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Letter

A study of the Al-rich region of the Al–Cu–Mo alloy system

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ABSTRACT

Partial isothermal sections at 810, 700 and 585 °C are presented for a high-Al compositional range of Al–Cu–Mo. The maximal solubility of Cu in the Al_5Mo phase(s) was found to be ~3 at.%. The previously reported Al_3Ti-type phase was found to be formed around the $Al_{68.5}Cu_{6.5}Mo_{25}$ composition. The other ternary phase forming in a small compositional range around Al_7Cu_2Mo has a hexagonal structure with $a = 0.86796(8)$ and $c = 1.51948(12)$ nm.

1. Introduction

An investigation of the Al–Cu–Mo phase diagram was carried out in Ref. [1]. The 600 °C isothermal section was determined in the whole compositional range. This work revealed the low solubility of a third element in binary phases and confirmed the formation of the Al_5CuMo_2 ternary phase with the Al_3Ti-type structure ($I4/mmm$, $a = 0.3716$, $c = 0.8445$ nm). Another ternary phase, Al_7Cu_2Mo was reported to be orthorhombic with $a = 0.505$, $b = 0.841$, $c = 1.968$ nm. Surprisingly, the isothermal section presented in Ref. [1] is inconsistent with the binary Al–Cu phase diagram accepted there. Also the Al–Mo phase diagram was quite poorly known at that time. The Al–Cu–Mo phase diagram compiled more recently in Ref. [2] was modified (without any additional experimental work) in order to be more consistent with the updated binaries. Particularly, Al_5Mo replaced Al_7Mo and "$Al_{17}Mo_4$" replaced "Al_3Mo", which required some shift of the corresponding compositional regions. Also, in Ref. [1] both $AlCu_3$ (existing above 567 °C) and Al_2Cu (existing below 591 °C) are shown. This discrepancy was eliminated in Ref. [2] by a suggestion that the true equilibrium temperature of the section was $567 < T < 591$ °C instead of 600 °C as proposed in Ref. [1].

In the present contribution the phase equilibria were specified at 585–810 °C in a high-Al compositional region of Al–Cu–Mo including the above-mentioned ternary phases. We also specified the structure of the phase forming around Al_7Cu_2Mo. Our analysis is based on the Al–Mo phase diagram from Refs. [3,4] and the Al–Cu phase diagram from Ref. [5].

2. Experimental

The alloys were produced by levitation induction melting in a water-cooled copper crucible under a pure Ar atmosphere. The purity of Al and Cu was 99.999%, and of Mo 99.97%. The ingot weights were typically ~5 g. Since Mo dissolved only slowly in the alloys, they were re-melted several times in order to improve homogeneity. Parts of the ingots were thermally annealed at 810–585 °C for 117–430 h. The alloys were examined by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA) 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. Powder XRD was carried out in the transmission mode using Cu $K_{\alpha 1}$ radiation and an image plate detector. For TEM examinations, powdered materials were dispersed on grids with carbon film. DTA was carried out in alumina crucibles at heating and cooling rates of 20 K/min.

3. Results and discussion

The high-Al region of the Al–Mo phase diagram is naturally separated from its low-Al part by the congruent Al_8Mo_3 phase melting at 1546 °C [4]. This temperature is much higher than the melting temperature of any phase in the Al–Cu alloy system, which also contains a deep eutectic (548 °C) at $Al_{82.9}Cu_{17.1}$ [5]. Due to these sharp temperature differences the studied compositions were significantly more limited from the Al–Mo side than from the Al–Cu side.

Within this compositional range Al–Mo contains a great number of phases [3,4], of which only Al_5Mo and $Al_{12}Mo$ were revealed in the studied alloys. The maximal solubility of Cu in the Al_5Mo phase(s) was found to be ~3 at.%, while in $Al_{12}Mo$ it was below 1.0 at.%. The solubility of Mo in all Al–Cu phases observed in the studied samples was found to be below 0.5 at.%.

Our study confirmed the formation of the two ternary phases. One has the above-mentioned Al_3Ti-type structure (designated

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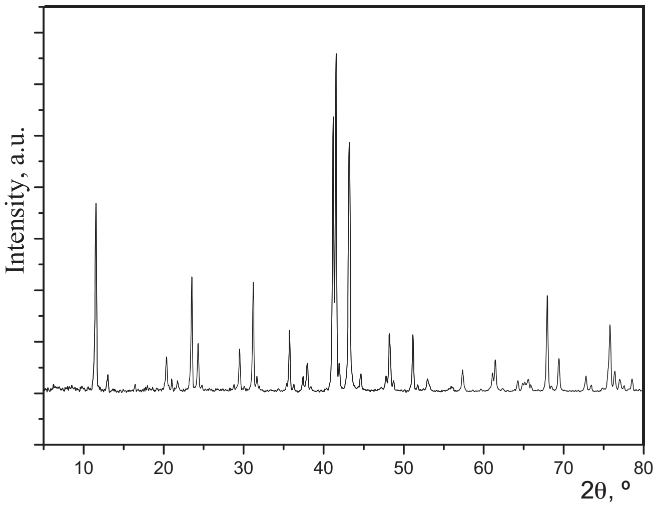

Fig. 1. Powder XRD pattern of the X-phase (Cu $K_{\alpha1}$ radiation).

Table 1
Diffraction data of the X-phase of Al_7Cu_2Mo (hexagonal, $a = 0.86798(8)$, $c = 1.51948(12)$ nm, the reflections with intensities below 4% are not presented).

No.	*h*	*k*	*l*	I/I_0	d_{obs}	d_{calc}
1	0	0	2	56	0.76130	0.75974
2	1	0	1	5	0.67529	0.67375
3	1	1	0	10	0.43418	0.43399
4	1	0	3	4	0.42086	0.42004
5	1	1	2	34	0.37679	0.37684
6	2	0	1	14	0.36476	0.36485
7	2	0	3	13	0.30185	0.30182
8	1	1	4	32	0.28579	0.28584
9	1	0	5	4	0.28166	0.28174
10	3	0	0	18	0.25056	0.25056
11	1	0	6	4	0.23967	0.23999
12	2	0	5	8	0.23638	0.23631
13	1	1	6	82	0.21863	0.21873
14	0	0	7	100	0.21685	0.21707
	2	2	0			0.21699
15	2	2	1	8	0.21487	0.21481
16	2	2	2	75	0.20888	0.20865
17	0	0	8	5	0.18983	0.18994
18	2	2	4	17	0.18824	0.18842
19	3	0	6	17	0.17817	0.17812
20	2	1	7	4	0.17246	0.17249
	3	2	0			0.17245
21	4	1	2	6	0.16031	0.16034
22	3	0	8	5	0.15133	0.15136
23	4	1	4	9	0.15056	0.15059
24	3	3	0	3	0.14466	0.14466
25	4	1	6	29	0.13770	0.13768
26	3	3	4	10	0.13517	0.13519
27	2	0	11	5	0.12970	0.12966
28	6	0	0	20	0.12529	0.12528
29	2	2	10	6	0.12448	0.12447
30	6	0	2	4	0.12362	0.12361
	5	0	7			0.12359
31	6	0	3	4	0.12158	0.12162
	1	1	12			0.12156
32	5	2	2	5	0.11887	0.11888
	4	2	7			0.11886
33	5	2	4	4	0.11473	0.11474
34	3	0	12	6	0.11303	0.11301
35	5	2	6	12	0.10870	0.10871
	4	2	9			0.10870
36	0	0	14	8	0.10853	0.10853
	6	0	7			0.10851
37	1	0	14	5	0.10740	0.10742
	4	4	2			0.10741
38	7	1	6	6	0.09265	0.09266
39	6	3	4	4	0.09189	0.09189

in following N-phase). It was found to be formed around the $Al_{68.5}Cu_{6.5}Mo_{25}$ composition, i.e. containing almost two times less Cu than is reported in Ref. [1]. However, this composition also fits the formula $(Al,Cu)_3Mo$ well. The lattice parameters $a = 0.37320(3)$ and $c = 0.84411(5)$ nm obtained in our work are close to those in Ref. [1]. The melting of the N-phase was not observed by DTA up to 1400 °C.

On the other hand, a phase with a composition close to Al_7Cu_2Mo exhibited a powder diffraction pattern (Fig. 1) which could not be indexed according to the orthorhombic structure with the lattice parameters reported in Ref. [1]. This phase designated X was found to be formed in a small compositional region around $\sim Al_7Cu_2Mo$, in agreement with Ref. [1]. The onset of its incongruent melting was observed by DTA at 803 °C.

Electron diffraction examinations of the X-phase revealed a hexagonal structure with the lattice parameters $a = 0.87$ and $c = 1.52$ nm (see Fig. 2). Using this information the powder XRD pattern of the X-phase was indexed (see Table 1, in total 60 reflections were observed in the range of 10–125°, average $\Delta(2\theta) = 0.016$, maximum $\Delta(2\theta) = 0.052$, figure of merit $F(30) = 15.7$). The lattice parameters refined from the powder XRD were $a = 0.86796(8)$ and $c = 1.51948(12)$ nm.

Annealing experiments were carried out at 810, 700 and 585 °C, and the results are presented in the isothermal sections in Fig. 3a–c. The upper annealing temperature is above the melting point of X (803 °C) and $Al_{12}Mo$ (712 °C [4]), but below that of h-Al_5Mo (846 °C [4]). At 700 °C the ternary X-phase is in equilibrium with the liquid, N, h-Al_5Mo and Al-Cu ε_2. The $Al_{12}Mo$ phase dissolving only a little of the Cu was not observed at ternary compositions. The lower applied temperature of 585 °C is just below the melting temperature of the Al_2Cu phase (θ-phase) but above the eutectic temperature in Al–Cu.

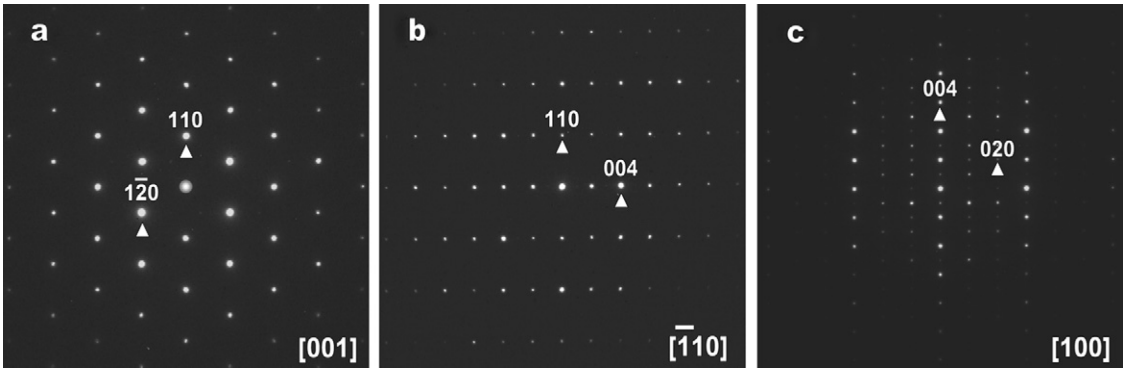

Fig. 2. Electron diffraction patterns of the X-phase: (a) Z.A = [0 0 1], (b) Z.A = $[\bar{1}\,1\,0]$ and (c) Z.A = [1 0 0].

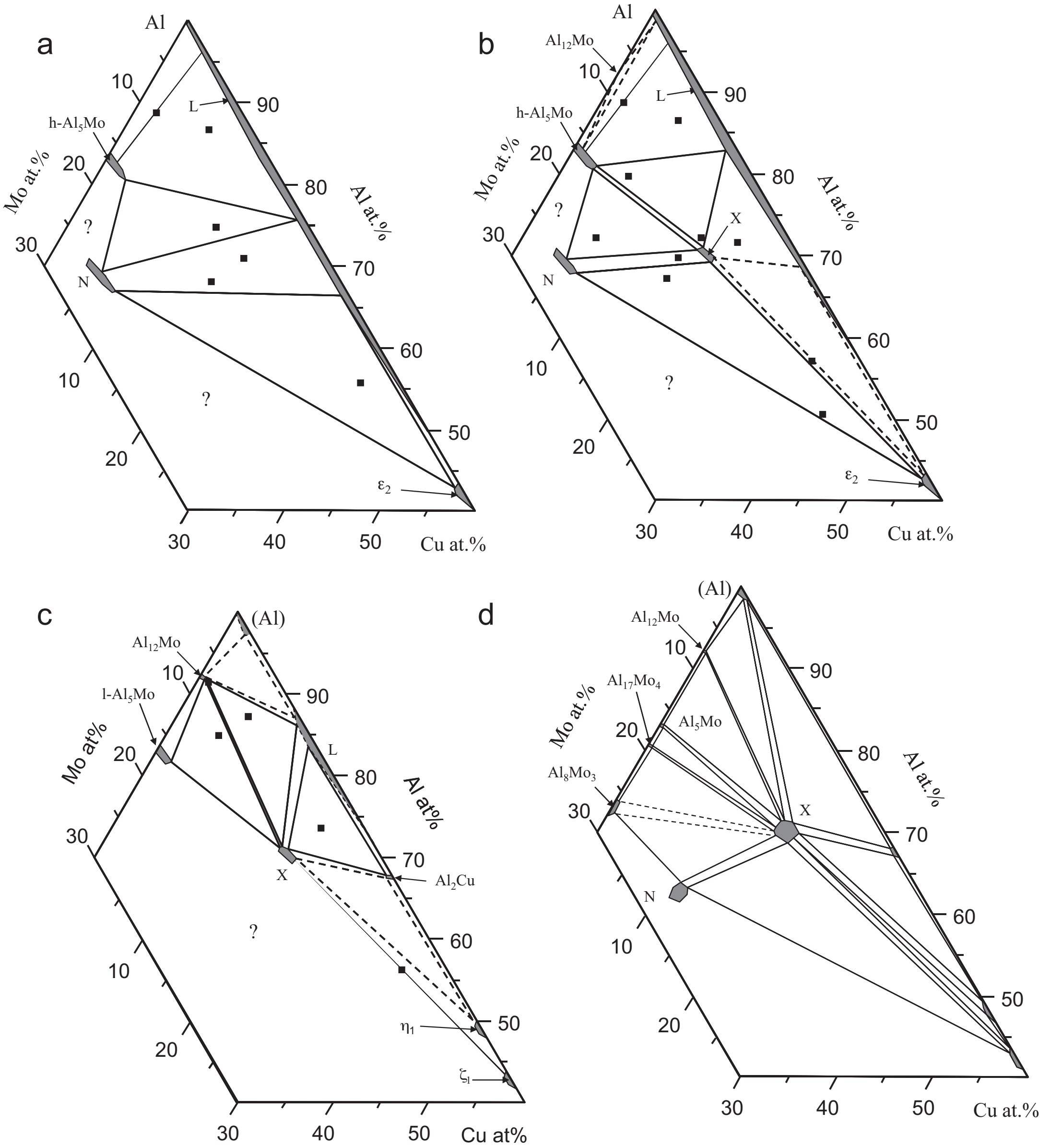

Fig. 3. Partial isothermal sections of the Al–Cu–Mo phase diagram: (a) at 810 °C, (b) at 700 °C, (c) at 585 °C and (d) redrawn from Ref. [1] with corrections made in Ref. [2]. Provisional lines are shown by broken lines. The alloy compositions are marked by squares. *L* is the liquid. The ranges where the equilibria were not clarified are marked by (?).

Our work revealed several items different from those presented in Ref. [1]. A direct comparison of the isothermal sections in the two contributions is not obvious due to differences in the applied temperatures. Actually, it is not very clear which temperature should be associated with the section in Ref. [1]. Indeed, apart from the above-mentioned inconsistency of that diagram with the Al–Cu phase diagram, revealed in Ref. [2], one more discrepancy was ignored there. The (Al) and Al_2Cu phases are in equilibrium in the binary system below 548 °C [5], i.e. below the temperatures given in Ref. [2]. On the other hand, at 548 °C and below, the high-temperature $AlCu_3$ phase does not exist. Concerning the equilibria of the X-phase with the Al–Mo phases, it is unclear what phases were really observed in Ref. [1]: the updated Al–Mo phase diagram is quite different from that known then. The equilibrium between the N-phase and Al_5Mo revealed in our work at 810 and 700 °C does not allow the X-phase to be in equilibrium with Al_8Mo_3 (shown provisionally in Ref. [1]) or $Al_{17}Mo_4$ (see Fig. 3d). At lower temperatures this item was not studied in our work due to difficulties with the equilibration of the relevant alloys.

The constitution of the studied compositional region of Al–Cu–Mo shows some similarity to that of the corresponding region of the Al–Ni–Mo alloy system [6]. The N-phase of the Al_3Ti-type structure was also observed in the latter. Its composition lies along about 25 at.% Mo between 1.6 and 6.0 at.% Ni. The second ternary phase is formed around $Al_{75.1}Ni_{14.2}Mo_{10.7}$ [6], i.e. its composition is quite close to that of the Al–Cu–Mo X-phase, but it has a different structure, namely orthorhombic with $a = 1.0054$, $b = 1.5288$ and $c = 0.8519$ nm [6]. It is worth noting that such an orthorhombic structure is also formed in Al–Ni–Re at quite a close composition [7], while the $Al_{65}Cu_{25}Re_{10}$ phase has a hexagonal structure ($P6_3$, $a = 1.1029$, $c = 1.2764$ nm [8]), different from that in Al–Cu–Mo.

4. Conclusions

The Al-rich region of Al–Cu–Mo was studied by SEM, powder XRD and electron diffraction. The maximal solubility of Cu in the Al_5Mo phases was found to be ~3 at.%. The previously reported

Al_3Ti-type phase ($I4/mmm$, $a = 0.37320(3)$ and $c = 0.84411(5)$ nm) was found to be formed around the $Al_{68.5}Cu_{6.5}Mo_{25}$ composition. The other ternary phase forming in a small compositional range around Al_7Cu_2Mo has a hexagonal structure with $a = 0.86796(8)$ and $c = 1.51948(12)$ nm. Partial isothermal sections at 810, 700 and 585 °C were determined.

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