

Al-Cu-Ru (Aluminum-Copper-Ruthenium)

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Recently, [2004Mi] determined six isothermal sections for Al-rich alloys of this system between 1100 and 600 °C, which depict a number of ternary phases.

Binary Systems

The Al-Cu phase diagram [Massalski2] depicts a number of intermediate phases. CuAl_2 (θ) is a C16-type tetragonal phase. CuAl (η) has two crystal modifications, the high-temperature orthorhombic and the low-temperature monoclinic forms. The two forms of the ζ phase occur in the composition range of 55.2-59.8 at.% Cu and are stable below 590 °C. Two modifications of the ϵ phase occur around the composition Cu_3Al_2 and are stable above 560 °C. The structures of the phases, δ , γ_1 (Cu_9Al_4), and γ_0 , which are stable between 58 and 70 at.% Cu, are based on the γ -brass structure. The β phase (70.6-82 at.% Cu) is body-centered cubic (bcc) and is stable above 567 °C. There are five intermediate phases in the Al-Ru system [2004Oka]. RuAl_6 is orthorhombic and $\text{Ru}_4\text{Al}_{13}$ is $\text{Fe}_4\text{Al}_{13}$ -type monoclinic. RuAl_2 has the C54, TiSi_2 -type orthorhombic structure. Ru_2Al_3 is a high-temperature phase stable between 1705 and 970 °C. RuAl is a B2, CsCl-type cubic structure. There are no intermediate phases in the Cu-Ru system. The mutual solubility between Cu and Ru is negligible [Massalski2].

Ternary Phases

There are four established ternary phases in this system [2004Mi]. Around the composition $\text{Al}_{70}\text{Cu}_{20}\text{Ru}_{10}$, a tetragonal phase (isostructural with $\text{Al}_7\text{Cu}_2\text{Fe}$ and labeled ω) forms peritectically and has the lattice parameters $a = 0.6433$ nm and $c = 1.489$ nm. [2004Mi] found a smaller homogeneity range for this phase than that reported by [1993Shi]. Around the composition $\text{Al}_{58}\text{Cu}_{30}\text{Ru}_{12}$, a cubic phase labeled C (space group $Pm\bar{3}$) is found at 800 and 600 °C and has a lattice parameter of 1.2386 nm. The third ternary phase around the composition $\text{Al}_{70.5}\text{Cu}_{8.5}\text{Ru}_{21}$ labeled C_1 (space group $Fm\bar{3}$) has a face-centered cubic structure with $a = 1.5511$ nm [2004Mi]. The face-centered icosahedral phase (labeled I) has a composition range of $\text{Al}_{61}\text{Cu}_{26}\text{Ru}_{13}$ - $\text{Al}_{70.5}\text{Cu}_{12.5}\text{Ru}_{17}$. It forms peritectically at 1057 °C and is stable down to at least 600 °C [2004Mi].

The third component solubility in the binary phases is significant in some cases. The CsCl-type B2 phase found by [2004Mi] with the copper range of 31-50 at.% is probably an extension of the binary phase RuAl into the ternary region, with Cu substituting for most of Ru. RuAl_6 dissolves up to 5 at.% Cu. $\text{Ru}_4\text{Al}_{13}$ and RuAl_2 dissolve about 2.5 and 1.5 at.% Cu, respectively.

Liquid-Solid Equilibria

[1996Log] and [2002Guo] investigated the liquid-solid phase equilibria of this system in the region surrounding the icosahedral phase. With starting metals of 99.999% purity, [2002Guo] arc-melted under Ar atm about 20 alloys with the composition range of 55-70Al, 22.5-42.5Cu, and 2.5-25Ru (all at.%). The phase equilibria were studied with differential thermal analysis, x-ray diffraction, and transmission electron microscopy. The compositions were determined by energy dispersive spectroscopy. The partial vertical section at 62.5 at.% Al constructed by [2002Guo] is redrawn in Fig. 1. The phase at $\text{Al}_{68}\text{Cu}_{12}\text{Ru}_{20}$ that forms peritectically at 1090 °C appears to be the C_1 phase reported by [2004Mi]. In Fig. 1, a second peritectic reaction between liquid and C_1 (?) occurs at 1020 °C, which yields the icosahedral phase I. This is in fair agreement with the observation of [2004Mi] that I forms peritectically at 1057 °C. [2002Guo] presented this vertical section as a pseudobinary section, which needs confirmation. By bracketing the narrow composition range (2.5-4 at.% Ru), where I forms as a primary phase, [2002Guo] obtained large grains of I from a partially solidified and quenched alloy.

[1996Log] presented a partial liquidus projection around the icosahedral region. This projection depicts a ternary

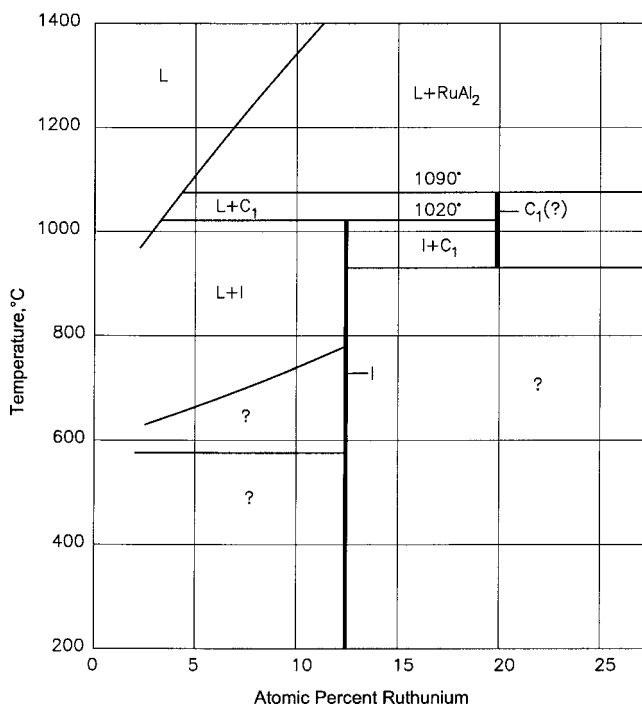


Fig. 1 Al-Cu-Ru partial vertical section at 62.5 at.% Al [2002Guo]

Section II: Phase Diagram Evaluations

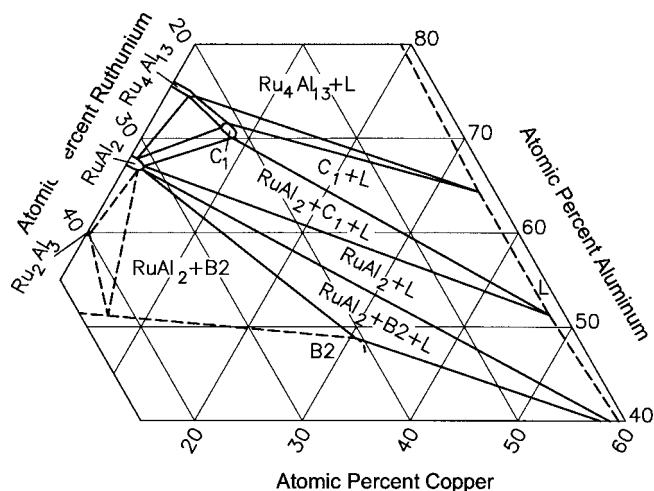


Fig. 2 Al-Cu-Ru partial isothermal section at 1100 °C [2004Mi]

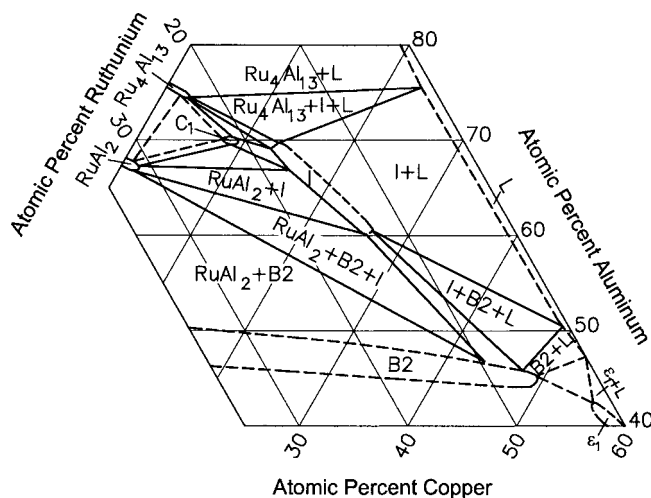


Fig. 4 Al-Cu-Ru partial isothermal section at 890 °C [2004Mi]

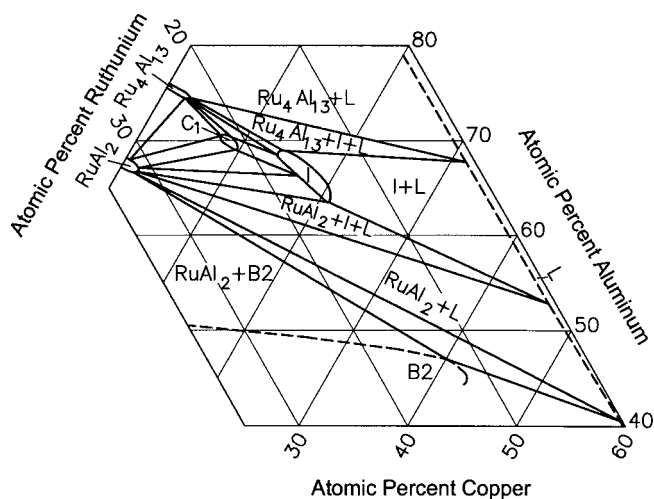


Fig. 3 Al-Cu-Ru partial isothermal section at 1000 °C [2004Mi]

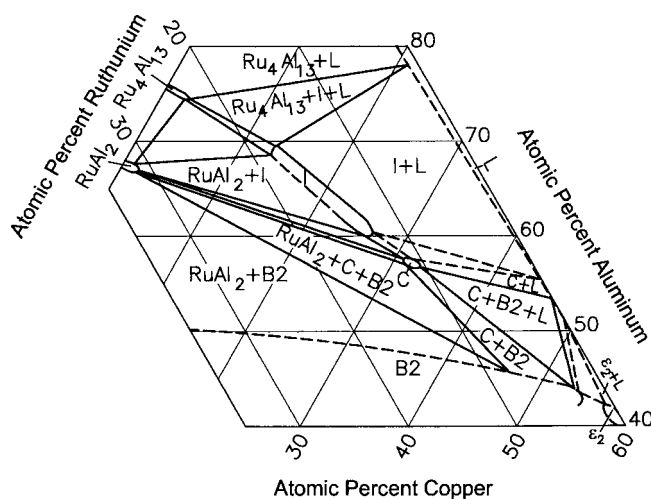


Fig. 5 Al-Cu-Ru partial isothermal section at 800 °C [2004Mi]

peritectic reaction at ~ 1200 °C, which yields *I*. This appears unlikely, in light of the more recent results of [2002Guo] and [2004Mi], which show that *I* forms at a much lower temperature.

Isothermal Sections

With starting metals of 99.999% Al, 99.99% Cu, and 99.9% Ru, [2004Mi] levitation-melted a number of alloys under Ar atm. The alloys were annealed in the range 1100-600 °C for 40-4392 h. The phase equilibria were studied by transmission electron microscopy, x-ray powder diffraction, and energy dispersive x-ray spectroscopy. The composition of the single phase alloys was determined by inductively coupled plasma optical emission spectroscopy. Differential thermal analysis was performed at a heating rate of 20 °C per min. The six partial isothermal sections constructed by [2004Mi] between 1100 and 600 °C are redrawn in Fig. 2-7

to agree with the accepted binary data. At 1100 °C (Fig. 2), only one ternary phase *C*₁ is present. The RuAl (*B*2) phase dissolves 31.5 at.% Cu, with Cu substituting for Ru. At 1000 °C (Fig. 3), the icosahedral phase *I* is present and forms tie-lines with Ru₄Al₁₃, *C*₁, RuAl₂, and the liquid. The solubility of Cu in *B*2 is more than 40 at.%. The partial isothermal section at 890 °C is shown in Fig. 4. Between 1000 and 890 °C, the U-type transition reaction: RuAl₂ + *L* \leftrightarrow *I* + *B*2 has occurred. At 800 °C (Fig. 5), the *C*₁ phase is not stable, but the *C* phase is present, forming tie-lines with *B*2, RuAl₂, *I*, and *L*. The solubility of Cu in *B*2 has increased to more than 50 at.%, with Cu substituting mostly for Ru. At 680 °C (Fig. 6), the ω phase is present and forms tie-lines with the icosahedral phase *I*. The binary phase RuAl₆, which is stable below 724 °C, dissolves 5 at.% Cu at 680 °C, forming tie-lines with ω . At 600 °C (Fig. 7), the binary phase CuAl is stable. [2004Mi] determined a tie-triangle between ω , *C*, and CuAl at 600 °C.

[1992Shi] and [1993Shi] studied eleven Al-rich alloys in

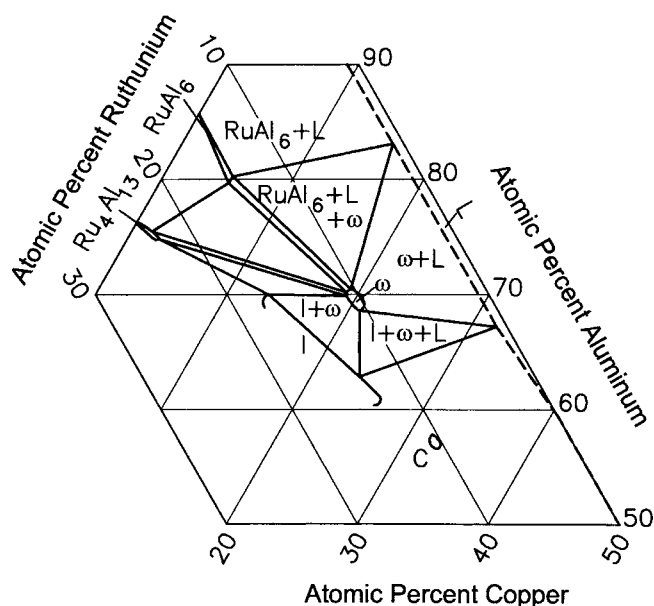


Fig. 6 Al-Cu-Ru partial isothermal section at 680 °C [2004Mi]

the icosahedral region and constructed partial isothermal sections at 800 and 500 °C. Their conclusion that the *I* phase transforms directly to the tetragonal ω phase at lower temperatures appears unlikely. The compositions of the *I* and ω phases are different and there is no convincing evidence for the direct $I \rightarrow \omega$ transition [1994Gru]. Their isothermal section at 500 °C shows only the ω phase, with a rather large composition range. [2004Mi] used an annealing time of 4392 h (6 months) at 600 °C. The attainment of equilibrium at 500 °C in the experiments of [1993Shi] with annealing times not exceeding 10 d is doubtful.

References

1992Shi: J.E. Shield, C. Hoppe, R.W. McCallum, A.I. Goldman, K.F. Kelton, and P.C. Gibbons, Icosahedral Phase Stabilities in Al-Cu-Ru Alloys, *Phys. Rev. B*, 1992, **45**(5), p 2063-2072

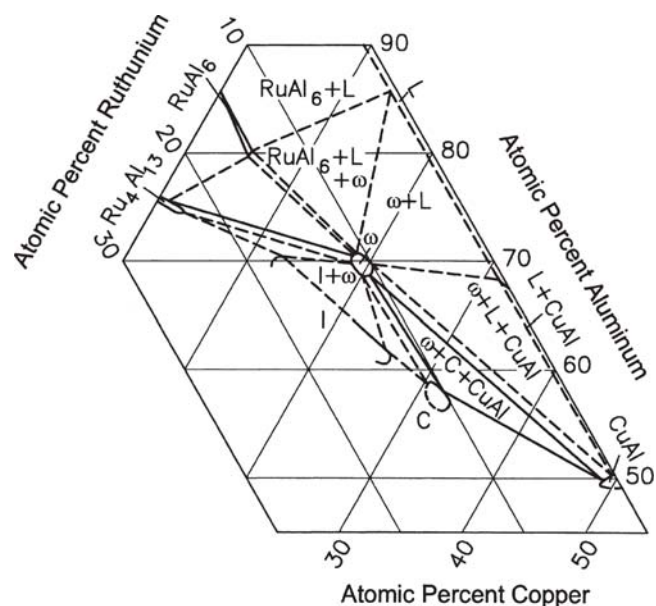


Fig. 7 Al-Cu-Ru partial isothermal section at 600 °C [2004Mi]

1993Shi: J.E. Shield, R.W. McCallum, A.I. Goldman, P.C. Gibbons, and K.F. Kelton, Phase Stabilities in the Al-Cu-Ru System, *J. Non-Cryst. Solids*, 1993, **153-154**, p 504-507

1994Gru: B. Grushko, U. Lemmerz, and C. Freiburg, On a Reaction Involving Al-Cu-Ru Icosahedral Phase and $\text{Al}_7\text{Cu}_2\text{Ru}$, *Philos. Mag. Lett.*, 1994, **70**(5), p 261-267

1996Log: T.A. Lograsso and S.A. Haines, Determination of the Liquidus Surface in the Quasicrystalline Region of the Al-Cu-Ru System, *J. Non-Cryst. Solids*, 1996, **197**, p 197-204

2002Guo: J.Q. Guo, H. Hasegawa, A.P. Tsai, and S. Takeuchi, Single-Crystal Growth of the Al-Cu-Ru Icosahedral Quasicrystal from the Ternary Melt, *J. Cryst. Growth*, 2002, **236**, p 477-481

2004Mi: S. Mi and B. Grushko, Investigation of the High-Al Region of Al-Cu-Ru, *Intermetallics*, 2004, **12**, p 425-435

2004Oka: H. Okamoto, Al-Ru (Aluminum-Ruthenium), *J. Phase Equilibria Diffusion*, 2004, **25**(2), p 196