ELSEVIER

Materials Science and Engineering A234–236 (1997) 253–257

MATERIALS SCIENCE & ENGINEERING A

Evolution of precipitates in AlLiCu and AlLiCuSc alloys after age-hardening treatment

J. Dutkiewicz [a], O. Simmich [b], R. Scholz [c], R. Ciach [a,*]

[a] *Institute of Metallurgy and Materials Science of the Polish Academy of Sciences, 30-059 Kraków, Poland*
[b] *Martin-Luther University Halle-Wittemberg, Halle, Germany*
[c] *Max-Planck Institute of Microstructure Physics, Halle, Germany*

Received 29 January 1997; received in revised form 1 April 1997

Abstract

The structure of precipitates formed during ageing at 200°C of AlLiCu and AlLiCuSc alloys containing 2.5 wt.% Li, 2.0 wt.% Cu and 0.2 wt.% Sc was studied using conventional and high resolution electron microscopy (HREM). Both alloys show similar hardness maximum and the main hardening phases were identified as Θ' (Al_2Cu), T_1 (Al_2LiCu) and δ' (Al_3Li). The first one is formed in the shape of thin plates of thickness of a few atomic layers. The HREM allowed to identify the structure of plates, its crystallographic relationship with the matrix and nucleation of δ' phase at the edges of plates preserving their coherency with the matrix. The T_1 was identified in thicker areas of foils using electron diffraction method. The radius of δ' increases rapidly in the first stage of ageing, what corresponds to the increase of hardness, while the thickness of T_1 plates increases steadily during ageing. The following crystallographic relationship between the matrix and T_1 precipitates was observed: $[001]\alpha \| [\bar{1}2\bar{1}0]T_1$ and $(110)\alpha \| (10\bar{1}0)T_1$. © 1997 Elsevier Science S.A.

Keywords: AlLiCuSc alloys; Precipitation hardening; Atomic resolution electron microscopy

1. Introduction

The early stages of ageing of AlLi alloys cause formation of ordered δ' (Al_3Li) particles combined often with a modulated structure [1], which has been attributed to the spinodal decomposition mode. High resolution images [1] allowed to resolve ordered δ' precipitates already in the as quenched state what suggests the presence of spinodal ordering and decomposition. The alloying additions, like copper increase the strength of aged AlLi alloys [2,3] forming additionally plate like T_1 (Al_2LiCu) precipitates of hexagonal structure [3] in addition to the spherical δ'. The addition of scandium has been reported to improve the properties of most of age hardenable aluminium alloys including binary or multicomponent AlLi base alloys [4–6]. There are some contradictions regarding acceleration [4] or retardation [5] of the δ' precipitation, but in both papers [4,5] a two layer structure of the δ' precipitates on Al_3Sc spherical particles was observed. According to Berezina et al. [4] scandium improves hardness only in a two-step ageing (400°C followed by 200°C), while in the other papers [6] this effect is not mentioned. The aim of the present paper is to show the effect of scandium on the structure and evolution of precipitates in AlLiCu alloys aged at elevated temperatures applying HREM technique, particularly suitable to study the nucleation of precipitate complexes [7].

2. Experimental procedure

The alloys examined were cast in a special chamber under pure argon (under 1 ppm N_2). They were melted with nominal compositions: $Al_{2.5}Li_{2.0}Cu$ and $Al_{2.5}Li_{2.0}Cu_{0.2}Sc$, (all compositions in wt.%). The purity of the elements was: Al and Cu 4N, Sc and Li 3N. The alloys were homogenised in argon atmosphere at 550°C and quenched into RT water. The ageing was performed in silicon oil bath at 200°C. Hardness was measured using Vickers method at the 5 kg load. The

---

* Corresponding author. Tel: +48 12 374200; fax: +48 12 372192.

PII S0921-5093(97)00229-3

transmission electron microscopy (TEM) examinations were carried out using PHILIPS CM-20 transmission electron microscope operating at 200 kV or JEOL 4000E at 400 kV for the high resolution investigations. Thin foils for TEM observations were obtained by jet electropolishing in a solution of perchloric acid in methyl alcohol at temperatures below 0°C.

3. Results and discussion

The results of measurements of the hardness changes of AlLiCu and AlLiCuSc alloys during ageing at 200°C are shown in Fig. 1. The higher hardness maximum of 125 HV attains AlLiCu alloy contrary to the statements in [5,6] that scandium increases hardness during ageing of AlLiCu alloys. Fig. 2 shows a set of transmission electron micrograph taken just after quenching of AlLiCuSc alloy. In the bright field one can see large spherical Al_3Sc precipitates of size close to 50 nm with a strong strain field contrast. In the dark field image taken using 110 superlattice spot one can see very small bright spots of size of a few nanometers, similar to those observed in [1] due to $L1_2$ spinodal ordering of lithium rich precipitates. It means that additions of copper and scandium do not modify tendency of Al–Li alloys to form δ' precipitates in the as quenched state. Next micrograph (Fig. 3) taken after 4 h of ageing at 200°C shows a significant growth of $L1_2$ domains representing δ' precipitates up to 10 nm and Al_3Sc up to 100 nm. At the same time the strain field contrast of the latter precipitates becomes much weaker and their interface is well defined. This indicates a loss of coherency at scandium rich precipitates caused by lithium deposition on them, explaining lack of hardening effect due to scandium addition. Since it is not the case in other aluminium alloys [2] the loss of coherency is most probably due to δ' precipitation on the Al_3Sc particles causing their growth and break of coherency. Indeed, dark field micrographs taken using superlattice $L1_2$ show in some cases bright rings over the large Al_3Sc particles, reported also in earlier works on AlLiSc alloys [6] where no hardening after conventional quenching and ageing treatment was observed.

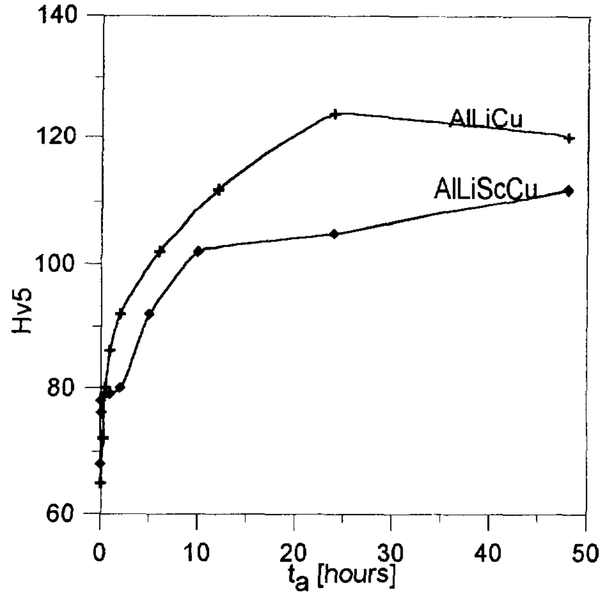

Fig. 1. Hardness vs. ageing time at 200°C of AlLiCu and AlLiCuSc alloys.

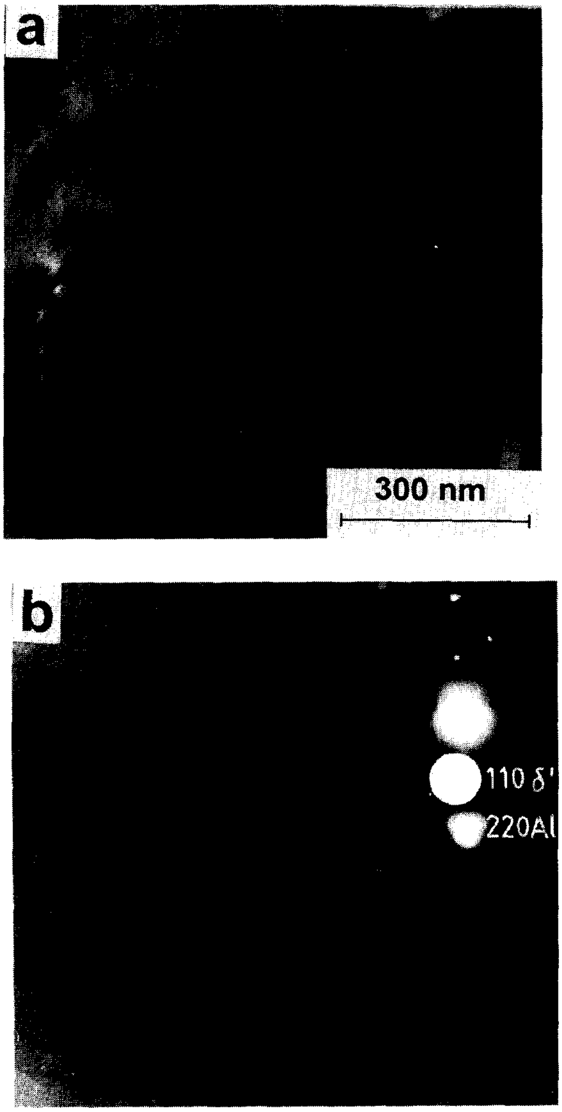

Fig. 2. The AlLiCuSc alloy in the as quenched state. (a) Transmission electron micrograph. (b) Dark field micrograph taken using 110 superlattice spot with the selected area diffration pattern (SADP) insert.

Next micrograph shows a bright field micrograph taken form AlLiCuSc after 24 h of ageing at 200°C. It shows spherical δ' and rings over Al_3Sc particles and plate like precipitates giving characteristic diffraction pattern (Fig. 4(b)) which indexing shows following crystallographic relationship between the matrix and T_1: $[001]\alpha \| [\bar{1}2\bar{1}0]T_1$ and $[100]\alpha \| [10\bar{1}0]T_1$, the same as observed in {8}.

High resolution electron microscopy of samples aged 24 h at 200°C allowed to identify the atomic structure of needles running in <100>Al direction at [001] and [110] zone axis orientation. Fig. 5 shows the atomic resolution micrograph taken from alloy AlLiCuSc at [001] zone axis orientation. The analysis of SADP (placed as an insert in Fig. 4) indicates that only Θ' reflections can be seen, what is in accord with the symmetry of bright points distribution representing columns of atoms within Θ' lattice at [010] zone axis orientation parallel to [001]Al. At the edges of Θ' precipitates the symmetry of atomic positions changes taking that of aluminium. It is most probably caused by lithium atoms attached to the Θ' precipitates forming δ' layer over Θ'. The bright atoms represent the same symmetry as aluminium and double space distance within this system can indicate only δ'. At several high

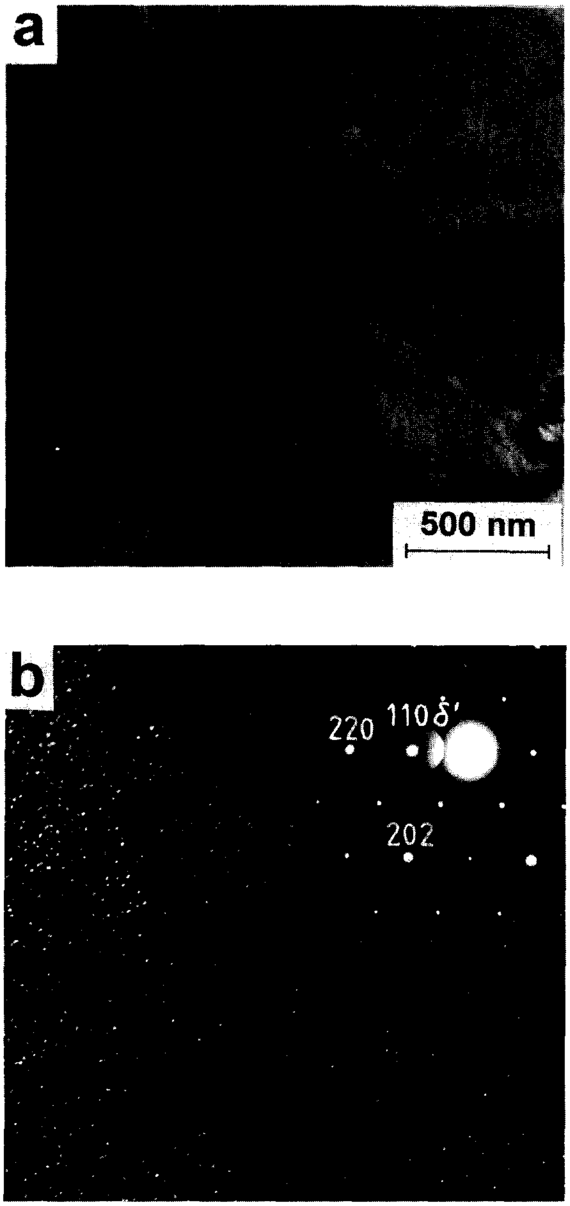

Fig. 3. The AlLiCuSc alloy after 4 h ageing at 200°C. (a) Transmission electron micrograph (b) Dark field micrograph taken using 110 δ' spot with SADP insert.

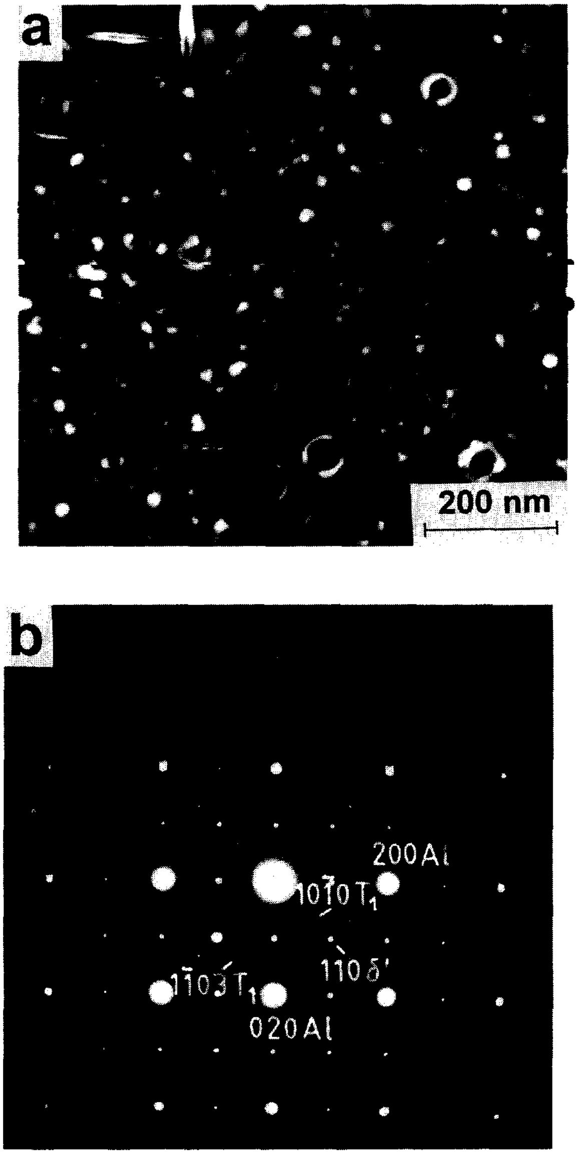

Fig. 4. The AlLiCuSc alloy aged 24 h at 200°C. (a) Dark field micrograph taken using 110 δ' spot. (b) Corresponding SADP showing reflections from Al matrix, δ' and T_1 phase.

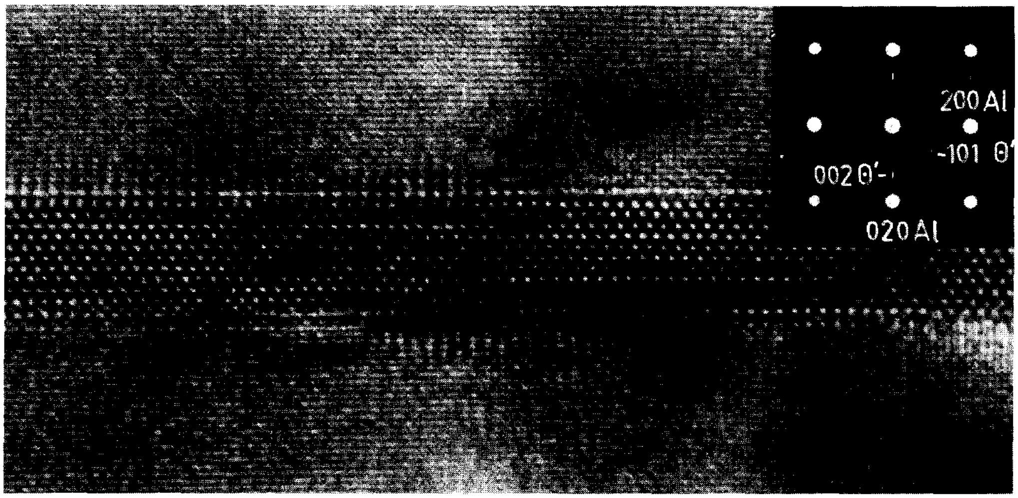

Fig. 5. The AlLiCuSc alloy aged for 24 h at 200°C. Atomic resolution micrograph of Θ' plate and Al matrix at [001] zone axis orientation with corresponding SADP insert.

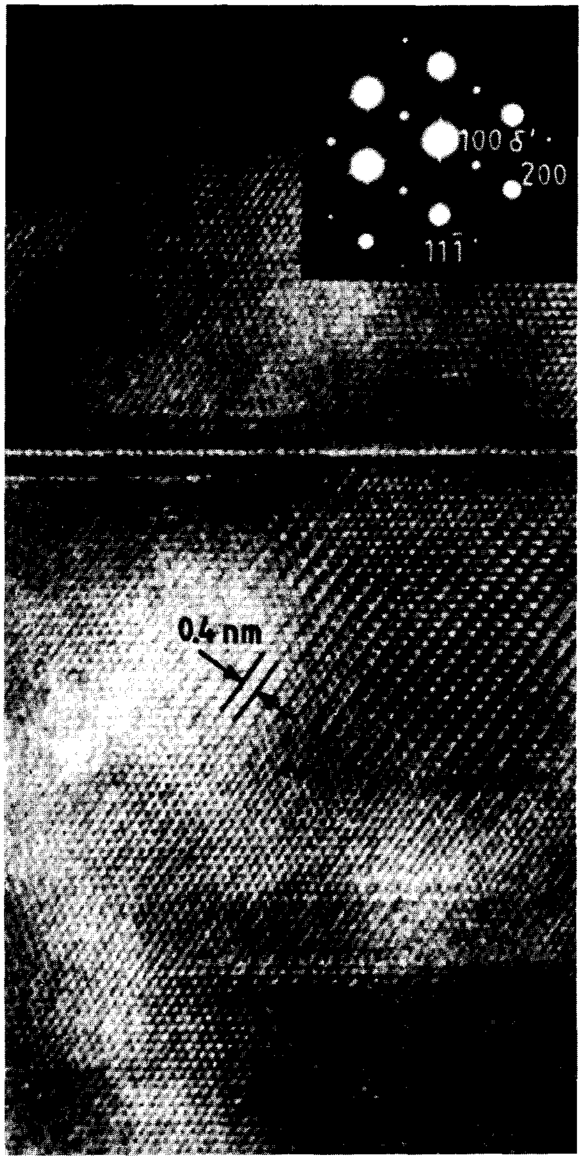

Fig. 6. The AlLiCuSc alloy aged for 24 h at 200°C. Atomic resolution micrograph of Θ' precipitate with δ' particle formed at the interface. Corresponding SADP insert is presented in the corner.

resolution micrographs only Θ' was identified. This means that in thinnest areas appropriate for high resolution microscopy T_1 phase was most probably etched out and cannot be observed. However, nucleation of δ' over Θ' is a probable mechanism of T_1 formation.

Next micrograph (Fig. 6) shows a high resolution image taken at [110] zone axis orientation taken after 24 h of ageing at 200°C. It shows long Θ' needle, with a growing ledge in the centre. At this place nucleated a large semisphere shaped δ' particle which at this orientation is visible as double spaced fringes perpendicular to ⟨100⟩ directions. The other small needles visible below the long one do not serve as nucleation site for δ'. This indicates that defects within Θ' precipitates promote nucleation of the ordered δ' precipitates.

4. Conclusions

(1) The addition of scandium does not cause strengthening of AlLiCu alloys after ageing at 200°C. The strong hardening effect is caused by copper addition. (2) The scandium rich Al_3Sc large spherical precipitates showing significant strain field contrast exist already after quenching together with finely dispersed δ' (Al_3Li) precipitates. (3) At the later stages of ageing corresponding to the hardness maximum formation of very thin Θ' (Al_2Cu) plates with the orientation relationship with the matrix: $[001]\alpha \| [010]\Theta'$ and $[100]\alpha \| [001]\Theta'$ (often with a semisphere of δ' on the

plate's surface) was observed using HREM. Their mutual reaction is likely to be a mechanism of $T_1(Al_2LiCu)$ plates formation. In thicker areas T_1 phase exhibited following crystallographic relationship with the matrix: $[001]\alpha \| [\bar{1}2\bar{1}0]T_1$ and $[100]\alpha \| [10\bar{1}0]T_1$.

Acknowledgements

This work was supported by the Foundation of German–Polish Cooperation. Donation Nr 1185/93/LN.

References

[1] T.A. Kassab, A. Menand, S. Chamberland, P. Haasen, Surf. Sci. 266 (1992) 333.

[2] S. Suresh, A.K. Vasudevan, Aluminium 63 (1987) 1020.

[3] A.J. Ardell, J.C. Huang, Mater. Sci Technol. 3 (1987) 176.

[4] A.L. Berezina, V.A. Volkov, S.V. Ivanov, N.I. Kolobniev, K.V. Chuistov, Fiz. Met. Metalloved. 2 (1991) 172.

[5] M. Miura, K. Horikawa, K. Yamada, M. Nakayama, in: T.H. Starke, E.A. Sanders (Eds.), Proc. 4th Int. Conf. Al Alloys, Atlanta, Georgia, 1994, p. 161.

[6] L.I. Kaigorova, A.M. Drits, Y.V. Zhingel, T.V. Krimova, V. Rassokhin, Fiz. met. Metalloved. 3 (1992) 94.

[7] V. Radmilovic, A.G. Fox, G. Thomas, Acta Metall. Mater. 37 (1987) 2385.

[8] J.C. Huang, A.J. Ardell, Mater. Sci Technol. 3 (1987) 176.