Isothermal Section of Ga–Ru–Cu Ternary Phase Diagram at 1073 K: Formation of New Ternary Phase, Ga₄Ru₃Cu, and Its Structural Relation with the GaRu β -Phase

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We have investigated the isothermal phase diagram of the Ga–Ru–Cu ternary system at 1073 K by X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy, and transmission electron microscopy to determine whether the stable icosahedral quasicrystal (*i*-phase) forms, as it does in the similar Al–Ru–Cu system, and new intermetallic phases exist. This is the first systematic investigation of the Ga–Ru–Cu system. No stable *i*-phase is identified in the Ga–Ru–Cu alloy system. However, we found a new ternary (τ) phase in the Ga–Ru–Cu system, which is characterized as a C-centered orthorhombic lattice with $a_\tau = 11.80 \text{ \AA}$, $b_\tau = 6.04 \text{ \AA}$, and $c_\tau = 3.07 \text{ \AA}$. The (ideal) chemical composition of the τ -phase is Ga₅₀Ru_{37.5}Cu_{12.5} (Ga₄Ru₃Cu). This new phase is stable up to 1073 K. Above 1173 K, the τ -phase transforms to the cubic GaRu (β) phase without any secondary phases. Thus, there is an order–disorder transition between the low-temperature τ -phase and the high-temperature cubic β -phase in this temperature range. [doi:10.2320/matertrans.MBW201706]

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1. Introduction

Quasicrystals have sharp Bragg peaks in reciprocal space, like conventional crystals, indicating a highly ordered structure of atoms, whereas their lattice translational symmetry is lost in real space.^{1,2)} The unusual behavior of icosahedral quasicrystals (*i*-phase) compared with common metallic alloys, such as high electrical resistivity and low lattice thermal conductivity, is of interest in materials physics and for their use in, for example, thermoelectrics. New *i*-phases in novel alloys may open a new research field in materials science.

Since the discovery of the stable *i*-phase of the ternary Al–Cu–Fe alloy,³⁾ Al-transition metal (TM)-based stable *i*-phases have been reported for Al–Pd–(Mn, Tc, Re, Ru, or Os) and Al–Cu–(Ru or Os) systems.^{4–7)} These *i*-phases were discovered using the empirical Hume-Rothery electronic stabilization mechanism, which is the tendency of a specific crystal structure to form using the characteristic ratio of the number of itinerant electrons per atom (e/a) as a guide.⁸⁾ For Al–TM type *i*-phases, the e/a value is commonly around 1.8.⁸⁾

In this study, we first applied the empirical Hume-Rothery rule to a Ga–TM alloy system to search for the stable *i*-phase similar to those in Al–TM systems, because Al and Ga have the same valence of +3 and similar atomic radii ($r_{\text{Al}} = 1.432 \text{ \AA}$ and $r_{\text{Ga}} = 1.411 \text{ \AA}$).⁹⁾ We chose the Ga–Ru–Cu system as a counterpart of the Al–Ru–Cu alloy, which has the widest formation range of the stable *i*-phase of all known Al–TM alloys.¹⁰⁾ No *i*-phases of Ga–TM alloys have been reported, except for in rapidly solidified metastable Ga–Pd–(Cr, Mn or Fe) alloys.¹¹⁾ The main reason for this is the lack

of information about the (equilibrium) phase diagrams of ternary Ga–TM alloys.

To clarify the presence or absence of a stable *i*-phase or the possibility of new intermetallic phases in the Ga–Ru–Cu alloy, we constructed the isothermal section of the ternary phase diagram of the Ga–Ru–Cu system at 1073 K over a wide composition range. Note that this is the first systematic investigation of the Ga–Ru–Cu system. We also report the formation, stability, and structural relation of a new ternary Ga–Ru–Cu compound, namely, the τ -phase with the (ideal) composition of Ga₅₀Ru_{37.5}Cu_{12.5} (Ga₄Ru₃Cu).

2. Experimental Methods

High-purity Ga (grains, 99.99999 wt.%), Ru (powder, 99.9 wt.%), and Cu (powder, 99.9 wt.%) (Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) were melted by the arc-melting method on a water-cooled Cu hearth (NEV-ACD-05, Nissin-Giken Co., Ltd., Saitama, Japan). To obtain a homogeneous sample, the ingot was turned over and remelted several times. After the melting procedure, the weight loss was $\sim 4.7\%$ (on average), possibly because of the use of raw powders of Ru and Cu. The nominal compositions are summarized in Table 1. The mother ingots were then directly sealed in a quartz ampoule under a pure Ar atmosphere ($\sim 0.05 \text{ MPa}$) and annealed at 1073 K for 48–72 h in an electronic furnace. There was no evidence for chemical reaction between the samples (especially molten Ga) and the quartz ampoule. The annealing temperature is comparable with the formation condition of the Al–Ru–Cu quasicrystal.¹²⁾ After the annealing process, the furnace was turned off and the samples were allowed to cool to room temperature inside the furnace (furnace cooling).

The phase constitutions were investigated by powder X-ray diffraction (XRD) using CuK α radiation (SmartLab, Rigaku Co., Ltd., Tokyo, Japan) at an operating voltage of

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Table 1 Phase constitutions and compositions of the investigated alloys.

Sample	Nominal composition			Observed phases in the XRD pattern	Composition determined by EDX		
	Ga (at.%)	Ru (at.%)	Cu (at.%)		Ga (at.%)	Ru (at.%)	Cu (at.%)
1 [†]	80	10	10	α -Ga*	98	0	2
				Ga ₃ Ru	74	25	1
				CuGa ₂ *	not observed by SEM		
2 [†]	70.5	17	12.5	Ga ₃ Ru	70	26	4
				Cu ₉ Ga ₄	39	1	60
				CuGa ₂ *	64	0	36
3	61	13	26	Ga ₃ Ru	74	24	2
				Cu ₉ Ga ₄	39	0	61
				CuGa ₂ *	65	0	35
4 [†]	66	15	19	Ga ₃ Ru	73	26	2
				Cu ₉ Ga ₄	38	0	62
				CuGa ₂ *	64	0	36
5	61	22	17	Ga ₃ Ru	72	25	3
				Ga ₂ Ru	67	32	1
				Cu ₉ Ga ₄	37	1	62
6	60	30	10	Ga ₂ Ru	64	34	2
				Cu	20	0	80
				Ga ₂ Ru	63	32	5
7	50	20	30	Cu	23	1	76
				Cu ₉ Ga ₄	33	0	67
				GaRu	47	46	7
8	40	40	20	Cu	10	0	90
				Ru	13	85	2
				GaRu	51	41	8
9	55	40	5	Ga ₂ Ru	65	32	3
				GaRu	51	36	13
				Ga ₂ Ru	66	32	2
10	48	36	16	Cu	16	0	84
				GaRu	51	40	9
				Cu	18	0	82
12	50	30	20	Ga ₂ Ru	65	32	3
				Cu	19	0	81
				T	50	37	13
13 [†]	50	35	15	Ga ₂ Ru	64	34	2
				Cu	20	4	75
				T	48	38	14
14 [†]	49	33	18	T	48	38	14

*Liquid phases at 1073 K.

[†]EDX analysis without a standard sample. EDX standards (GaSb, Ru and Cu) were used for composition analysis of the other samples. The compositional difference with and without standards is estimated to be less than ~2 at.%.

40 kV and a current of 30 mA. Except for the Ga-rich sample (sample 1), all of the samples were ground into powders for the measurements. Because of the difficulty of grinding, only sample 1 was polished and examined by XRD.

The alloy composition of each phase was determined by scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) measurements at an operating voltage of 20 kV (JSM-6010LA, JEOL Ltd., Tokyo, Japan). The phase compositions were determined from the average value of several EDX data points for each phase. The estimated compositional error for the EDX measurements was within a few atom percent for each element.

Transmission electron microscopy (TEM) was performed with a TOPCON EM-002B electron microscope (JEOL Ltd.)

with an acceleration voltage of 200 kV. The samples for the TEM observations were additionally annealed at 973 K for 72 h to obtain high structural perfection and then crushed with an agate mortar. Differential scanning calorimetry (DSC) was performed under Ar flow up to 1273 K with a heating rate of 10 K/min (DSC8020, NETZSCH Japan K.K., Kanagawa, Japan).

3. Results and Discussion

3.1 Isothermal diagram of the Ga–Ru–Cu alloy at 1073 K

A total of 14 different compositions were investigated in this study. The nominal compositions of the alloys are summarized in Table 1 along with the observed phases and chemical compositions determined by XRD and SEM/EDX measurements.

According to binary phase studies of Ga–Ru^{13,14)} and Cu–Ga¹⁵⁾ systems, four different binary solid phases and one liquid phase exist at 1073 K: Ga₃Ru,¹⁶⁾ Ga₂Ru,¹⁴⁾ GaRu,¹⁴⁾ Cu₉Ga₄,¹⁷⁾ and CuGa₂ (liquid phase at 1073 K),¹⁸⁾ in addition to pure Ga (liquid phase at 1073 K),¹⁹⁾ Ru,²⁰⁾ and Cu.²¹⁾ Note that Cu has a wide solubility limit of up to ~20 at.% Ga at 1073 K. There are no intermetallic compounds in the Cu–Ru binary system.²²⁾ The solubility range of Cu₉Ga₄ is about 30 at.% < Ga < 36 at.% at this temperature and several polymorphic structures have been reported.²³⁾ However, the diffraction patterns are very similar and difficult to distinguish in our work. Thus, we simply identify these polymorphs as “Cu₉Ga₄”. The detailed phase information is listed in Table 2.

Figure 1 shows the isothermal section of the Ga–Ru–Cu phase diagram at 1073 K. The solid lines show the phase boundary for each phase. The dark gray region represents the single-phase domain for each phase. There are at least 14 regions at 1073 K: Ga₃Ru + Cu₉Ga₄ + Ga₂Cu/Ga(liquid), Ga₃Ru + Cu₉Ga₄, Ga₃Ru + Ga₂Ru + Cu₉Ga₄, Ga₃Ru + Ga₂Ru, Ga₂Ru + Cu₉Ga₄, Ga₂Ru + Cu₉Ga₄ + Cu, Ga₂Ru + τ + Cu, Ga₂Ru + GaRu + τ , GaRu + τ + Cu, Ga₂Ru + GaRu, GaRu + Cu, GaRu + Ru + Cu, GaRu + Ru, and Ru + Cu. The GaRu phase has a relatively large solubility range of up to ~9 at.% Cu (gray region in Fig. 1 of GaRu). The liquid phase at 1073 K crystallizes as Ga + Ga₂Cu or Ga₂Cu during the cooling process. Note that in the SEM/EDX experiments, phase separation with a phase distribution was observed in the GaRu phase. Sample 10 has the constitution GaRu + Ga₂Ru + Cu, although this phase configuration does not exist in the diagram. This may be because the GaRu phase is not in equilibrium during furnace cooling. Furthermore, the τ -phase (black dot in Fig. 1) is the only ternary phase of the Ga–Ru–Cu alloy, which will be discussed in more detail later.

Figure 2(a) shows the XRD patterns in the formation range of the *i*-phase for the Al–Ru–Cu alloy with $e/a = \sim 1.8$ (light gray region surrounded by dotted lines in Fig. 1). All of the peaks can be indexed to known binary phases: Ga₃Ru, Ga₂Ru, and CuGa₂ (liquid phase at 1073 K). This is also consistent with the SEM image (Fig. 2(b)), where no ternary phases, including *i*-phases, are observed in this composition region, which is completely different from the case of the

Table 2 Crystallographic data of the observed phases in the Ga–Ru–Cu system at 1073 K.

	Phase	Space group	Structure type	<i>a</i> [Å]	<i>b</i> [Å]	<i>c</i> [Å]	α [°]	γ [°]	Comment	Ref.
Ga	α -Ga	<i>Cmca</i>	Ga	4.523	7.661	4.524	90	-	Liquid phase at 1073 K	(19)
Cu	Cu	<i>Fm$\bar{3}m$</i>	fcc-Cu	3.61505	-	-	90	-	Solubility range: <20 at.% Ga at 1073 K	(21)
Ru	Ru	<i>P6$_3$/mmc</i>	hcp-Mg	2.7508	-	4.2819	90	120		(20)
Ga–Ru binary	Ga ₃ Ru	<i>P4$_2$/mnm</i>	CoGa ₃	6.4734	-	-	90	-		(16)
	Ga ₂ Ru	<i>Fddd</i>	TiSi ₂	8.184	4.749	8.690	90	-		(14)
	GaRu	<i>Pm$\bar{3}m$</i>	CsCl	3.01	-	-	90	-		(14)
Ga–Cu binary	CuGa ₂	<i>P4/mmm</i>	FeSi ₂	2.830	-	5.839	90	-	Liquid phase at 1073 K	(18)
	Cu ₉ Ga ₄	<i>P$\bar{4}$3m</i>	Al ₄ Cu ₉	8.7355	-	-	90	-	Formation range: 30 < at.% Ga < 36 at 1073 K	(17)
Ternary	T	C-centered ortho.	-	11.8	6.04	3.07	90	-		This work

Fig. 1 Ternary phase diagram of the Ga–Ru–Cu alloy system at 1073 K determined from the experiments. The dark gray regions represent the single-phase domain for each phase. The black dot is the τ -phase. The light gray region surrounded by dotted lines represents the formation range of the i -phase in the Al–Ru–Cu system for comparison.¹⁰⁾ The circles are the nominal compositions from this study.

Al–Ru–Cu system.¹⁰⁾ Our results show that the Hume-Rothery rule does not hold for the Ga–Ru–Cu system. However, it does reveal that systematic phase information about other Ga–TM alloys is required, as is the case for Al–TM systems. It should be noted that we attempted low-temperature annealing of samples 2 and 3, but there was no significant difference in the XRD patterns compared with Fig. 2(a). The results also indicate that formation of the quasicrystal phase in the Ga–Ru–Cu system is not possible, even in the low-temperature region.

3.2 Structure and stability of the τ -phase

The τ -phase is the only ternary phase in the Ga–Ru–Cu system. Figure 3 shows the powder XRD pattern of this single phase with a nominal composition of Ga₄₉Ru₃₃Cu₁₈ (Sample 14 in Table 1). Note that no significant secondary phases are detected by XRD and SEM measurements. All of the XRD peaks can be indexed to an orthorhombic lattice with $a_\tau = 11.80$ Å, $b_\tau = 6.04$ Å, and $c_\tau = 3.07$ Å. Because the

Fig. 2 (a) XRD patterns of samples 2, 3, and 4, and (b) SEM image of the Ga–Ru–Cu alloy (sample 4) located within the formation range of the i -phase of the Al–Ru–Cu system.¹⁰⁾ Each sample consists of three known binary phases: Ga₃Ru, Cu₉Ga₄, and CuGa₂ (liquid phase at 1073 K). The determined chemical compositions are also given.

$h + k = 2n + 1$, where n is an integer, peak intensities are systematically eliminated, the Bravais lattice becomes a C-centered orthorhombic lattice. Considering that this τ -phase is located very close to the Cu solubility limit of the cubic GaRu phase, it is reasonable that its lattice parameter is almost equal to the $4 \times 2 \times 1$ cell size of GaRu ($a = 3.010$ Å, see the insert of Fig. 3). Thus, the basic crystal structure of the τ -phase should be very similar to that of cubic GaRu (β -phase).

Figure 4(a) shows the selected area electron diffraction (SAED) pattern of the τ -phase along the $[110]_{\text{Ortho}}$ zone axis of the $4a \times 2a \times a$ orthorhombic lattice. In addition to the main Bragg peaks, similar to those of the calculated SAED pattern of the β -phase along the $[210]_{\text{Cub}}$ zone axis (see Fig. 4(b)), additional superlattice reflections indexed by $h\bar{h}0$

Fig. 3 XRD pattern of the τ -phase (sample 14) of the Ga–Ru–Cu alloy. All of the peaks can be indexed to $a_\tau = 11.80 \text{ \AA}$, $b_\tau = 6.04 \text{ \AA}$, and $c_\tau = 3.07 \text{ \AA}$, which are almost equal to $4 \times 2 \times 1$ unit cell size of the cubic GaRu (β) phase. The insert shows the structural relationship between the cubic GaRu (β) phase and the τ -phase. The light-green, gray, and blue spheres represent Ga, Ru, and Cu, respectively. The crystal structure was visualized using the VESTA 3 program package.²⁴⁾ Note that the origin of the τ -phase in the insert is shifted by $(1/8, 1/4, 0)$ for comparison, i.e., the origin is specified at the Cu position in the general setting.

Fig. 4 (a) Experimental SAED pattern of the τ -phase along $[110]_{\text{Ortho.}}$ ($4a \times 2a \times a$ orthorhombic lattice). (b) Calculated SAED pattern of the GaRu β -phase along $[210]_{\text{Cub.}}$ (cubic lattice). There are superlattice reflections at the $\bar{h}h0$ positions indicated by triangles, whereas there are no superlattice reflections along $[00l]$.

are clearly observed, which are indicated by triangles in Fig. 4(a). There are no superlattice reflections along $[00l]$. This result is consistent with the above X-ray diffraction data; i.e., the τ -phase is definitely the orthorhombic lattice with $4 \times 2 \times 1$ cell size with respect to the β -phase.

From the above data, we constructed the structural model of the τ -phase (see the insert of Fig. 3). For the model structure, the Ga frameworks are essentially the same for the τ -phase and β -phase, whereas the Cu and Ru atoms are ordered with the relation of the C -centered symmetry for the τ -phase. The highest possible space group of the τ -phase becomes $Cmmm$. For this model, the chemical composition is $\text{Ga}_{50}\text{Ru}_{37.5}\text{Cu}_{12.5}$, which is in good agreement with the determined composition of $\text{Ga}_{50}\text{Ru}_{37}\text{Cu}_{13}$.

Figure 5 shows the XRD patterns of sample 14 annealed at various temperatures for 72 h. Spectrum (b) is the same data as that in Fig. 3, indicating the single τ -phase. When the sample is annealed at 1173 K (spectrum (a)), the τ -phase completely changes to the single cubic β -phase without any secondary phases. With subsequent low-temperature annealing (973 K, spectrum (c)), the β -phase reversibly changes to the single τ -phase. Note that DSC of the τ -phase (not shown here) shows an endothermic peak at around

Fig. 5 Annealing temperature dependence of the XRD pattern of sample 14. Diffraction pattern (b) is the same data as in Fig. 4. Pattern (a) is the XRD pattern after additional annealing of the sample at 1173 K for 72 h. All of the patterns are the β -phase. Pattern (c) was measured after additional heat treatment at 973 K for 72 h. Reversible change of the XRD patterns of the low-temperature τ -phase and high-temperature β -phase is observed.

1150 K, which supports that the order–disorder phase transition occurs at this temperature. A similar phenomenon to the Ga–Ru–Cu τ -phase is observed for the $\text{Al}_{50}\text{Ru}_{37.5}\text{Cu}_{12.5}$ ($\text{Al}_4\text{Ru}_3\text{Cu}$) alloy. Investigation of the transition mechanisms and structures is in progress.

4. Conclusion

Here, we report the isothermal section of the Ga–Ru–Cu ternary system at 1073 K. We could not identify formation of the i -phase in any composition range by XRD and SEM/EDX measurements. However, we discovered a new ternary phase (τ -phase) with the ideal composition of $\text{Ga}_{50}\text{Ru}_{37.5}\text{Cu}_{12.5}$ ($\text{Ga}_4\text{Ru}_3\text{Cu}$), which is the only ternary compound in this system. The crystal structure of the τ -phase is a C -centered orthorhombic lattice ($a_\tau = 11.80 \text{ \AA}$, $b_\tau = 6.04 \text{ \AA}$, and $c_\tau = 3.07 \text{ \AA}$) with $4 \times 2 \times 1$ unit cell size with respect to the binary cubic GaRu β -phase. The experimental results suggest that the τ -phase is the low-temperature chemically ordered phase of Cu and Ru, and at temperatures above 1150 K its structure transforms to the cubic β -phase.

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