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Metastable precipitation in the Al-Mg,Si,Cu system: an atomic STEM-EELS study

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Precipitation hardening is still an important and efficient way to improve the mechanical resistance of aluminium alloys. We focus here on the 6061 grade, namely with the composition Al - Mg 1 wt. % - Si 0.6 wt. % - Cu 0.25 wt. %. This system belongs to the so-called 6xxx series, based on the Al-Mg-Si system. It was previously shown [1,2] that a complex precipitation sequence occurs, which is greatly affected by the presence of any further addition of minor element(s), such as copper:

Low Cu quantity (i.e. 0,07 wt. %): o.s.s.s. □ zones GP □ □" □ [□' + Q'] □ [□ + Si]

High Cu quantity (0,9 wt. %): o.s.s.s. □ GP zones □ □ ' □ Q' □ [Q + Si]

o.s.s.s. mean over saturated solid solution; GP zones are aggregates of solute atoms, comparable to well-known Guinier-Preston zones – see for example original references cited in [3]). Labels □", □', Q', refer to metastable phases, whereas □ (Mg_2Si) Si and Q ($Al_xCu_2Mg_{12-x}Si_7$ [4]) refer to stable phases. Typically, at 573 K, the precipitation sequence can be summarized as [5]: □" → QP + QC → QC + Q' → Q' → □ where QP, QC are metastable phases closely-related to the □' in the Al-Mg-Si system [6]. Although a large number of (HR)TEM studies exist in the literature on this particular alloy (see the recent review [7]), their atomic structures are not accurately known. A major difficulty encountered is indeed that 'composite' particles frequently develop, the HRTEM contrast of which is perturbed by dynamical scattering, local misorientations and possible strain effects. In a recent study by means of STEM-HAADF imaging, a better structural description of some atomic arrangements could be obtained, thanks to Z-contrast images which are much less sensitive to the previous undesirable effects [8]. Starting from a model initially proposed by [6], we were able to refine atomic positions and suggest new atomic occupancies, as well as a different space group for the QC phase. But confirmation of these observations requires chemical analysis at the atomic level.

This is the purpose of the present work. We have carried out STEM-EELS (Electron Energy-Loss Spectroscopy) measurements at the atomic level, using a double Cs-corrected FEI-TITAN microscope recently installed at CEA-Grenoble, Minatec. To minimize as much as possible irradiation effects during 'column-by-column' analysis with a sub-Angström probe, we have performed these experiments at 80 kV. Results are illustrated by figures 1 and 2. In figure 1, we use the Q' phase as a 'standard' in order to ascertain the chemistry of expected Cu-columns, as deduced from the structure refined in the case of the stable phase (Q: $Al_xCu_2Mg_{12-x}Si_7$ [4]). In figure 2, EELS imaging reveals that the brighter dots resolved in the STEM-HAADF images are not those containing the higher content of Cu, but that they are Si-enriched. These experimental results, which would be probably impossible to obtain by another technique, will be used to refine the model of the QC phase [9].

1. W.F. Miao, D.E. Laughlin, *Metall. Mater. Trans. A*, 31A (2000) 361-371.
2. K. Matsuda, Y. Uetani, T. Sato, S. Ikeno, *Metall. Mater. Trans. A*, 32A (2001) 1293-1299.
3. O.B.M. Hardouin Duparc, *Metall. Mater. Trans. A*, 41A (2010) 1873-1882.
4. L. Arnberg, B. Aurivillius, *Acta Chem. Scand.*, A34, (1980), 1-5.
5. V. Massardier, T. Epicier, *Mat. Sci. Forum*, 396-402, (2002), 851-856.
6. C. Cayron, P.A. Buffat, *Acta mater.* 48, (2000), 2639-2653.
7. C.D. Marioara, S.J. Andersen, T.N. Stene, H. Hasting, J. Walmsley, A.T.J. Van Helvoort,
8. R. Holmestad, *Philos. Mag.*, 87, 23, (2007), 3385-341.
9. T. Epicier, C. Cayron, *Rev. Metall.* 109, (2012), 393-407.
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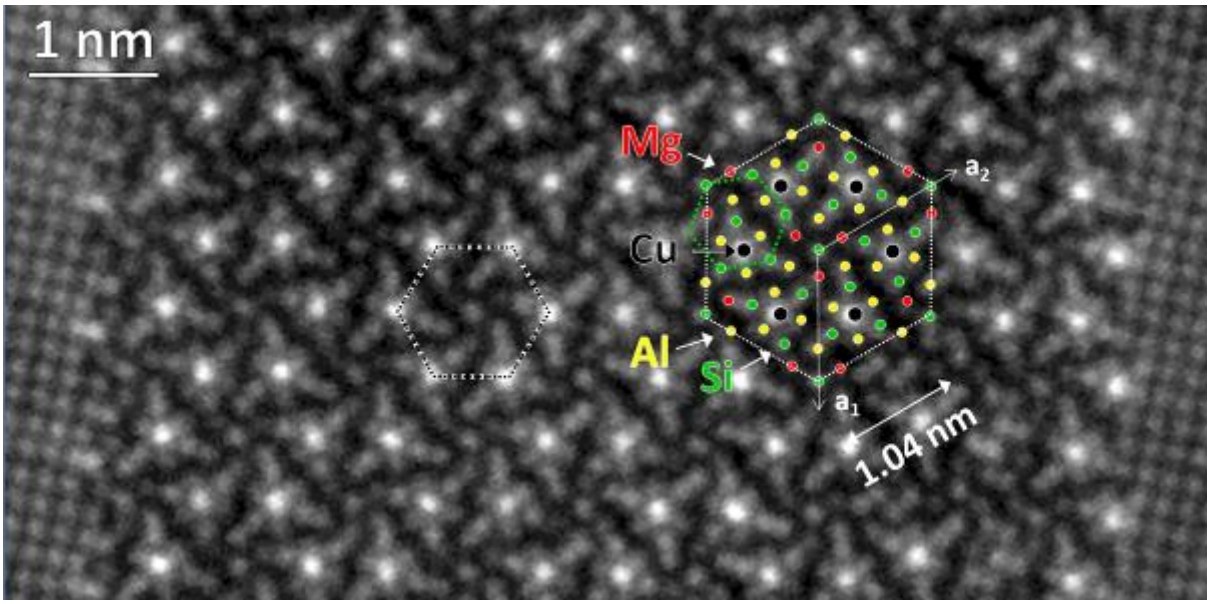

Figure 1. Atomic STEM image of a Q' precipitate, showing a one-to-one correspondence with the model of the stable Q hexagonal phase (P-6, with a = 1.04 nm, c ≈ 0.405 nm [4]); brighter dots image Cu sites.

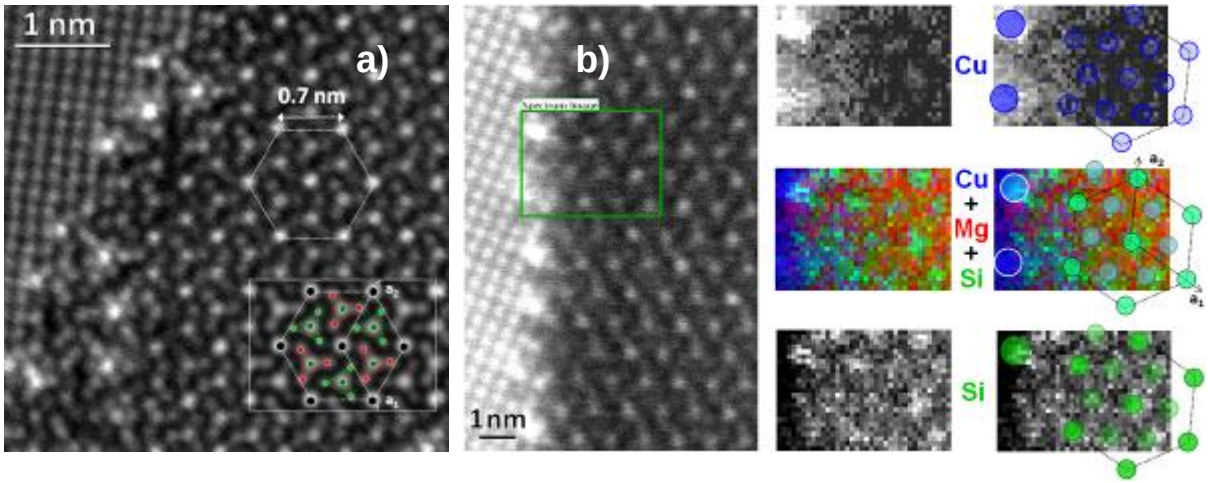

Figure 2. STEM-EELS analysis of the QC phase. a): STEM image and simulation corresponding to the refined model proposed in [8] (hexagonal P-6, a ≈ 0.7 nm, c = 0.405 nm): the hexagonal lattice at 0.7 nm is defined by brighter dots imaging mixed Cu-Si columns. b): STEM-EELS imaging of another QC precipitate showing the respective Cu, Si and composite Cu+Mg+Si *maps* (middle row). Both top and bottom maps show that the brighter dots (0.7 nm lattice) are Si-enriched and not Cu-enriched (note that Cu segregation at the precipitate-matric interface is clearly evidenced).