Aluminium - Copper - Dysprosium

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Literature Data

After the assessment previously carried out by [1991Ran] all the data have been reviewed by Riani et al. [2003Ria], considering also the more recent literature data. [1989Kuz] studied the isothermal section at 500°C of the Al-Cu-Dy system by X-ray diffraction on 109 samples prepared from 99.5% Dy and purer Cu and Al. The samples were then annealed at 500°C for 600 h and the solubility of the third component was determined in some of the binary compounds. All other works on this system are devoted to ternary compounds. The following compounds were found: DyCuAl [1968Dwi, 1973Oes], DyCuAl₃ [1988Kuz], DyCu₄Al [1978Tak], DyCu₄Al₈ [1979Fel], DyCu₆Al₆ [1980Fel, 1981Fel], Dy₂Cu₇Al₁₀ [1982Pre], DyCu_{0.9}Al_{2.1} [1992Kuz] and Dy₃Cu_{2.6}Al_{8.4} [2000Ste]. The alloys were prepared from 99.5 to 99.9% pure Dy [1968Dwi, 1973Oes, 1978Tak, 1979Fel, 1980Fel, 1981Fel, 1982Pre] and Cu and Al of higher purity, either by arc melting or in an induction furnace under inert protective atmosphere.

A high pressure modification of the compound DyCuAl and its structure are reported by [1987Tsv1] and [1987Tsv2]. Samples made from 99.9% pure metals were either rapidly quenched from a melt at a constant pressure of 7.7 GPa or annealed at 1450 to 1500°C. After vacuum annealing at 700°C for 6 h, this high pressure modification was reported to decompose into the initial phases obtained at atmospheric pressure.

Binary Systems

In this ternary evaluation the edge binary system Al-Dy is accepted as reported by [2003Gry] and the Al-Cu system as reported by [2003Gro] with changes being applied in the crystal structure data. The Cu-Dy is used as published by [1988Sub, 1994Sub].

Solid Phases

[1989Kuz] confirmed the existence of the earlier reported ternary compounds τ_1 , DyCu₄Al₈, $\tau_2, Dy_2Cu_7Al_{10}, \ \tau_3, Dy(Cu_{1-x}Al_x)_5, \ \tau_5, DyCuAl_3 \ and \ \tau_6, DyCuAl, \ and \ found \ two \ new \ ternary \ compounds,$ τ_4 ,Dy₅Cu₆Al₉ and τ_7 ,Dy₄Cu₄Al₁₁. The DyCu₆Al₆ compound reported by [1980Fel] identified to be the τ_1 ,DyCu₄Al₈ compound. Both, τ_1 ,DyCu₄Al₈ and DyCu₆Al₆ have the same structure (ThMn₁₂ type) and possibly belong to the same solid solution range, although the investigators did not mention this point. Two of the ternary phases, τ_2 and τ_3 , are reported to have a homogeneity range with constant Dy content: τ_2 , Dy₂(Cu_{1-x}Al_x)₁₇ and τ_3 , Dy(Cu_{1-x}Al_x)₅. For τ_3 [1989Kuz] gives a homogeneity range with a maximum $Cu \ content \ at \ DyCu_{3.8}Al_{1.2} \ which \ does \ not \ cover \ the \ composition \ DyCu_4Al, \ for \ which \ [1978Tak] \ reported$ the same crystal structure as was allocated to τ_3 by [1989Kuz]. [2000Ste] gave a slightly different composition and structure for the τ₅,DyCuAl₃ compound (BaAl₄-type) previously proposed by [1988Kuz], i.e. τ_5 ,Dy₃Cu_{2.6}Al_{8.4} and a La₃Al₁₁ type structure. The structure of the τ_4 ,Dy₅Cu₆Al₉ compound is not given. For the τ_4 ,DyCu_{0.9}Al_{2.1} phase [1992Kuz] observed the hR36 structure of the PuNi₃-type or NbBe₃ type and assumed that it is identical with the Dy₅Cu₆Al₉ compound identified in the earlier work [1989Kuz]. It is isostructural with HoCuAl₂ with some Al atoms substituting Cu. The τ_8 ,Dy₆Cu₁₆Al₇ phase has been identified as pertaining to the cubic Th₆Mn₂₃-type structure by [1990Ste]. Crystallographic data for the ternary and binary phases are given in Table 1.

Isothermal Sections

The isothermal section at 500°C, studied by [1989Kuz], is used as base for Fig. 1. The Al rich part of the [1989Kuz] diagram was later supported by the observations of [1997Sok] at 400°C, by the tie lines of Al- τ_1 , DyAl₃- τ_1 and DyAl₃- τ_5 . However, we brought some modifications to the original diagram to make it consistent with the accepted binary diagrams: on the Al-Cu edge, the ϵ phase, unstable at 500°C is omitted; on the Al-Dy edge [1989Kuz] indicated a compound Dy₃Al, which is not a stable phase of the binary system

but more probably stabilized by impurities, therefore it is omitted in Fig. 1. On the other hand, the Dy_2Cu_9 compound, whose stability is doubtful, was not observed by [1989Kuz]. The copper rich part of the diagram has also been slightly modified for the sake of thermodynamic consistency. Seven ternary phases have been identified and included. Three of them τ_4 , $Dy_5Cu_6Al_9$, τ_5 , $DyCuAl_3$ and τ_7 , $Dy_4Cu_4Al_{11}$ have been described as point compounds. For the remaining phases, the following solubility ranges are accepted: τ_1 , $Dy(Cu_xAl_{1-x})_{12}$ (0.33 < x < 0.37), τ_2 , $Dy_2(Cu_xAl_{1-x})_{17}$ (0.394 < x < 0.588), τ_3 , $Dy(Cu_xAl_{1-x})_5$ (0.46 < x < 0.8) and τ_6 , $DyCu_{2-x}Al_x$ (0.95 < x < 1). The point phase given by [1989Kuz] as corresponding to the composition τ_5 , $DyCuAl_3$ was subsequently [2000Ste] described as τ_5 , $Dy_3Cu_{2.6}Al_{8.4}$ with the La₃Al₁₁ type structure. The composition of the τ_5 , $DyCuAl_3$ phase is rather close to that of the τ_7 , $Dy_4Cu_4Al_{11}$ (or τ_7 , $DyCuAl_{2.75}$) and the crystal structure of τ_7 , is unknown. However, we did not consider these two phases as belonging to the same solid solution because the general trend in the Al-Cu-Dy system is the mutual exchange of Al and Cu atoms on a same crystallographic site. The τ_8 , $Dy_6Cu_{16}Al_7$ phase described by [1990Ste] was not observed when [1989Kuz] examined the equilibria at 500°C. Its position is shown in the Fig. 1, but no reliable equilibrium lines can be drawn between τ_8 and the surrounding phases.

Notes on Materials Properties and Applications

Much of the research effort done in the recent years on Rare Earth-Al-Cu compounds has been focused on their magnetic behavior. Basic information is mainly obtained from magnetization curves at various temperatures. The paramagnetic Curie temperature of the compound τ_6 , DyCuAl compound, once determined as 35 K by [1973Oes] was later estimated to be lower, at 25.9 K by [1998Jav] or 28 K by [2001Hav].

[1979Fel] studied the magnetism and hyperfine interactions of 151 Eu, 155 Gd, 161 Dy, 166 Er and 170 Yb in RCu₄Al₈ and reported a Neel temperature of 19 K for the τ_1 ,DyCu₄Al₈ compound. [1981Fel] reported 3.9 K for τ_1 ,DyCu₆Al₆. [1998Jav] studied the magnetic properties of the RCuAl (R = Y, Ce to Sm, Gd to Tm and Lu) intermetallic compounds measuring susceptibility, magnetization and specific heat and observed a magnetic ordering at low temperatures in most of these materials: PrCuAl and NdCuAl showed an antiferromagnetic behavior while in the heavy rare-earth compounds (R=Gd-Er) a ferromagnetic coupling was found. Moreover [1999And] studied the magnetic anisotropy and the spontaneous magnetostriction of DyCuAl by means of X-ray diffraction.

The interaction of H_2 with RCuAl (R = Dy, Ho, Er) was studied by [1996Mit].

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Table 1: Crystallographic Data of Solid Phases

Assessment, 267)

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Al) <660	<i>cF</i> 4 <i>Fm</i> 3 <i>m</i> Cu	a = 404.96	pure Al at 25°C [Mas2] Cu solubility 2.48 at.% [Mas2] Negligible solid solubility of Dy [1988Gsc]
(Cu) < 1084.62 Cu _{1-x} Al _x	<i>cF4 Fm3m</i> Cu	a = 361.46 $a = 361.52$ $a = 365.36$	pure Cu at 25°C [Mas2], 0 to 19.7 at.% A1 [Mas2] negligible solid solubility of Dy [1994Sub] [2003Gro], $x = 0$, quenched from 600°C [2003Gro], $x = 0.152$, quenched from 600°C
(βDy) 1412-1381	cI2 Im3m W	a = 398.0	[Mas2] dissolves up to ~12 at.% Cu at 800°C [1994Sub] dissolves up to ~3 at.% Al at 1300°C [1988Gsc]

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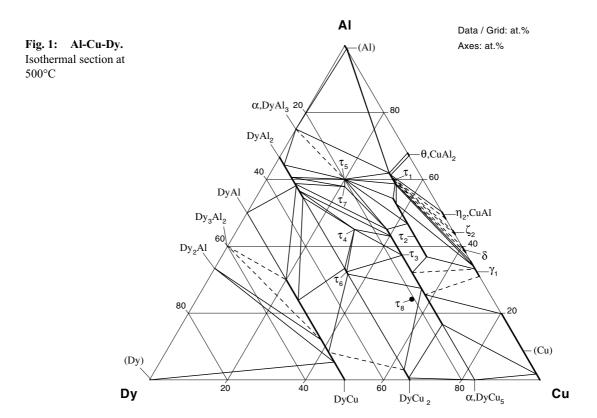
Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αDy) < 1381	hP2 P6 ₃ /mmc Mg	a = 359.15 c = 565.01	[Mas2] dissolves up to ≤ 1 at.% Al at 1300°C [1988Gsc]
β, Cu ₃ Al(h) 1049-559	cI2 Im3m W	<i>a</i> = 294.6 <i>a</i> = 295.64	~70 to 82 at.% Cu [1994Mur], [1998Liu] at 580°C at 672°C in two-phase (Cu)+β alloy
$ \frac{\alpha_2, \operatorname{Cu}_{100-x} \operatorname{Al}_x}{< 363} $	t**		22 ≤ <i>x</i> ≤ 23.5 [1994Mur]
.303	TiAl ₃ Long period super-lattice	a = 366.8 c = 368.0	76.5 to 78.0 at.% Cu at 76.4 at.% Cu (subcell only)
$ \gamma_0, Cu_{100-x}Al_x $ $ Cu_{-2}Al $ 1037-800	cI52 I43m Cu ₅ Zn ₈		$31.5 \le x \le 40.2$ [Mas2], $32.0 \le x \le 38.0$ [1998Liu]
γ ₁ , Cu ₉ Al ₄ < 890	cP52 P43m	070.22	62 to 68 at.% Cu [Mas2, 1998Liu]
δ, Cu _{100-x} Al _x < 686	$ \begin{array}{c} \text{Cu}_{9}\text{Al}_{4} \\ hR^{*} \\ R\overline{3}m \end{array} $	a = 870.23	From single crystal [V-C2] at 68 at.% Cu $38.1 \le x \le 40.7$ [1994Mur] 59.3 to 61.9 at.% Cu at $x = 38.9$ [V-C2]
$\frac{\varepsilon_1, \operatorname{Cu}_{100-x} \operatorname{Al}_x}{958-848}$	Cubic?		40.6 ≥ <i>x</i> ≥ 37.9 59.4 to 62.1 at.% Cu [Mas2, 1994Mur]
ε ₂ , Cu _{2-x} Al 850-560	<i>hP</i> 6 <i>P6₃/mmc</i> Ni ₂ In	a = 414.6 c = 506.3	0.78 ≥ x ≥ 0.45 55 to 61 at.% Cu [Mas, 1994Mur, V-C2], NiAs type in [Mas2, 1994Mur]
ζ ₁ , Cu _{47.8} Al _{35.5} (h) 590-530	oF88 - 4.7 Fmm2 Cu _{47.8} Al _{35.5}	a = 812 b = 1419.85 c = 999.28	55 to 57 at.% Cu [Mas2, 1994Mur] structure: [2002Gul]
ζ ₂ , Cu _{11.5} Al ₉ (r) < 570	oI24 - 3.5 Imm2 Cu _{11.5} Al ₉	a = 409.72 b = 713.13 c = 997.93	55.2 to 56.3 at.% Cu [V-C, Mas2, 2003Gro] structure: [2002Gul]
η ₁ , CuAl(h) 624-560	o*32	a = 408.7 $b = 1200$ $c = 863.5$	49.8 to 52.4 at.% Cu [V-C, Mas2, 1994Mur] Pearson symbol: [1931Pre]
η ₂ , CuAl(r) < 560	mC20 C2/m CuAl	a = 1206.6 b = 410.5 c = 691.3 $\beta = 55.04^{\circ}$	49.8 to 52.3 at.% Cu [V-C2]
θ, CuAl ₂ < 591	tI12 I4/mcm CuAl ₂	a = 606.7 $c = 487.7$	32.05 to 32.6 at.% Cu at 549°C 32.4 to 32.8 at.% Cu at 250°C [1996Goe] single crystal [V-C2, 1989Mee]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
DyCu _{1-x} Al _x	cP2 Pm3m CsCl	a = 357 a = 344 to 346	$0 \le x \le 0.6$ x = 0.6 [1989 Kuz] [1994 Sub]
DyCu < 955			
DyCu ₂ < 890	oI12 Imma CeCu ₂	a = 430 b = 680 c = 729	[1994Sub] Al solubility ~3 at.% [1989Kuz]
Dy ₂ Cu ₇ ~905 - ~855	?		[1994Sub]
Dy ₂ Cu ₉ < 970	t**	a = 499.9 c = 1394	[1994Sub]. The existence of this phase was questioned by [1994Sub] and can not be confirmed by ternary data
β, DyCu ₅ 965 - 930	hP6 P6/mmm CaCu ₅	a = 502 $c = 408$	Lattice parameters interpolated from the systematics of crystal data of RE-Cu alloys [1994Sub]
$ \overline{\mathrm{Dy}(\mathrm{Al}_{x}\mathrm{Cu}_{1-x})_{5}} < 930 $	cF24 F43m		$0 \le x \le 0.012$ from figure in [1989Kuz]
αDyCu ₅	AuBe ₅	a = 702.5	[1994Sub]
DyCu ₇ ~860 - ~775	hP8 TbCu ₇ Closely related to hP6 - CaCu ₅	a = 493.2 c = 415.6	[1994Sub]
βDyAl ₃ 1090-1005	<i>hR</i> 60 <i>R</i> 3̄ <i>m</i> HoAl ₃	a = 607.0 c = 3594	[1988Gsc]
αDyAl ₃ < 1005	hP16 P6 ₃ /mmc TiNi ₃	a = 609.1 c = 953.3	[1988Gsc]
$\overline{\text{DyCu}_x \text{Al}_{2-x}}$ $\overline{\text{DyAl}_2}$ < 1500	cF24 Fd3̄m MgCu ₂	a = 778 a = 783.6	$0 \le x \le 0.32$ at $x = 0.32$ [1989Kuz] at $x = 0$ [1988Gsc], [2000Sac]
DyA1 < 1100	oP16 Pbcm ErAl	a = 582.2 b = 1137 to 1134 c = 560 to 559	[1988Gsc], [2000Sac]
Dy ₃ Al ₂ < 1025	tP20 P4 ₂ /mnm Zr ₃ Al ₂	a = 817 to 820 c = 754 to 755	[1988Gsc], [2000Sac]
Dy ₂ Al < 990	oP12 Pnma Co ₂ Si	a = 654 to 653 b = 508 c = 940 to 938	[1988Gsc] [2000Sac]

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Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\overline{\tau_1, \operatorname{Dy}(\operatorname{Cu}_x \operatorname{Al}_{1-x})_{12}}$	tI26 I4/mmm ThMn ₁₂		$0.33 \le x \le 0.50$ at 800° C [1980Fel] $0.33 \le x \le 0.37$ at 500° C (x range estimated from figure in [1989Kuz])
DyCu ₄ Al ₈	-	a = 872.5 c = 513.7 a = 869.0	at $x = 0.33$, as cast sample [1979Fel] at $x = 0.33$, 500°C [1989Kuz]
DyCu ₆ Al ₆		c = 506.2 a = 866.2 c = 504.2	at $x = 0.5$, 800°C [1980Fel]
τ_2 , Dy ₂ (Cu _x Al _{1-x}) ₁₇	$hR57$ $R\overline{3}m$ Th_2Zn_{17}	a = 881.2 $c = 1284.4$ $a = 871.6$	$0.394 \le x \le 0.588 [1989 \text{Kuz}]$ at $x = 0.394 [1989 \text{Kuz}]$ at $x = 0.588 [1982 \text{Pre}]$
τ_3 , Dy(Cu _x Al _{1-x}) ₅	hP6 P6/mmm CaCu ₅	c = 1273.5 $a = 506.4$ $c = 415.2$ $a = 520$	$0.46 \le x \le 0.8 \text{ [1989Kuz]}$ at $x = 0.8 \text{ [1978Tak]}$ at $x = 0.46 \text{ [1989Kuz]}$
$\overline{\tau_4, DyCu_{0.9}Al_{2.1}}$	<i>hR</i> 36 <i>R3m</i> PuNi ₃	c = 408 $a = 545.7$ $c = 2531.7$	[1992Kuz] Previously reported as Dy ₅ Cu ₆ Al ₉ [1989Kuz]
τ ₅ , DyCuAl ₃	oI10 Immm HoCuAl ₃	a = 420.5 b = 414.3 c = 981.3	[1988Kuz, 1997Sok] Melting point higher than 1550°C [1989Kuz]
	oI12 Immm La ₃ Al ₁₁	a = 421.25 b = 1243.2 c = 982.67	[2000Ste] for τ_5 -Dy ₃ Cu _{2.6} Al _{8.4} This cell possibly is a superstructure of that described above (3 <i>b</i>)
τ_6 , DyCu _{2-x} Al _x	<i>hP</i> 9 <i>P</i> 62 <i>m</i> ZrNiAl	a = 701.5 c = 402.4 a = 702.29 c = 402.49	$0.95 \le x \le 1$ (from figure in [1989Kuz]) [1999And, 2001Hav] at 25°C [1968Dwi] (<i>hP</i> 9 type Fe ₂ P)
τ_7 , Dy ₄ Cu ₄ Al ₁₁			[1989Kuz]
τ ₈ , Dy ₆ Cu ₁₆ Al ₇	$cF1\underline{16}$ $Fm\overline{3}m$ Th_6Mn_{23}	a = 1227.5	[1990Ste] not observed by [1989Kuz] in the investigation of the isothermal section

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