# Hardening phases evolution in the QE22 magnesium alloy 

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The increasing demand of weight reduction in the automotive and aeronautical industry has renewed the interest in the study of magnesium alloys, despite its relatively high production costs. It is well known that the ageing response of magnesium alloys is not as effective as that of aluminium alloys, but the addition of particular solute atoms has proved to increase the tensile properties as well as the hardness of several Mg -based compositions [1]. In particular, it was demonstrated that the addition of $2-3 \mathrm{wt} \%$ of Ag in rare earths-based Mg alloys markedly improves their age hardening response and hence their mechanical properties.

In this paper we study the phase transformations occurring in a $\mathrm{Mg}-2.2 \mathrm{Nd}-2.1 \mathrm{Ag}-0.6 \mathrm{Zr}$ (wt.\%) commercial alloy (commonly named QE22) when submitted to different thermal treatments, because there is still a certain degree of uncertainty in literature about its precipitation sequence and the structure and composition of its hardening phases.

In order to follow the precipitation sequence of the alloy, the solution heat treated samples were submitted to thermal treatments at $150^{\circ} \mathrm{C}, 204^{\circ} \mathrm{C}$ and $275^{\circ} \mathrm{C}$ for different ageing times. Then all samples were analyzed by transmission electron microscopy (TEM) techniques.

TEM observation of the solution heat treated sample shows a fine precipitation of nanometric structures uniformly distributed inside the grains. Although this precipitation is clearly visible in bright field images, it does not give rise to any remarkable effect on the diffraction pattern, suggesting the coherency of such nanometric structures. It is most probable that these nanometric structures are co-clusters or Guinier-Preston zones [2].

TEM analysis of the sample aged at $204^{\circ} \mathrm{C}$ for 10 hours ( T 6 condition), performed in the $\langle 001\rangle_{\mathrm{Mg}}$ zone axis orientation, reveals the presence of fine precipitates uniformly distributed inside the grains with dimension ranging from 10 to 50 nm (figure 1a). The corresponding Selected Area Diffraction (SAD) pattern is shown in figure 1 b while the simulation of the whole SAD pattern performed by the CrystalKit program is reported in figure 1c. The triangular structures located at about $1 / 3\{110\}_{\mathrm{Mg}}$ are attributable to a new second phase that we indicate here as $\chi$. The $\chi$ phase is hexagonal with $\mathrm{a}=0.286 \mathrm{~nm}$ and $\mathrm{c}=0.521 \mathrm{~nm}$ and it precipitates according to the following relationships with Mg : $(001)_{\chi} / /(001)_{\mathrm{Mg}}$, $[1-10]_{\chi} / /[110]_{\mathrm{Mg}}$. Figure 1 b also shows faint extra spots located at $1 / 3\{1-10\}_{\mathrm{Mg}}$ due to the hexagonal $\gamma$ phase. From the SAD pattern we obtain the following lattice parameters and orientation relationships with the matrix for the $\gamma$ precipitate: $\mathrm{a}_{\gamma}=0.963 \mathrm{~nm}, \mathrm{c}_{\gamma}=1.035 \mathrm{~nm}$ and $(001)_{\gamma} / /(001)_{\mathrm{Mg}},[100]_{\gamma} / /[100]_{\mathrm{Mg}}$. The $\mathrm{c}_{\gamma}$ value measured from our SAD pattern results to be in-between those proposed in literature for this phase [1,3].

TEM observation of the sample aged 16 hours at $150^{\circ} \mathrm{C}$ shows the presence of fine elongated $\chi$ precipitates uniformly distributed inside the grains.

The main TEM results obtained for the sample aged 30 minutes at $275^{\circ} \mathrm{C}$ and observed in $<001\rangle_{\mathrm{Mg}}$ zone axis are reported in figure 2. In this sample, coarse precipitates are present preferentially located on dislocations and grain boundaries with dimensions ranging from 30
to 170 nm , (figure 2a). The SAD pattern reported in figure 2 b exhibits extra spots arranged in a triangular structure located at about $1 / 3\{110\}_{\mathrm{Mg}}$. These spots are due to the stable $(\mathrm{Mg}, \mathrm{Ag})_{12} \mathrm{Nd}$ phase as well as to double diffraction effects, as indicated on the simulated SAD pattern in figure 2c. Measurements carried out on the SAD pattern provide for the $(\mathrm{Mg}, \mathrm{Ag})_{12} \mathrm{Nd}$ phase a tetragonal structure with $\mathrm{a}=1.03 \mathrm{~nm}$ and $\mathrm{c}=0.59 \mathrm{~nm}$ and the following orientation relationships with $\mathrm{Mg}:(100)_{(\mathrm{Mg}, \mathrm{Ag}) 12 \mathrm{Nd}} /(001)_{\mathrm{Mg}},[0-11]_{(\mathrm{Mg}, \mathrm{Ag}) 12 \mathrm{Nd}} /[110]_{\mathrm{Mg}}$. This phase was already reported in literature with different orientation relationships [4].

In conclusion, the results obtained so far indicate that the decomposition of the supersaturated solid solution occurs via the formation of nanosized coherent structures (coclusters or GP zones) followed by the co-precipitation of two metastable hardening phases, $\gamma$ and $\chi$. The stable phase $(\mathrm{Mg}, \mathrm{Ag})_{12} \mathrm{Nd}$ appears at the highest annealing times or temperatures. TEM observations provided information on the crystallographic structure of the different phases and allowed to clarify some inconsistencies present in literature.

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Figure1. Sample T6 in $\langle 001\rangle_{\mathrm{Mg}}$ zone axis orientation: a) TEM bright field, b) SAD pattern, c) SAD pattern simulation: large dots-Mg, stars- $\chi$ phase, open dots $-\gamma$ phase, small dots-double diffraction.


Figure2. Sample aged at $275^{\circ} \mathrm{C}$ for 30 minutes in $\langle 001\rangle_{\mathrm{Mg}}$ zone axis: a) TEM bright field, b) SAD pattern, c) SAD pattern simulation: large dots- Mg , open dots- $(\mathrm{Mg}, \mathrm{Ag})_{12} \mathrm{Nd}$ phase, small dots-double diffraction.

