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Identification of a new hexagonal phase in the Al–Cu–Re system

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ABSTRACT

Particles of an unknown intermetallic phase with the approximate composition $Al_{65}Cu_{25}Re_{10}$ were observed in a ternary Al–Cu–Re alloy. The structure of this phase was investigated in a transmission electron microscope using the precession electron diffraction (PED) technique. This phase has a hexagonal unit cell with lattice parameters $a = 11.029(6)$ and $c = 12.746(1)$ Å; its crystal symmetry can be described by the $P6_3$ (173) space group.

1. Introduction

An investigation of the Al–Cu–Re phase diagram, which had been carried out at 600 °C in the whole compositional range in [1], revealed the existence of five ternary phases. In the Al-rich corner of the Al–Cu–Re phase diagram the Al_8CuRe and Al_7Cu_2Re ternary phases were reported. The crystal structure of the former phase was characterized by a monoclinic unit cell with lattice parameters $a = 5.12$, $b = 8.75$, $c = 17.44$ Å and $\beta = 90.3°$. The crystal structure of Al_7Cu_2Re was not reported. In our recent investigation of the Al-rich part of the Al–Cu–Re phase diagram (to be published) we have revealed only one ternary phase forming at the same temperature of 600 °C in the relevant compositional range. It was not associated with the above-mentioned monoclinic structure reported in [1].

In the present work we report our results on structural characterization of a new ternary aluminide observed in Al-rich corner of the Al–Cu–Re system. First, we address the characterization of the unit cell parameters and the symmetry of a new compound, before undertaking a study for full structure solution. The main techniques used in this work are powder X-ray diffraction (XRD) and transmission electron microscopy (TEM), in particular newly developed precession electron diffraction (PED) method.

2. Materials and methods

The alloys 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 99.98% and of Re 99.95%. The ingot weights were typically ~5 g. Since Re dissolved only slowly in the alloys, they were re-melted several times in order to improve homogeneity. Parts of the ingots were annealed at 600–650 °C for up to 307 h. The materials were examined by 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. Selected samples were examined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the corresponding compositions were used for verification of the EDX analyses.

Samples for XRD experiments were prepared from the crushed material by a standard technique, and powder XRD pattern was recorded on a Rigaku D/MAX-2000 diffractometer equipped with a graphite monochromator for Cu Kα radiation. The measurements were performed within 2θ range from 5° to 85° at 2θ-step size of 0.02° with a rate 10 s/step.

Transmission electron microscopy and precession electron diffraction experiments were carried out on a 200 kV JEOL FasTEM-2010 electron microscope equipped with an energy-dispersive X-ray spectrometer (NORAN) and Spinning Star Precessing Unit (Nanomegas). Precession Electron Diffraction Patterns were taken with nearly parallel beam and the degree of precession was in the range of 18.5–46.6 mrad. Images and diffraction patterns were recorded by a Gatan slow-scan digital camera. TEM study was preformed on powdered materials dispersed on Cu grids with amorphous carbon film.

3. Results and discussion

After preliminary experiments a sample of the nominal composition $Al_{65}Cu_{25}Re_{10}$ was selected for further examinations. After annealing it was found to contain a major ternary phase and some fraction of $CuAl_2$ forming from the residual liquid. The composition of the ternary phase, as determined by EDX in SEM, was very close

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to the nominal composition of the studied alloy. DTA examination indicated its melting at 740 °C. The powder XRD pattern taken from the sample is shown in Fig. 1.

In order to determine the unit cell geometry, a series of conventional selected area electron diffraction patterns (SAD) at different orientations were recorded from the same area of particles of a new ternary phase. Then two diffraction zones of highest symmetry, shown in Fig. 2a and b, were selected and indexed on the basis of hexagonal unit cell with lattice parameters $a = 11.00$ and $c = 12.75$ Å (within an accuracy of ±0.04 Å). The zone axes of these patterns were $[0001]$ and $[2\bar{1}\bar{1}0]$, respectively. In terms of this unit cell a successful indexing of all observed diffraction zones was performed thus indicating that the dimensions of the unit cell are correct. Fig. 3a and b show, as an example, two indexed SAD patterns corresponding to $[01\bar{1}\bar{2}]$ and $[\bar{2}113]$ zone axes, respectively. Electron diffraction pattern taken at $[2\bar{1}\bar{1}0]$ orientation exhibits some extra reflections (indicated in the inset in Fig. 2b as ER). These reflections are forbidden and they disappear while tilting the specimen around the reflections row containing them (they also disappear at larger precession angles because the double diffraction paths to them are no longer available).

The next step in the structural characterization of the new phase was the determination of the space group. The methodology used

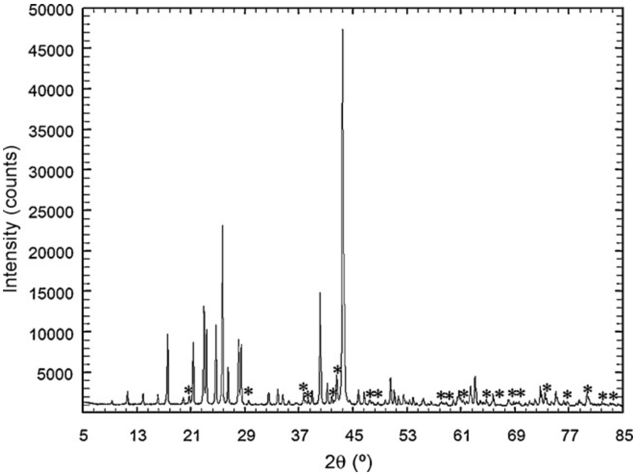

Fig. 1. Powder X-ray diffractogram taken from the investigated Al–Cu–Re alloy. Positions of peaks related to the binary $CuAl_2$ phase are marked by asterisks; other peaks correspond to the new ternary Al–Cu–Re phase.

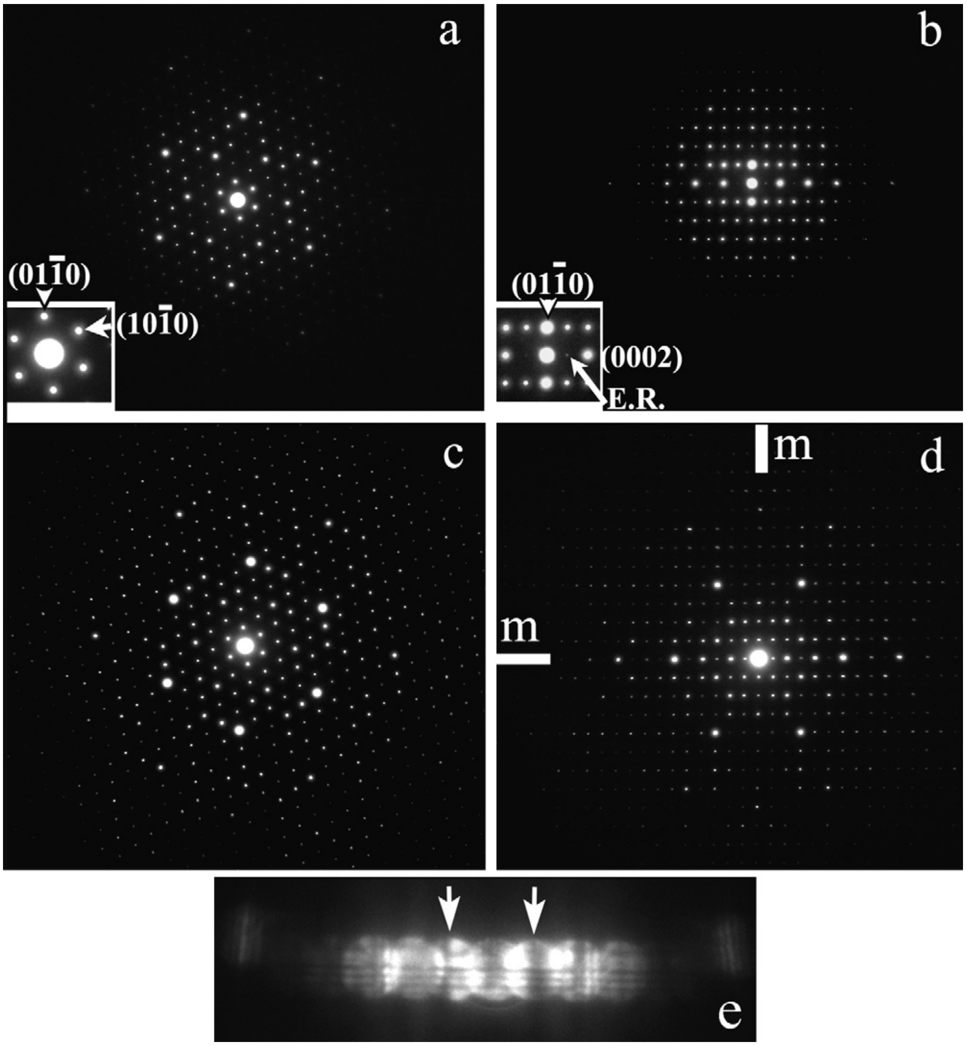

Fig. 2. The most symmetrical electron diffraction patterns taken from the particles of the new phase. (a) SAD pattern taken along $[0001]$ orientation (schematic indexed pattern is shown in the inset); (b) SAD pattern taken along $[2\bar{1}\bar{1}0]$ orientation (schematic indexed pattern is shown in the inset, ER denote extra reflection appearing due to double diffraction phenomenon); (c and d) PED patterns of the $[0001]$ and $[2\bar{1}\bar{1}0]$ ZA, respectively. Precession patterns received with precession angle of 2° (34.9 mrad); (e) CBED pattern with (0002) and $(000\bar{2})$ diffraction disks marked by arrows.

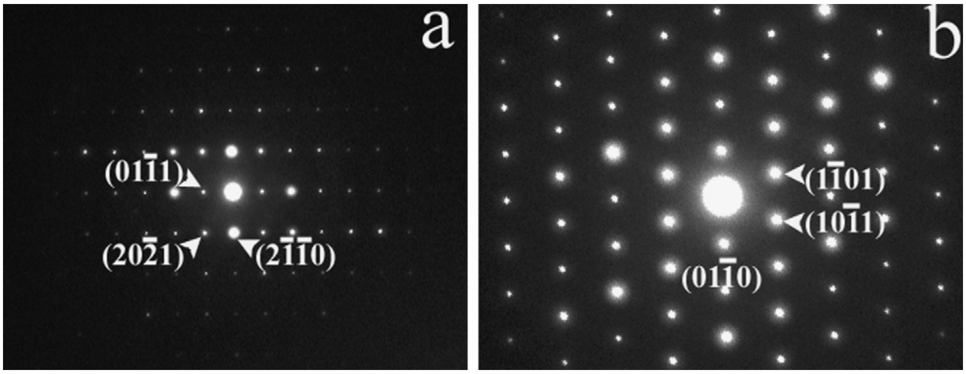

Fig. 3. SAD patterns taken from the particles of the new phase at (a) $[01\bar{1}\bar{2}]$ and (b) $[\bar{2}113]$ orientations.

was based on the analysis of symmetry of the electron diffraction patterns [2,3]. As seen on SAD pattern shown in Fig. 2a, symmetry of [0001] pattern can be evaluated as *6mm* or *6*, and it was difficult to distinguish between these two possibilities due to dynamical nature of the intensities. Determination of symmetry of other diffraction patterns also met same difficulties: all <uv.w> patterns exhibited either *2* or *2mm* symmetry (see Fig. 3a and b) and it was almost impossible to determine unambiguously the correct symmetry of these patterns and, as a consequence, to deduce the correct symmetry associated with the new Al–Cu–Re phase.

Thus, in order to proceed with this task, precise (more kinematic) intensity distribution of the reflections on the electron diffraction patterns was needed. The technique that was chosen for this purpose was PED [4]. PED patterns have three main features: (1) the number of reflections present on these patterns is much larger than the number of those present on a conventional pattern [3–5]; (2) the intensities of the diffracted beams are integrated intensities and are closer to the kinematical intensities [3–6]; and (3) due to the precession of the beam the dynamical interactions are substantially reduced [6]. PED patterns taken from the new phase at [0001] and $[2\bar{1}\bar{1}0]$ orientations are shown in Fig. 2c and d, respectively.

As it follows from the original work of Buxton et al. [7] among the possible point groups, corresponding to the hexagonal system, only two point groups *6/m* or *6* can be associated with *6* symmetry that was observed in the diffraction pattern taken along the [0001] zone axis (see Table 1. These two point groups differ in the centrosymmetry: *6/m* point group is centrosymmetric while *6* point group is non-centrosymmetric. In order to decide which of them, *6/m* or *6*, is correct, it was useful to perform the experiment with convergent beam electron diffraction (CBED) containing (0002) and $(000\bar{2})$ reflections. It is known that in the case of non-centrosymmetrical point group, differences in intensity distribution within (0002) and $(000\bar{2})$ diffraction disks should be observed [8,9]. These differences are due to strong coherent multiple scattering affecting the intensities of the reflections in the CBED patterns. Fig. 2e shows CBED pattern taken from the particle of the new phase so that both (0002) and $(000\bar{2})$ diffraction disks are observed. The asymmetry between these two disks is clearly seen, thus leading to a conclusion that the correct symmetry of the $[2\bar{1}\bar{1}0]$ pattern is *m* and the point group associated with the new structure is *6*. Bearing in mind that systematic absence of the $(000l)$ reflections with $l = 2n + 1$ in the $[2\bar{1}\bar{1}0]$ pattern takes place, it becomes evident that $P6_3$ (number 173) is the only space group that can describe the symmetry of the unit cell of this new ternary phase.

Using the electron diffraction data, powder XRD pattern, taken from the alloy, was successfully indexed. The list of observed and calculated interplanar distances is presented in Table 2. Using the data in Table 2 the lattice parameters were refined by the least-

Table 1
Determination of the point group following the methodology described in [2,3,7]. Possible ideal symmetries of electron diffraction patterns corresponding to hexagonal crystal system. (ZOLZ – Zero Order Laue Zone and HOLZ – High Order Laue Zone.).

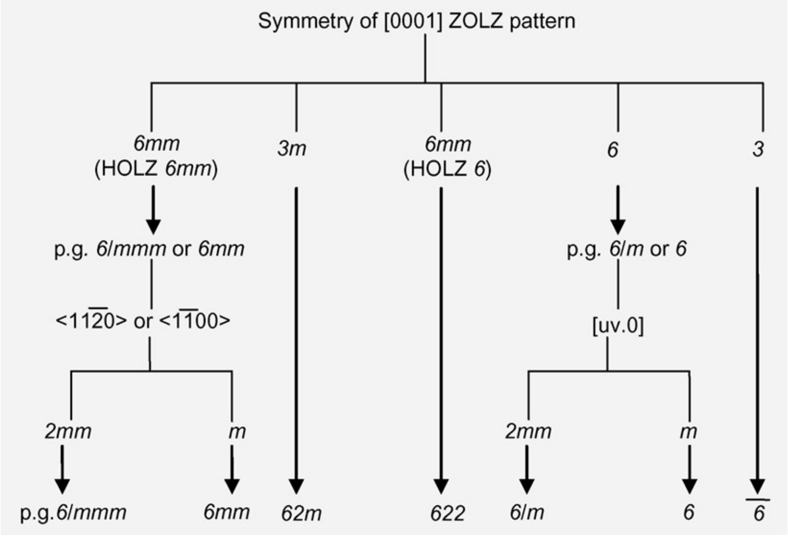

Table 2
List of 25 first most intense peaks corresponding to the new phase as obtained from powder X-ray diffractogram for the $Al_{65}Cu_{25}Re_{10}$ phase (space group $P6_3$, $a = 11.029(6)$ and $c = 12.746(1)$ Å, $V = 1342.7$ Å^3).

No.	(*h k l*)	d_{obs} (Å)	d_{calc} (Å)	$2\theta_{obs}$ (°)	Rel. Int. (%)
1	0 1 1	7.644	7.643	11.567	9.79
2	0 0 2	6.373	6.373	13.884	8.09
3	1 1 0	5.515	5.515	16.058	6.90
4	1 1 1	5.061	5.061	17.508	51.08
5	0 2 1	4.472	4.472	19.835	5.01
6	1 1 2	4.170	4.170	21.288	44.91
7	0 1 3	3.882	3.882	22.890	70.08
8	0 2 2	3.822	3.822	23.255	51.80
9	1 2 0	3.610	3.610	24.638	28.10
10	1 2 1	3.474	3.473	25.624	64.74
11	1 1 3	3.366	3.366	26.46	27.39
12	0 0 4	3.187	3.187	27.977	13.40
13	0 3 0	3.184	3.184	28.000	35.64
14	1 2 2	3.141	3.141	28.389	21.35
15	0 2 4	2.651	2.651	33.787	6.71
16	1 1 5	2.314	2.314	38.888	12.30
17	0 2 5	2.249	2.249	40.060	28.46
18	3 1 3	2.248	2.248	40.077	33.04
19	3 2 0	2.191	2.191	41.159	9.77
20	0 0 6	2.124	2.124	42.519	31.23
21	2 2 4	2.085	2.085	43.360	19.56
22	4 1 0	2.084	2.084	43.375	100.00
23	2 1 5	2.082	2.082	43.418	44.88
24	0 4 3	2.082	2.082	43.434	48.63
25	0 1 6	2.074	2.074	43.611	52.71

square fitting procedure and more precise unit cell dimensions were received: $a = 11.029(6)$ and $c = 12.746(1)$ Å.

4. Conclusions

A new intermetallic phase has been identified in the Al–Cu–Re ternary system. The composition of this phase was specified as Al–25 at.%Cu–10 at.%Re. This phase has a hexagonal unit cell with lattice parameters $a = 11.029(6)$ and $c = 12.746(1)$ Å; its crystal symmetry can be described by the $P6_3$ space group. Development of the complete structural model and the determination of the atomic positions in the structural building unit are now in progress.

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