An investigation of the Al-rich region of the Al-Cu-Ir phase diagram

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Received February 2, 2009; accepted June 10, 2009; available on-line November 16, 2009

The Al-Cu-Ir alloy system was studied in the range above 35 at.% Al. Partial 900 and 540°C isothermal sections were determined. Congruent equiatomic AlIr extends at approximately constant Al concentration up to 30 at.% Cu. Cubic C-Al12Ir (C-phase) dissolves up to 12 at.% Cu, Al13Ir up to 8.5 at.% Cu, Al2Ir5 (γ-phase) and Al2Ir13 (β-phase) up to 3 at.% Cu, and Al1Ir up to 2.5 at.% Cu. Increase of the Cu concentration results in a decrease of the Al concentration of these phases. The Al-Cu ε-phase dissolves up to 3 at.% Ir, while the solubility of Ir in 0 and η2 is below 0.5 at.%. Close to the high-Cu limit of the C-phase region an fcc C2-phase (Fm3, a = 1.53928 nm) structurally related to the C-phase is formed. A stable decagonal phase (D10-phase) is formed below ~1200°C in a compositional range extending from Al41.2Cu20.5Ir8.5 to Al59Cu25.3Ir15.5. A ternary orthorhombic c2-phase (a = 2.34 nm, b = 1.65 nm, c = 1.24 nm) was found below ~1200°C in a compositional range extending from Al11.5Cu3Ir22.5 to Al9Cu12Ir19.3. An additional ternary ω-phase (P4/mnm, a = 0.6414 nm, c = 1.4842 nm) forming around the Al16Cu20Ir10 composition below 683°C was revealed.

Phase diagram / Intermetallics / Quasicrystals

Introduction

This work continues an investigation of the Al-rich part of the Al-Cu-Ir alloy system, which was carried out in [1], following the first report on the formation of stable quasicrystals in Al65Cu25.3Ir15 [2]. The Al–Cu–Ir alloy system belongs to a group of Al-based systems where quasicrystals and related periodic phases have been extensively studied for two decades (see [3] for references). Also the related ternary alloy systems Al–Cu–Co (see [4,5] and references therein) and Al–Cu–Rh [6] were recently investigated (Co, Rh and Ir belong to the same column of the periodic table). In the present communication we show the results concerning the phase equilibria in a compositional range of above 35 at.% Al at 900°C and in a smaller compositional range close to the Al corner at 540°C. The corresponding partial isothermal sections contain all four ternary phases revealed in [1]. The binary Al-Ir phase diagram was accepted from the recent update in [7], and the binary Al-Cu phase diagram was accepted from [8].

Experimental

Alloys of 3 to 5 g were produced by levitation induction melting in a water-cooled copper crucible under a pure Ar atmosphere. The purity of Al was 99.999%, of Cu 99.95%, and of Ir 99.9%. Parts of solidified ingots were thermally annealed under vacuum at 540°C for 232 h and at 900°C for 186 h, subsequently water quenched. The as-cast and annealed samples were studied by powder X-ray diffraction (XRD, Cu Kα radiation was used), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The local phase compositions were determined in SEM by energy-dispersive X-ray analysis (EDX) on polished unetched cross sections. TEM examinations were carried out on powdered materials dispersed on grids with carbon film. Differential thermal analysis (DTA) was carried out for selected samples at heating and cooling rates of 10 to 50°C/min.

Results

The Al-Ir alloy system [7] contains a number of intermetallics (see Table 1). Congruent AlIr (β-phase) and congruent C-Al12Ir (C-phase) melt at temperatures above 2000 and 1600°C, respectively. At higher Al concentration the Al2Ir, Al2Ir5 (γ-phase), Al4Ir13 (φ-phase) and Al1Ir phases are formed by subsequent peritectic reactions at 1466, 1446, 993 and 877°C. Finally, an (Al) + Al1Ir2 eutectic is formed at 657°C.
Table 1 Crystallographic data of the periodic Al-Cu, Al-Ir and Al-Cu-Ir phases mentioned in isothermal sections.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>a, nm</th>
<th>b, nm</th>
<th>c, nm</th>
<th>β, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ (Al₂Cu)</td>
<td>Imc</td>
<td>0.60662</td>
<td></td>
<td></td>
<td>0.48738</td>
</tr>
<tr>
<td>η₂ (AlCu)</td>
<td>C2/m</td>
<td>1.2066</td>
<td>0.4105</td>
<td>0.6913</td>
<td>55.04</td>
</tr>
<tr>
<td>AlIr₂</td>
<td>P2₁/c</td>
<td>0.63779</td>
<td>0.64318</td>
<td>0.87337</td>
<td>94.78</td>
</tr>
<tr>
<td>θ (Al₂Ir₁₃)</td>
<td>P3₁c</td>
<td>1.2286</td>
<td></td>
<td>2.7375</td>
<td>-</td>
</tr>
<tr>
<td>AlIr</td>
<td>P6₅/mmc</td>
<td>0.4246</td>
<td></td>
<td>0.7756</td>
<td>-</td>
</tr>
<tr>
<td>C (Al₃Ir)</td>
<td>Pm₃</td>
<td>0.7694</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>β (AlIr)</td>
<td>Pm3m</td>
<td>0.2969</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ε₆</td>
<td>Orth.</td>
<td>2.34</td>
<td>1.65</td>
<td>1.24</td>
<td>-</td>
</tr>
<tr>
<td>C₂</td>
<td>Fm3</td>
<td>1.53928</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ω (Al₃Cu₂Ir)</td>
<td>P4/mnc</td>
<td>0.64142</td>
<td></td>
<td>1.4842</td>
<td>-</td>
</tr>
</tbody>
</table>

*Electron diffraction data.

Fig. 1 Powder XRD patterns (Cu Kα₁ radiation) of the: a) decagonal phase (D₁₁), b) ω-phase, c) C₂-phase and d) ε₆-phase.

In Al-Cu the phases forming in the relevant compositional range are high-temperature and low-temperatures couples of the ε, ζ and η phases and Al₃Cu (θ) [8]. Apart from c₁ they are molten at the temperature of 900°C selected for our major investigation. The θ-phase presented in the partial 540°C isothermal section (see below) is formed by a peritectic reaction at 591°C. The (Al) + θ eutectic is formed at 548°C [8]. The Al-Cu phases were usually minor in the majority of the studied alloys and were identified according to their compositions compared to those in the binary phase diagram.

In solidified materials equiatomic AlIr was found to extend at approximately constant Al concentration up to 25 at.% Cu. The C-phase dissolves up to 12 at.% Cu, Al₃Ir up to 8.5 at.% Cu, the χ-phase and ϕ-phase up to 3 at.% Cu, and Al₉Ir₂ up to 2.5 at.% Cu. With the increase of the Cu concentration the compositional ranges of the above-mentioned binary Al-Ir phases, apart from the β-phase, become wider and sharply shifted towards lower Al concentrations. The dissolution of Cu also results in a decrease of the melting temperatures of the Al-Ir phases.

The Al-Cu ε₁-phase dissolves up to 3 at.% Ir, while the solubility of Ir in θ and η₂ is below 0.5 at.%. The formation of a stable ternary decagonal phase and three ternary periodic phases was also observed in the above-mentioned compositional range. Their powder X-ray diffraction patterns are shown in Fig. 1. The decagonal phase of ~Al₆₀Cu₂₄Ir₁₆ examined by electron diffraction exhibited a periodicity of ~0.4 nm in the specific direction (D₁₁-structure, Fig. 2a-c). Of the periodic phases, one was found around the Al₇₀Cu₂₀Ir₁₀ composition (ω-phase, see Table 1). It is isostructural to the Al₃Cu-Rh ω-phase, also observed at similar compositions in Al-Cu-Co(Fe, Ru) [1]. The second ternary C₂-phase (see Table 1) is formed in a range around Al₉₀Cu₃₇Ir₂₆, i.e. close to the high-Cu limit of the C-phase compositional range. It exhibits a structure typical of the C₂-phases that are also formed in Al-Cu-Rh and a number of other aluminum-transition metal alloy systems [1]. Around the Al₉₀Cu₃₇Ir₂₀ composition, the third ternary phase was revealed, which belongs to the family of so-called ε₆-phases [9]. Electron diffraction examinations in TEM...
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Fig. 2 Electron diffraction patterns of the Al-Cu-Ir phases: a-c) decagonal phase ($D_1$), d-f) $\varepsilon_6$-phase.

(see Fig. 2d-f) revealed the $\varepsilon_6$ structure, also observed in Al-(Cu)-Rh [6]. While in binary Al-Rh the $\varepsilon_6$-phase is stable and can dissolve up to ~15 at.% Cu, it does not exist as a stable phase in Al-Ir, but is stabilized by Cu in a ternary compositional range.

Fig. 3 Partial isothermal section at 900°C. The compositions of the studied samples are shown by spots. Provisional tie-lines are shown by broken lines. L is liquid. The compositional region marked by (?) was not studied.

The $D_1$-phase melts at about 1002°C, the $\varepsilon_6$-phase at ~1200°C, the $\omega$-phase at 683°C whereas the $C_2$-phase was not melted up to 1400°C.

The partial 900°C isothermal section of Al-Cu-Ir is shown in Fig. 3. In the studied compositional range the Al-Ir phases $\beta$, C, Al$_3$Ir, $\chi$ and $\phi$ are solid at this temperature, while a wide region adjacent to Al-Cu is occupied by the liquid and only the $\varepsilon_6$-phase is solid. The ternary $\varepsilon_6$-phase is formed in a compositional range from Al$_{71.5}$Cu$_{6}$Ir$_{22.5}$ to Al$_{68}$Cu$_{12.5}$Ir$_{19.5}$. The $D_1$-phase is also solid at this temperature and is formed in a compositional range from Al$_{71.5}$Cu$_{6}$Ir$_{22.5}$ to Al$_{68}$Cu$_{12.5}$Ir$_{19.5}$. The compositional gap between the existence regions of the C-phase and $C_2$-phase was not detected and the separation of their compositional ranges is shown conditionally in Fig. 3 by a broken line. It is worth noting that in the Al-Cu-Rh [6] and Al-Pd-Rh [10] alloy systems similar C and $C_2$ phases were found to coexist in narrow ranges, which was very difficult to detect. The three-phase equilibria Al$_3$Ir-$\varepsilon_6$-$\chi$, Al$_3$Ir-$\varepsilon_6$-$D_1$, L-$\varepsilon_6$-$D_1$ and L-$\varepsilon_6$-$D_1$ were established with certainty from the existence of the corresponding boundary two-phase equilibria. The three-phase equilibria between the $\phi$, $\chi$, $\varepsilon_6$ phases and the liquid have not been clarified yet due to difficulties to obtain samples in the corresponding small compositional ranges. In Fig. 3 one of the possibilities is assumed.

The partial 540°C isothermal section is shown in Fig. 4. At this temperature equilibration of only a few alloys adjacent to the Al corner was achieved after a
Fig. 4 Partial isothermal section at 540°C. The compositions of the studied samples are shown by spots. Provisional tie-lines are shown by broken lines. L is liquid. The compositional region marked by (?) was not studied.

Conclusions

We report a first study of the Al-Cu-Ir alloy system in the compositional range above 35 at.% Al. Partial 900 and 540°C isothermal sections were determined. The Al-Ir phases were found to dissolve Cu: 30 at.% for AlIr, 12, 8.5, 3 and 2.5 at.% for Al$_2$Ir, Al$_3$Ir, $\chi$, $\varphi$ and Al$_6$Ir$_2$, respectively. One stable ternary decagonal phase (D1-phase) and three ternary periodic phases designated C$_2$, $\epsilon_6$ and $\omega$ were revealed.

Acknowledgements

We thank V. Lenzen and M. Schmidt for technical contributions. D. Kapush and T.Ya. Velikanova thank Forschungszentrum Jülich for financial support.

References