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Al-Co-Cu-Si and Al-Co-Cu microcrystalline and quasicrystalline phases of decagonal symmetry

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Résumé. — D'après une étude en HREM et diffraction électronique et de précédents résultats de diffraction des rayons X sur monocristal, nous confirmons qu'à température ambiante, l'état de l'alliage décagonal $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ n'est pas quasicristallin mais microcristallin. Les résultats HREM sont comparés à ceux obtenus sur l'alliage $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$. De plus, pour la première fois, une transition de phase à haute température, vers un état quasicristallin est révélée dans les deux composés.

Abstract. — On the basis of HREM and electron diffraction studies and of previous X-ray single crystal diffraction results, we confirm the existence on a non-quasicrystalline microcrystalline state for the decagonal $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ alloy at room temperature. The HREM results are compared to those obtained for the $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ alloy. Moreover for the first time, a high temperature phase transition towards a quasicrystalline state is revealed in the two compounds.

1. Introduction.

Recently, Al-Co-Cu and Al-Co-Cu-Si systems have been reported to be stable decagonal quasicrystals with decaprismatic solidification morphology [1]; the effect of Si is to improve both the crystal size and the prismatic morphology. From high resolution electron microscopy (HREM) [2], electron diffraction [1,3], tunneling microscopy [4] and X-ray single crystal diffraction analyses [5], it has been pointed out that such materials exhibit a decagonal quasicrystalline structure, which can be inconsistent with the conventional Penrose tiling [2].

We have reproduced the crystal growth of decaprismatic cylinders of a few 100μ length from an alloy of nominal composition $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ and crystals of much more smaller size from an $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ alloy. The $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ crystal size has allowed us to carry out a study using conjointly X-ray single crystal diffraction and HREM: the two complementary techniques show that the sample is not in a 2D quasicrystalline state but in a microcrystalline state (with very large unit cells) which restores the overall tenfold symmetry in diffraction patterns, being formed of coherent crystalline domains having orientational relationships (rotations of 36° or 72°) [6].

In this paper: first, previous X-ray diffraction and HREM results are recalled and the corresponding electron diffraction pattern is shown and discussed; second, the Al-Co-Cu-Si HREM results are compared to the Al-Co-Cu ones; and third, for the first time, we exhibit the phase transition between microcrystalline and quasicrystalline states.

2. Comparison of HREM, X-ray and electron diffraction results for the Al-Co-Cu-Si compound.

2.1 HREM AND X-RAY RESULTS. — By X-ray diffraction, the sample is found to be periodic in the direction of the cylinder long axis ($c \sim 4.2 \text{ \AA}$), and the $l = 0$ plane perpendicular to the c^* axis presents tenfold symmetry (cf. Fig. 1 in Ref. [6]).

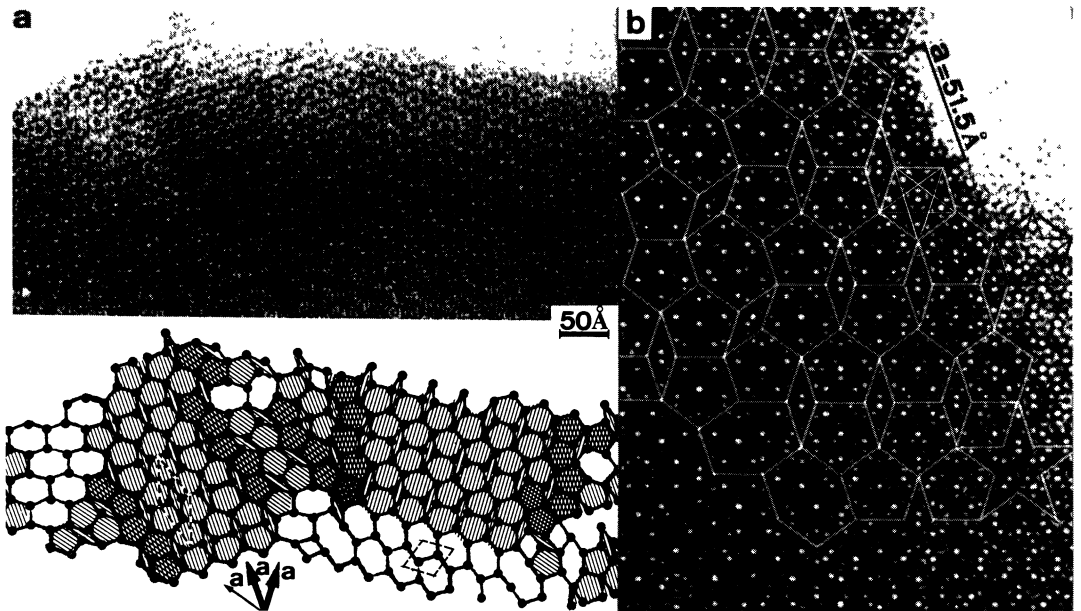


Fig. 1. — HREM micrographs of the Al-Co-Cu-Si phase, observed following its pseudo 10-fold zone axis; a) structural arrangement exhibiting two types of rhomb cell outlined by dotted lines on the drawing and corresponding to cell parameters, $a = 51.5 \text{ \AA}$, $\alpha = 36^\circ$ and $a = 51.5/r \text{ \AA}$, $\alpha = 72^\circ$; b) higher magnified image showing details of the previous structural arrangement: wheels of ten white dots situated at vertices of pentagons and thin rhombs (the distance of 51.5 \AA , indicated on this micrograph, corresponds the edge length of the rhomb cell of 36° angle).

HREM micrograph observed following the c axis is shown in figure 1. The figure 1a, borrowed to reference 6, displays an arrangement of pentagons and rhombs with a 36° angle, from which a

large "36°" rhomb with edge $a = 51.5 \text{ \AA}$ can be deduced. At higher magnification, the micrograph of figure 1b shows wheels of ten white dots whose centers are in fact at pentagon and small rhomb vertices; a 5-fold symmetry is observed inside pentagons. The large rhombs form periodic domains (Fig. 1a). Orthogonal 2-fold symmetries of the structural arrangement (Fig. 1b) indicates that the 2D-space group must be related to rectangular Bravais lattice of cell parameters $a_1 = 2a \cos 18^\circ = 98 \text{ \AA}$ and $b_1 = a_1 \tan 18^\circ = 32 \text{ \AA}$.

Moreover, the periodic domains have orientational relationship: they are turned by 36° (Fig. 1a) which explains the 10-fold symmetry observed on diffraction patterns. Indeed, all X-ray diffraction peaks measured in the $l = 0$ plane are fitted by superimposing the reciprocal lattices of the ten rotated twins formed of rhombs with edge length $r = 51.58 \pm 0.5 \text{ \AA}$ and with a 36° angle [6].

Another periodic arrangement is also seen on the HREM micrograph (Fig. 1a). It is characteristic of a rhomb cell with a 72° angle, but with edge length 31.8 \AA : τ times smaller than the 36° rhomb edge ($\tau = (1 + \sqrt{5})/2$). Here again, crystalline domains have orientational relationships: they are turned by 72° . Taking into account the inversion symmetry in the reciprocal space, it explains tenfold symmetry in the diffraction pattern. These 72° domains allow the indexing of almost all the diffraction peaks [6].

We have also pointed out that all X-ray diffraction peaks can be fitted by 72° domains but formed of rhombs with the same edge length 51.58 \AA than the 36° ones [6]. The existence of such a rhomb has not yet been proved, and we shall illustrate its "fitting" on an electron diffraction pattern.

3. Electron diffraction data.

The figure 2a shows an example of electron diffraction pattern with tenfold symmetry. The tenfold symmetry is not perfect: a few peaks are not always found after a rotation by 36° , contrary to what is found by X-ray diffraction. This can be due to the fact that a much smaller volume is diffracting, where the rotated domains are possibly present in the different proportions. Although the electron diffraction pattern is not yet corrected from multiple diffraction effects [7], we illustrate the fitting of diffraction data by 72° rhombs of edge length $a = 51.5 \text{ \AA}$ in figure 2b; it represents an enlarged part of figure 2a and the reciprocal lattices of the periodic domains rotated by $n \times 72^\circ$ (n integer). Note that many peak positions are fitted but intensity conditions when rotating the domains have also to be taken into account and leads us to reject some of them.

4. Comparison between Al-Co-Cu-Si and Al-Co-Cu compounds.

The electron diffraction pattern of the Al-Co-Cu sample presents tenfold symmetry like that of the Al-Co-Cu-Si sample (Fig. 2). But HREM results are somewhat different. The figure 3 shows an HREM micrograph of the Al-Co-Cu-Si sample, where the large 36° rhombs correspond to the white line drawings. Moreover, much larger domains than the 36° rhomb ones and exhibiting only one periodicity are found. In the figure 3, such a periodicity extends to all the image: it can be seen in the direction of the arrows. To visualize more clearly these larger domains, we have marked some centers of ten white dot wheels with black points, such that a periodic lattice (possibly with no true existence) is respected. For the Al-Co-Cu sample, domains of the 36° rhomb cell nearly not exist but domains with one periodicity are clearly defined.

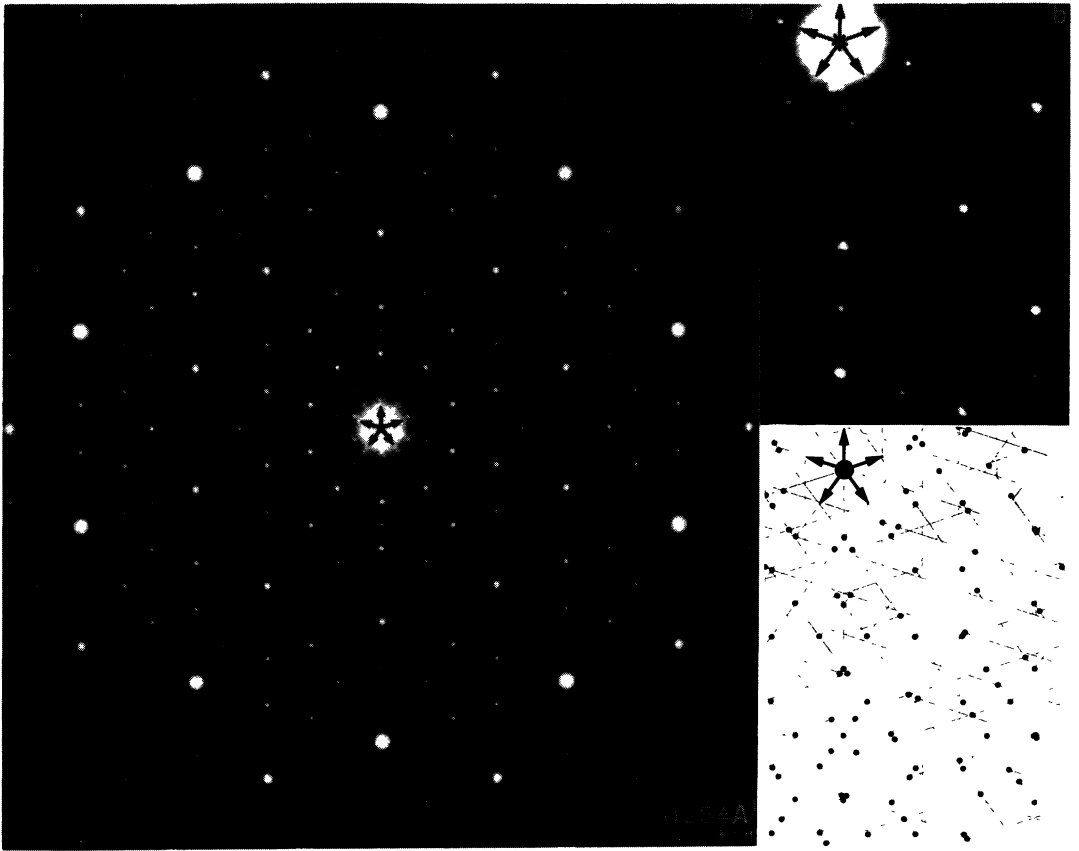


Fig. 2. — a) electron diffraction pattern of pseudo 10-fold zone axis, observed on an Al-Co-Cu-Si sample, b) comparison of observed and calculated reflections (see text).

5. Phase transitions.

Preliminary *in situ* heating experiments on an $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ sample show that the “crystalline” state transforms into quasicrystal. Both micrographs of the figure 4a and b give an example of the structural change observed before and after an electron beam irradiation heating and where it can be noticed that structural arrangements of 10-fold symmetry have formed in the quasicrystalline state. Similar features are also observed on a heat treated $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ sample (Fig. 4c).

Although no thermodynamic characterization of these phase transformations have yet been performed, the HREM results give strong arguments in favour of phase transformations.

6. Conclusion.

In summary, contrary to what has been found in $\text{Al}_{65}\text{Cu}_{20}\text{Co}_{15}$ [1-5], we have found that at room temperature the $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ alloy is in a non-quasicrystalline microcrystalline state, which restores the overall tenfold symmetry in diffraction patterns. We present also first results concerning the $\text{Al}_{63}\text{Cu}_{17.5}\text{Co}_{17.5}\text{Si}_2$ and $\text{Al}_{65}\text{Cu}_{17.5}\text{Co}_{17.5}$ alloys showing a transition towards a quasicrys-



Fig. 3. — HREM micrograph observed along a pseudo 10-fold zone axis of an Al-Co-Cu-Si phase. A periodicity can be seen at glance, in the direction of arrows (see text).

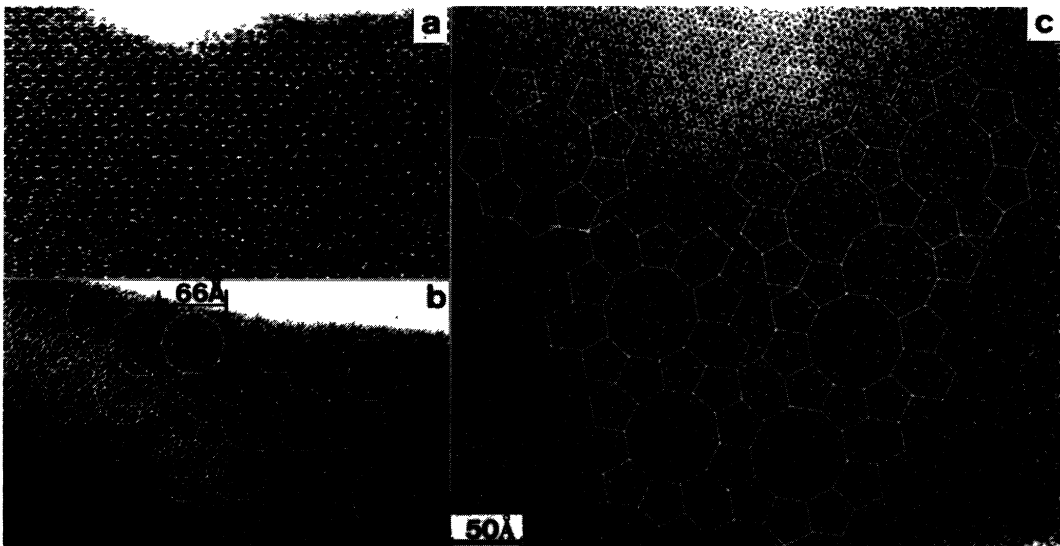


Fig. 4. — Phase transformation of the Al-Co-Cu alloy, a) before and b) after heating; c) quasicrystalline state observed in the Al-Co-Cu-Si alloy phase transformation (see text).

talline phase at high temperature. Further HREM and X-ray diffraction studies of this phase transition could allow to discriminate between deterministic packing or random tiling models for this high temperature phase, a question still opened for quasicrystalline structures.

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