Aluminium - Chromium - Magnesium

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Literature Data

Information about the phase equilibria in the aluminium-rich region are due to the results obtained by different investigators [1940Erd, 1940Hof, 1943Mon, 1948Lit, 1956Vul, 1960Zol1, 1960Zol2, 1973Ohn1, 1973Ohn2]. [1940Erd] was the first to examine the phase relations in the Al-rich corner within the range of 0 to 23 mass% Cr and 0 to 37 mass% Mg by means of thermal analysis (±0.5°C, 60 grams of alloy) and optical metallography of a total of 140 alloys. A liquidus projection was established for the Al-rich and Cr-poor region (3 mass% Cr and 35 mass% Mg, see also [1941Han]). All samples were prepared by melting the Al in a graphite crucible internally-lined with sintered Al₂O₃ prior to adding the proper amounts of Cr in the form of an Al-10 mass% Cr master alloy followed by the Mg. To prevent oxidation, a protective layer of Hydrasal was used and, due to a retarded solubility of Al-Cr crystals, the melts had to be kept for prolonged periods at temperature. Starting materials were 99.99 % Al and Mg and 99.86 % pure electrolyte Cr containing 0.095 mass% H, 0.03 % Fe, 0.01 % Si, 0.01 % Cr and 0.003 % S. To avoid separation by gravity, melts were cast in flat 10 × 15 mm thin-walled iron molds. Phases were specified by selective etching using NaOH (1 %) at 50°C for $CrAl_7$ (15-45 s, brown, no attack on Cr_2Al_{11} and T), and HNO_3 (20 %) at 70°C for Mg₂Al₃ (dark brown, no attack on Al). For an isothermal section at 400°C, the alloys were sealed in silica ampoules under 1 bar of air with addition of Mg filings as a getter material, and heat treated for 720 h at 400°C. Solid solubility limits of a series of alloys (1.96 to 2.07 mass% Mg, 0.12 to 1.6 mass% Cr, balance Al) have been derived at three different temperatures (400, 500 and 600°C) from electrical resistivity measurements and by X-ray examination [1940Hof]; alloys were prepared by casting into thick-walled brass crucibles, annealing at 600 to 620°C for 48 h and subsequently hot drawing (at 420 to 450°C) into a wire of 4 mm diameter, quenching, sealing in silica capsules and finally annealing at 400, 500 and 600°C, respectively. The results of [1940Erd], in particular the existence of a ternary phase T, were essentially confirmed by [1948Lit] in a reinvestigation of the ternary system in the region of 0 to 20 mass% Mg and 0 to 10 mass% Cr on a series of more than 60 samples which were prepared by melting Al and proper amounts of an Al-8.6 mass% Cr master alloy in fluorspar-lined Al₂O₃ crucibles before adding the Mg. The reguli were then sealed in evacuated hard glass tubes, annealed for 380 to 720 h at 460°C and examined by chemical analysis (some), by optical metallography and by X-ray analysis and a partial isothermal section at 460°C was established. Etchants used were hot alkaline permanganate solutions at 60 to 70°C. T was generally outlined by a 1 min swab etch with aqueous hydrofluoric acid. In contradiction to these observations by [1940Erd], [1941Han] and [1948Lit], the ternary phase T was considered by [1943Mon] to constitute a solid solution of Mg in binary Cr₂Al₁₁ (in this assessment called CrAl₅) rather than a true ternary compound - as a consequence the primary field of the T phase is eliminated in the liquidus projection and the primary field of CrAl₇ will extend further up to 20 mass% of Mg; similarly, the isothermal section proposed by [1943Mon] for a temperature of 447°C is without a ternary compound. In a later review by [1952Han], Mondolfo's version of the phase diagram was rejected on the basis of significant differences between T and the proposed solution of Mg in Cr₂Al₁₁ as seen under polarized light.

The present evaluation was published in the MSIT Evaluation Program earlier and reflects today's state of knowledge.

Binary Systems

The binary system Al-Cr was accepted after [Mas2]. The binary Al-Cr compounds $CrAl_7$ and Cr_2Al_{11} are called here Θ and η , respectively. The new version of the Al-Mg binary system was accepted after [1998Lia]. It is modified according to the documented homogeneity range of the β phase [1997Su], which was not taken into account by the calculation. The small homogeneity range of the ϵ phase [1997Su] is not well established. The Al-Mg phase diagram is accepted from [2003Luk].

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Solid Phases

Despite arguments by [1943Mon] (see above) the ternary compound originally labeled T ("CrMgAl₈") by [1940Erd] and [1941Han] has been confirmed by [1948Lit, 1952Han, 1956Vul, 1973Ohn1] and [1973Ohn2] and an extended homogeneous range was indicated from X-ray and chemical analysis on electrochemically extracted single crystals, then revealing a Cr content of about 11.8 to 12.6 mass% Cr; a tie line construction furthermore resulted in a Mg content varying from 8.2 to 13.5 mass% Mg ("Cr₂Mg₃₋₄Al₂₄₋₂₅") [1948Lit]. The large lattice parameter, as observed by [1953Lit] for "Cr₂Mg₃Al₂₅" confirms the existence of an extended homogeneous range towards compositions richer in Mg than Cr₂Mg₃Al₁₈, as was also indicated from the investigation by [1948Lit]. Assuming complete occupation of all atom sites in the unit cell, and taking further into account the various results obtained from chemical analyses [1940Erd, 1948Lit], the homogeneous range, however, appears to be at higher Cr contents as indicated by [1948Lit], and thus might be represented by the formula: Cr₂Mg₄Al₁₇ to Cr₂Mg₂Al₁₉ (see also Fig. 6). In contrast to a preliminary X-ray investigation by [1953Lit], a complete determination of the crystal structure by means of single crystal X-ray Weissenberg photographs revealed cubic symmetry $Fd\overline{3}m$ due to observed extinctions (hhl) for h+l=2n+1 [1954Sam, 1958Sam]. At a reliability factor of R = 0.116 the atom parameters were (origin of cell at 1/8 1/8 from 1): Al1 in 96 g (0.0666(3), 0.0666, 0.2998(4)), Al2 in 48 f (0.1407(6), 0, 0), Mg1 in 16 d (5/8, 5/8, 5/8), Mg2 in 8 b (1/2, 1/2, 1/2) and Cr in 16 c (1/8, 1/8, 1/8)) [1958Sam]. The crystal structure was confirmed using X-ray powder data [1973Ohn1, 1987Ker]. Besides the existence of T ($Cr_2Mg_3Al_{18}$) the formation of at least one further ternary phase (denoted T_y) was claimed by [1940Erd], but no details were given. Solid solubility of Mg in CrAl₇ and in Cr₂Al₁₁ were observed to be very small [1940Erd] or negligible [1960Zol2]. Solid solubility limits for Cr and Mg in (Al) as derived by [1940Hof] were: 0.56 Cr mass% at 0.0 mass% Mg, 600°C, and 0.38 mass% Cr at 2.0 mass% Mg, 600°C; 0.3 mass% Cr at 0.0 mass% Mg, 500°C and 0.2 mass% Cr at 2.0 mass% Mg, 500°C. These data and later observations by [1948Lit] at 460°C (0.3 mass% Cr at 1.1 mass% Mg) are slightly higher than the more recent findings by [1973Ohn1] and [1973Ohn2] at 400, 450 and 550°C, respectively. Crystallographic data of the solid phases appearing in the diagrams are listed in Table 1.

Invariant Equilibria

Four ternary invariant equilibria were reported by [1940Erd] and [1941Han] in the Al-rich region of the system (35 mass% Mg, 3 mass% Cr; see Table 2): eutectic decomposition of the liquid at $447.3 \pm 0.5^{\circ}\text{C}$ and three transition type reactions U_1 , U_2 , U_3 , for which a reaction temperature was measured only for U_2 at 632.7°C . The compositions of the liquids are given explicitly [1940Erd, 1941Han], those of the solid phases are corrected in view of later investigations by [1948Lit] and [1973Ohn1, 1973Ohn2] (see also section Isothermal Sections). The anomalous nature of the ternary eutectic was also discussed by [1960Spe]. Based on the information by [1940Erd] on the formation of at least two ternary phases T and T_x , the reaction scheme (Fig. 1) and a projection of the invariant equilibrium planes and the connecting lines of double saturation (Fig. 2) are presented for the Al-rich region of the Al-Cr-Mg system. Due to the lack of detailed information, however, the diagram is partly estimated.

Liquidus Surface

Figure 3 shows some isotherms of the liquidus surface and the melting grooves separating five areas of primary crystallization in the Al-rich region of the system: α , Θ , η , β , T. Figure 3 is essentially based on the experimental results of [1940Erd] and [1960Zol2]. In contrast to [1940Erd], and based on liquid extraction experiments on a series of alloys with constant Mg contents of 1.5, 2.0 and 3.0 mass%, the experiments of [1960Zol2] revealed that with increasing Mg content up to 7 mass% Mg, the α field of primary crystallization contracts.

Isothermal Sections

Figures 4, 5 and 6 reveal the isothermal sections in the Al-rich region at 550, 450 and 400°C according to [1973Ohn1] and [1973Ohn2]. The phase field distribution at 400°C is mainly based on [1940Erd] with

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minor corrections regarding the position and homogeneous range of the ternary T phase [1958Sam] which was found from the 460°C section by [1948Lit]. Furthermore, according to the investigations by [1948Lit] and [1973Ohn1, 1973Ohn2], the vertex of the three phase field $\alpha+\Theta+T$ is generally located at smaller Mg and Cr contents, as also suggested by [1952Han] in view of the earlier data by [1940Hof].

Notes on Materials Properties and Applications

[1952Han] and [1956Vul] report on the hardness of the ternary compound T in comparison with binary Cr-aluminides. Whereas [1952Han] measured 540 kg·mm⁻², the variation of the microhardness of "CrMg₂Al₁₂" was given as 461 kg·mm⁻² at 20°C (30 s), 402 kg·mm⁻² at 300°C (30 s) and 358 kg·mm⁻² at 300°C after 60 min [1956Vul]. Furthermore, the influence of "Cr₂Mg₄Al₂₄" (Cr₂Mg₄Al₁₇) on the heat resistance of aluminium alloys was investigated at 300°C. The fatigue limit σ_{100} at 300°C for the alloy containing 0.63 mass% Cr and 2.30 mass% Mg was found to be 4.7 kg·mm⁻² [1956Vul].

Structure and mechanical properties of rapidly solidified Al-(3-6)Mg-(0-9)Cr (at.%) alloys were investigated by [1994Abr]. Authors report that Al-Cr-Mg alloys exhibit higher strength and hardness (Table 3) comparing with corresponding values of binary Al-Cr alloys. However, the use of magnesium as alloying element produced a drastic reduction in tensile ductility.

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Table 1: Crystallographic Data of Solid Phases

| Phase/ Temperature Range [°C] | Pearson Symbol/ Space Group/ Prototype | Lattice Parameters [pm] | Comments/References |
|---|--|---|--|
| α, (Al) < 660.452 | <i>cF4</i> <i>Fm3m</i> Cu | a = 404.96 | at 25°C [Mas2] |
| δ, (Mg) < 650 | hP2 P6 ₃ /mmc Mg | a = 320.94 c = 521.07 | at 25°C [Mas2] |
| β, Mg ₂ Al ₃ < 452 | cF1168 $Fd\overline{3}m$ Mg_2Al_3 | a = 2823.9 | 1168 atoms on 1704 sites per unit cell [2003Luk] 60-62 at.% Al [1997Su] |
| ε, Mg ₂₃ Al ₃₀ 410-250 | hR159 R3 Mg ₂₃ Al ₃₀ | $a = 1282.54 \pm 0.03$ $c = 2174.78 \pm 0.09$ | [V-C, 1968Sam, 1981Sch] 159 atoms refer to hexagonal unit cell [2003Luk] |

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| D1 / | D C 1 1/ | T 44' D | C /D C |
|---|--------------------|------------------------|---|
| Phase/ | | | Comments/References |
| Temperature Range | Space Group/ | [pm] | |
| [°C] | Prototype | | |
| γ , Mg ₁₇ Al ₁₂ | <i>c<u>I</u>58</i> | a = 1054.38 | [V-C], $\rho_{\rm X} = 2.068 {\rm Mg \cdot m^{-3}}$ |
| < 458 | $I\overline{4}3m$ | a = 1048.11 | 52.58 at.% Mg [L-B] |
| | α Mn | a = 1053.05 | 56.55 at.% Mg [L-B] |
| | | a = 1057.91 | 60.49 at.% Mg [L-B] |
| η, Cr ₂ Al ₁₁ | oC584 | | [2003Cor] |
| ≤ 940 | Cmcm | a = 1240 | quenched from 920°C |
| | | b = 3460 | 16.9 to 19.2 at. % Cr; |
| | | c = 2020 | , |
| | | a = 1252.1 | single crystal "ECrAl ₄ " |
| | | b = 3470.5 | 2 |
| | | c = 2022.3 | |
| | | a = 1260 | "εCrAl ₄ " |
| | | b = 3460 | 4 |
| | | c = 2000 | |
| $\overline{\Theta, \operatorname{CrAl}_7}$ | mC104 | a = 2519.6 | $\rho_{\rm obs} = 2.78 \; {\rm Mg \cdot m^{-3}} \; {\rm at}$ |
| ≤ 790 | C2/m | b = 757.4 | 13.2 at.% Cr [V-C] |
| | $Al_{45}V_7$ | c = 1094.9 | , |
| | 43 / | $\beta=128.80^{\circ}$ | |
| * T ^{a b} , Cr ₂ MgAl ₁₈ | cF184 | a = 1455 | [1958Sam], sp. group $Fd\overline{3}m$ |
| 2 2 10 | $Fd\overline{3}m$ | | $\rho_{\rm x} = 2.86 {\rm Mgm}^{-3} [1954 {\rm Sam}]$ |
| | $Al_{18}Cr_2Mg_3$ | | $\rho_{\rm exp} = 2.80 {\rm Mgm}^{-3} [1954 {\rm Sam}]$ |
| | 10 2 -5 | $a = 1453 \pm 1$ | [1987Ker] |
| | | a = 1468 | [1948Lit, 1953Lit] for "Al ₂ Cr ₂ Mg ₃ " |
| | | | converted from kX-units |
| * T _x | unknown structure | - | [1940Erd] |

^a Earlier denoted as "Al₈CrMg" by [1940Erd] or as E by [1948Lit] who, from X-ray powder and single crystal oscillation photographs, reported $Fm\overline{3}m$ as the most probable space group due to the lack of extinctions observed for the (hhl)-reflections.

b Assuming complete occupation of all atom sites in the structure, the large lattice parameter of [1953Lit] suggests an extended homogeneity range towards compositions richer in Mg than $Al_{18}Cr_2Mg_3$. Taking further into account the various results obtained from chemical analysis [1940Erd, 1948Lit] the homogeneity range might be $Al_{17-19}Cr_2Mg_{4-2}$ (this range is assumed in Fig. 6).

 Table 2: Invariant Equilibria

| Reaction | T [°C] | Type | Phase | Composition (at.%) | | |
|---|--------|----------------|----------------|--------------------|------|------|
| | | | | Al | Cr | Mg |
| $L + \eta \rightleftharpoons \Theta + T$ | ~ 750 | U ₁ | L ₁ | 84.9 | 1.2 | 13.9 |
| | | | η_1 | 84.6 | 15.4 | 0.0 |
| | | | Θ_1 | 87.2 | 12.8 | 0.0 |
| | | | T_1 | 78.3 | 8.7 | 13.0 |
| $L + \Theta \Rightarrow \alpha + T$ | 633 | U_2 | L ₂ | 85.0 | 0.9 | 14.1 |
| | | | Θ_2^- | 87.5 | 12.5 | 0.0 |
| | | | α_2^- | 97.5 | 0.3 | 2.2 |
| | | | T_2 | 81.3 | 8.6 | 10.1 |
| $L + T_x \rightleftharpoons \beta + T$ | 448 | U ₃ | L ₃ | 64.6 | 1.1 | 34.3 |
| | | | T_{x3} | unknov | vn | |
| | | | β_3 | 60.5 | 0.0 | 39.5 |
| | | | T_3 | 74.0 | 8.7 | 17.3 |
| $L \rightleftharpoons \alpha + \beta + T$ | 447 | Е | L_4 | 65.5 | 0.9 | 33.6 |
| | | | α_4 | 85.6 | 0.0 | 14.4 |
| | | | eta_4 | 61.5 | 0.0 | 38.5 |
| | | | T_4 | 78.6 | 8.4 | 13.0 |

Table 3: Mechanical Properties of Al-Cr-Mg and Al-Cr Alloys [1994Abr]

| Composition (at.%) | | Yield strength | UTS [MPa] | Elongation (%) | | |
|--------------------|-----|----------------|-----------|----------------|------|-------|
| Al | Cr | Mg | [MPa] | | | [MPa] |
| 99.5 | 0.5 | 0 | 185 | 198 | 16.5 | 566 |
| 98.5 | 1.5 | 0 | 233 | 235 | 8.5 | 755 |
| 98.0 | 2.0 | 0 | 241 | 257 | 8.0 | 950 |
| 92.0 | 2.0 | 6.0 | 498 | 520 | 4.0 | 1610 |

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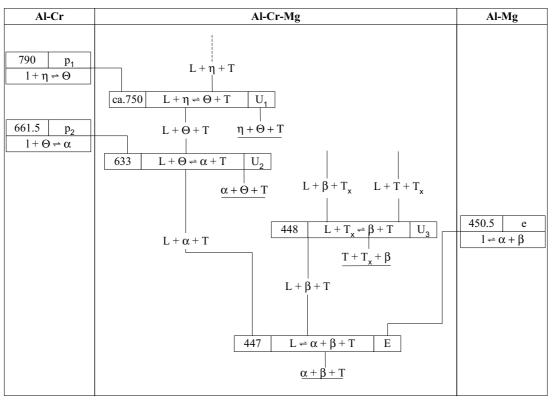
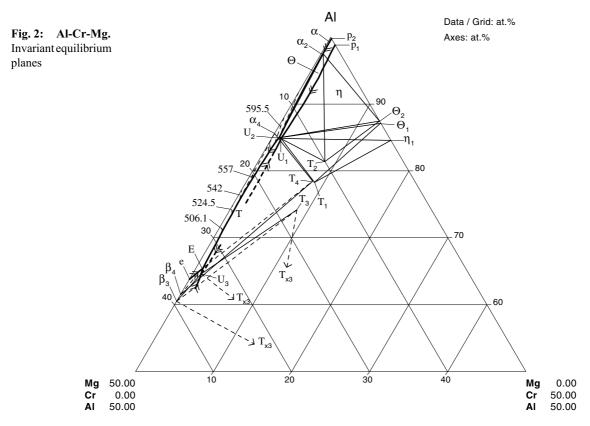


Fig. 1: Al-Cr-Mg. A partial reaction scheme



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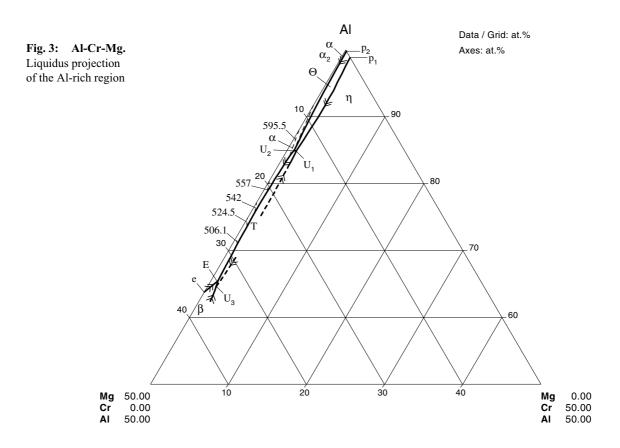
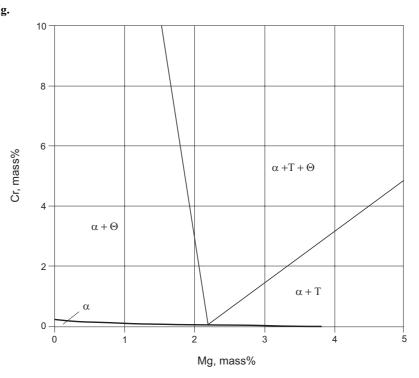
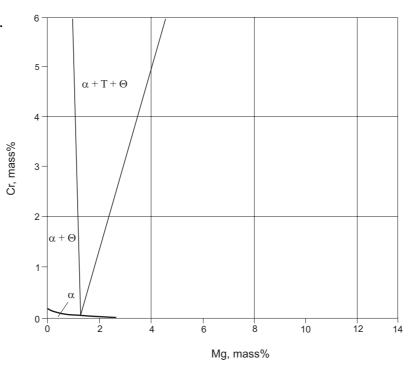


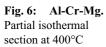
Fig. 4: Al-Cr-Mg. Phase equilibria in the Al corner at 550°C

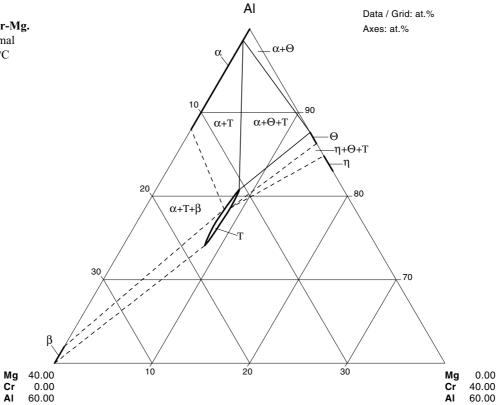


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Fig. 5: Al-Cr-Mg. Phase equilibria in the Al corner at 450°C







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