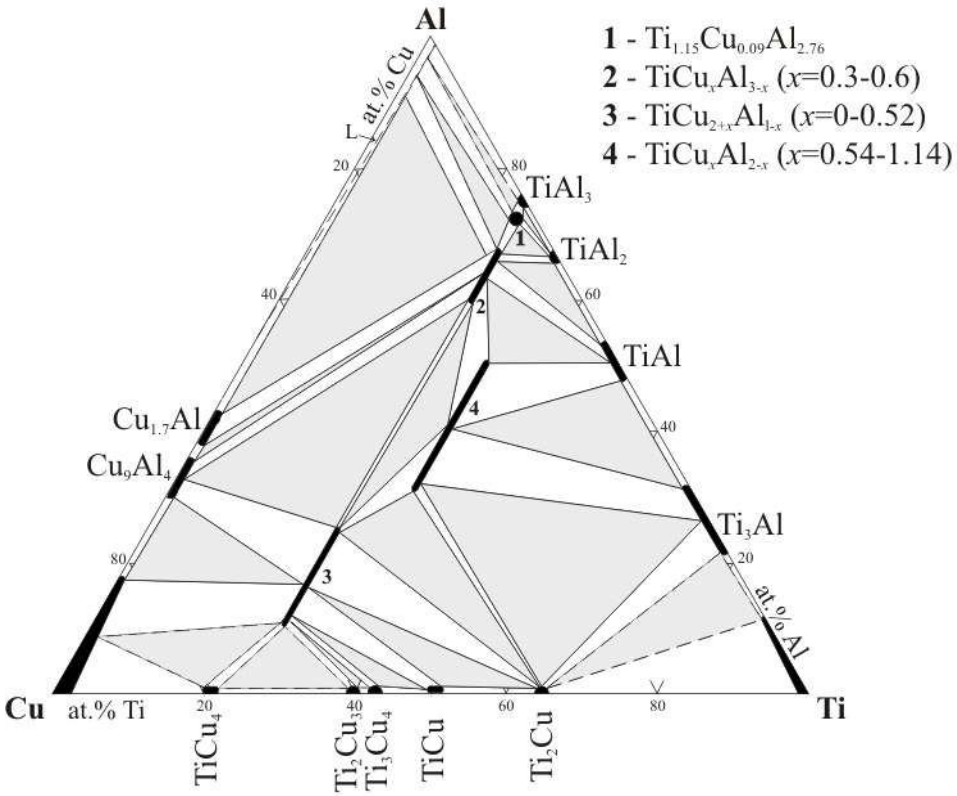


Fig. 8. Isothermal section of the phase diagram of the system Ti–Cu–Al at 800°C

ternary compounds in the system Ti–Cu–Al with large homogeneity ranges was confirmed (7.5, 13 and 20 at.% Al or Cu along the isoconcentrates 25 at.% Ti for the former two and 33.3 at.% for the last one). The additional compound with structure type $ZrAl_3$ is in equilibrium with $TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3) (structure type Cu_3Au) (Fig. 4), which in turn forms equilibria with one binary (Cu_9Al_4) and two ternary compounds ($TiCu_{2+x}Al_{1-x}$, x=0–0.52(2) (structure type $MnCu_2Al$) and $TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3) (structure type $MgZn_2$). The compounds $TiCu_{2+x}Al_{1-x}$ and $TiCu_xAl_{2-x}$ are in equilibrium with each other; in addition the former is in equilibrium with TiCu, Ti_2Cu, and Cu_9Al_4, whereas the latter forms equilibria with Ti_2Cu, TiAl, and Ti_3Al.

The isothermal section of the phase diagram of the system Ti–Cu–Al at 800°C proposed by Markiv et al. [5] does not contain any compound with structure type $ZrAl_3$ (Fig. 3). However, Schubert et al. [4] observed a compound with this structure type at the composition $TiCu_{0.16}Al_{2.84}$. They assume that this apparently ternary compound is in fact part of the solid solution of the high-temperature phase reported in the binary Ti–Al system at the approximate composition Ti_3Al_{11}. This opinion is also supported by Ran and Stadelmaier [1] in their review of the Ti–Cu–Al system. The structure type Zr_3Al adopted by the Ti-rich high-temperature phase was confirmed by Bulanova et al. [14] during an investigation of the Ti–Al–Si system, where this phase was also found to incorporate small amounts of Si.

Concerning the homogeneity ranges of the ternary phases, a certain variation of the Ti content cannot be excluded, but the main extension is clearly along the isoconcentrate 25 at.% Ti for the cubic close-packed and the Heusler phases, and along 33 at.% Ti for the Laves phase. In this aspect, the isothermal section constructed here is closer to those determined by Markiv et al. than to that proposed by Virlis and Zwicker. However, in the present investigation the Cu-rich boundary of the Laves phase was found to form equilibrium with Ti_2Cu. Such equilibrium is present in the section at 540°C drawn by Virlis and Zwicker, but not in those published by Markiv et al., where, instead, the Heusler phase forms equilibrium with Ti_3Al.

Crystal structure of $Ti_{1.15}Cu_{0.09}Al_{2.76}$

The crystal structure of the ternary aluminide discovered near the composition $TiAl_3$ was solved by direct methods in space group *I*4/*mmm* [15] on X-ray powder diffraction data of the sample $Ti_{27}Cu_2Al_{71}$. In agreement with the findings by Schubert et al. [4] it crystallizes in the $ZrAl_3$ structure type (Pearson symbol *tI*26, space group *I*4/*mmm*, a=3.9159(3), c=16.556(2) Å). Experimental details of the structure refinement and crystallographic data are given in Table 5. Atomic coordinates and isotropic displacement parameters are given in Table 6. The tetragonal unit cell of the $ZrAl_3$ type contains 16 atoms distributed over four sites, one occupied by Zr and the other three by Al. For the refinement, the Zr site was assumed to be occupied by Ti atoms, and the other sites by mixtures of Al, Ti and Cu. The site in Wyckoff position 4d was found to be occupied exclusively by Al atoms. The final atom coordinates and site occupancies are listed in Table 6.

Table 5

Details of the Rietveld refinement of the sample $Ti_{27}Cu_2Al_{71}$

Composition	$Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$
Structure type	$ZrAl_3$
Space group	*I*4/*mmm*
Cell parameters: a, Å	3.9159(3)
c, Å	16.556(2)
Cell volume V, Å^3	253.87(6)
Formula units per cell Z	4
Density D_X, g cm^{-3}	3.5370(8)
Reliability factor R_B	0.0279
FWHM parameters U, V, W	0.021(4), 0.001(1), 0.0469(6)
Mixing parameter η	0.864(6)
Asymmetry parameter C_M	–0.051(1)
Reliability factors R_p, R_{wp}	0.0563, 0.2476

Table 6

Atomic coordinates and isotropic displacement parameters for $Ti_{1.15}Cu_{0.09}Al_{2.76}$

Site	Wyckoff position	x	y	z	B_{iso}, Å^2
Ti	4e	0	0	0.1293(3)	0.76(12)
Al	4d	0	½	¼	0.8(2)
M1[1]	4c	0	½	0	0.8(2)
M2[2]	4e	0	0	0.3599(3)	0.6(2)

Note: [1] – M1=0.85(2) Al+0.15(2) Ti; [2] – M2=0.91(1) Al+0.09(1) Cu.

Microhardness

The microhardness of a substance is an important parameter to define the strength of the material. This property is basically related to the crystal structure of the material or in other words, the way in which the atoms are packed and the electronic factors operating to make the structure. Microhardness values of the four ternary phases of Ti–Cu–Al system investigated here are given in Table 7.

Table 7

Microhardness of the ternary phases in the Ti–Cu–Al system, compactness (occupied fraction f) density (D_x) and selected interatomic distances (δ) from X-ray diffraction

Sample	$Ti_{25}Cu_{6.25}Al_{68.75}$		$Ti_{25}Cu_{50}Al_{25}$	$Ti_{33.3}Cu_{23}Al_{43.7}$
Phase	$TiCu_{0.45(4)}Al_{2.55(4)}$ (Cu_3Au type)	$Ti_{1.15}Cu_{0.09}Al_{2.76}$ ($ZrAl_3$ type)	$TiCu_{2.11(4)}Al_{0.89(4)}$ ($MnCu_2Al$ type)	$TiCu_{0.72(3)}Al_{1.28(3)}$ ($MgZn_2$ type)
Microhardness, GPa	0.324(5)	0.517(5)	0.524(2)	0.894(6)
Compactness f, %	79	79	77	84
Density D_X, g cm^{-3}	3.679	4.344	6.097	5.019
δ, Å	Ti–M 2.785 M–M 2.785	Ti–M 2.752 M–M 2.758	Ti–M 2.605 M–M 2.598	Ti–M 2.455 M–M 2.430

The microhardness of the samples ranges from 0.324 to 0.894 GPa. The larger value (0.894 GPa) is for the phase that has the largest Ti content (sample $Ti_{33.3}Cu_{23}Al_{43.7}$). It should be noted that the microhardness does not depend on the atomic weight, but on the coefficient of compactness (occupied fraction, f). The microhardness increases to the tetrahedrally close-packed structure $MgZn_2$ which coefficient of compactness (84%) is larger than in the cubic close-packed structure Cu_3Au (79%).

Conclusions

The isothermal cross-section of the phase diagram of the system Ti–Cu–Al at 800°C was constructed. Three purely ternary compounds with relatively large homogeneity ranges corresponding to substitution of Cu for Al form. A fourth ternary compound with $ZrAl_3$-type structure was observed near the composition $TiAl_3$. The largest microhardness was observed for the Laves phase.

Acknowledgements

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ПОВТОРНЕ ДОСЛІДЖЕННЯ СИСТЕМИ Ti–Cu–Al ПРИ 800°C

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Ізотермічний переріз діаграми стану системи Ti–Cu–Al при 800°C досліджено рентгенівським методом порошку, мікроструктурним аналізом та енергодисперсійною рентгенівською спектроскопією. Для трьох тернарних сполук визначено області гомогенності при 800°C: $TiCu_xAl_{3-x}$, x=0,30(3)–0,60(3) (структурний тип Cu_3Au), $TiCu_{2+x}Al_{1-x}$, x=0–0,52(2) (структурний тип $MnCu_2Al$) та $TiCu_xAl_{2-x}$, x=0,54(3)–1,14(3) (структурний тип $MgZn_2$). Кристалічну структуру додаткової сполуки поблизу складу $TiAl_3$ уточнено з даних рентгенівської порошкової дифракції ($Ti_{1,15(2)}Cu_{0,09(1)}Al_{2,76(3)}$, структурний тип $ZrAl_3$; символ Пірсона tI16, просторова група I4/mmm, a=3,9159(3), c=16,556(2) Å). Ця тернарна сполука, виявлена при 800°C, ймовірно є продовженням твердого розчину на основі бінарної високотемпературної фази, наданої як Ti_5Al_{11}, із аналогічним структурним типом. Поміряно мікротвердість тернарних сполук.

Ключові слова: алюміній, купрум, титан, рентгенівська порошкова дифракція, діаграма стану, тернарна сполука, мікроструктура, твердість.

REINVESTIGATION OF THE SYSTEM Ti–Cu–Al AT 800°C

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The isothermal section of the phase diagram of the ternary system Ti–Cu–Al at the temperature of 800°C was investigated using X-ray powder diffraction, microstructural analysis and energy-dispersive X-ray spectroscopy. The homogeneity ranges at 800°C of three purely ternary compounds were determined: $TiCu_xAl_{3-x}$, x=0.30(3)–0.60(3) (structure type Cu_3Au), $TiCu_{2+x}Al_{1-x}$, x=0–0.52(2) (structure type $MnCu_2Al$) and $TiCu_xAl_{2-x}$, x=0.54(3)–1.14(3) (structure type $MgZn_2$). The crystal structure of an additional compound near the composition $TiAl_3$ was refined on X-ray powder diffraction data ($Ti_{1.15(2)}Cu_{0.09(1)}Al_{2.76(3)}$, structure type $ZrAl_3$; Pearson symbol tI16, space group I4/mmm, a=3.9159(3), c=16.556(2) Å). This ternary compound, observed at 800°C, is probably an extension of the solid solution of the binary high-temperature phase reported as Ti_5Al_{11} with the same structure type. The microhardness of the ternary compounds was measured.

Keywords: aluminum; copper; titanium; X-ray powder diffraction; phase diagram; ternary compound; microstructure; hardness.

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