Short Communications

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On the structure of the $M'$ phase in Al–Zn–Mg alloys. By J. H. AULD and S. MCK. COUSLAND, Aeronautical Research Laboratories, Department of Defence, Box 4331, GPO, Melbourne, Australia

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Abstract

Recently published work on the metastable phase $M'$, while agreeing with most of the earlier findings regarding its nature and morphology, raised doubts regarding the previously proposed structure. The basis of these doubts is discussed; reasons, based mainly on the experimental conditions employed, and evidence are given as to why the objections are not valid.

Régnier, Bouvaist & Simon (1982) recently re-examined the nature of the transition phase $M'$ (often alternatively referred to as $\eta'$), which can form in heat-treated aluminium-rich Al–Zn–Mg alloys whose composition lies in the $(\alpha + M)$ equilibrium phase field ($M$ is the Laves phase MgZn$_2$). Most of their results confirmed the earlier findings of Graf (1957) and of Auld & Cousland (1974). These findings were:

(i) the $M'$ phase can be assigned a hexagonal unit cell with parameters $a = 3d_{112\text{Al}} = 4.96\ \text{Å}$ and $c = 6d_{111\text{Al}} = 14.03\ \text{Å}$;
(ii) the $M'$ lattice is always oriented with $(0001)_M$ parallel to $(111)_\text{Al}$ and $(10\overline{1}0)_M$ parallel to $(110)_\text{Al}$;
(iii) the $M'$ phase forms as platelets, 100 to 200 Å broad and only about 30 Å thick, lying parallel to $(111)_\text{Al}$ planes.

However, Régnier et al. suggested that the structure determined by the present authors (Auld & Cousland, 1974) did not appear to be correct on two grounds: (i) it was suggested that since the reflections observed by Régnier et al. appeared as chains of diffuse reflections, calculations of intensity should be based on a 'global' structure factor; (ii) Régnier et al. failed to observe a number of reflections detected by us and for which our calculated intensities were not zero; they suggested that this may have been due to $M'$ reflections being confused with $M$ reflections, both of which were present in our case. We deal with these grounds for objection in turn.

(i) As a preliminary to our structural study, specimens were aged at various temperatures for various times to find the aging treatment giving maximum intensity of $M'$ reflections this condition occurred when some $M$ had already commenced to form and was the one used for our intensity measurements. No confusion arose as to whether any particular reflection originated from $M'$ or from $M$ because, firstly, the positions of all such reflections were calculated and compared with those observed and, secondly, a comparison of films taken after progressively longer aging times showed $M'$ reflections fading as $M$ reflections intensified. Furthermore, we did not use the integrating mechanism of the precession camera as this would have increased the recorded breadth of the reflections. A high-quality curved quartz monochromator was used to give a sharp line focus and, since the line focus integrates each reflection in the direction of the line, the integrated intensity was measured by traversing a microdensitometer beam across the centre of the reflection line in

![Fig. 1. (a) Zero-level precession-camera photograph of reciprocal space parallel to $(110)_\text{Al}$. (b) Key to (a).](image-url)
the direction of the streaking caused by the thinness of the precipitates. Except for the few cases indicated in our table of observed and calculated structure factors (Auld & Coudland, 1974), the reflections were sufficiently well separated to allow true integrated intensities to be measured for each reflection. For the above reasons, our recorded $M'$ reflections were not chains of diffuse reflections and the comparison of observed intensities with those calculated by the usual structure factor method is appropriate.

(ii) As to the second objection, the chief disagreement between Régnier et al. and ourselves concerns the intensities of the 007, 113, 034 and 125 reflections of $M'$. Régnier et al. did not observe any of these reflections whereas we observed all four; furthermore, the intensities of these four reflections, calculated for our proposed $M'$ structure, were reasonably high. In the discussion that follows, the positions of $M'$ and $M$ reflections are given by coordinates referred to the $(100)^*$ axes of the aluminium reciprocal lattice, taking $d_{100}^A$ as one unit. The 007$_M$ reflection is found at positions of the type 1-17, 1-17, 1-17. As stated in our original Table 2, it was impossible to measure its intensity reliably, as it lies close to the 004$_M$ reflection at 1-09, 1-09, 1-09 and also to the very strong 111$_A$ reflection, Fig. 1. (Note that exposure times of about 100 h, used to record reflections from the $M'$ phase, cause each aluminium reflection to be highly overexposed and so visible diffuse scattering extends a considerable distance from each node of the aluminium reciprocal lattice.) However, although the intensities of 007$_M$ and of 004$_M$ could not be reliably measured by the microdensitometer, both were definitely detectable by eye, with 007$_M$ fading and 004$_M$ strengthening as aging progressed. Similarly, the 113$_M$ reflections occur at positions of the type 1-17, 1-17, 0-83, also fairly close to 111$_A$, and to 112$_M$ at 1-19, 1-19, 0-73, Fig. 1; these 113$_M$ reflections are nevertheless sufficiently well separated from the neighbouring reflections to permit approximate measurement. The 113$_M$ reflections also occur at positions of the type 0-17, 0-17, 1-83, in the vicinity of 200$_A$, and fairly close to 112$_M$ at 0-09, 0-09, 1-83. While the intensities of the 007$_M$ and the 113$_M$ reflections were difficult to measure, these difficulties do not apply to the 034 and the 125 reflections of the $M'$ phase, as these are well clear of any $M$ or $A1$ reflections. The 034$_M$ reflections are computed to lie at positions of the type 1-33, 2-67, 0-67 and were observed at this position on a zero-level $[112]_A$ film. The 125$_M$ reflections are computed to occur at positions of the type 1-17, 1-50, 2-17 and 0-17, 0-50, 2-83. These positions are best found on upper-level photographs of $[112]_A$ with $\zeta = \frac{1}{3}d_{112}^A$ or of $[011]^*_A$ with $\zeta = \frac{1}{3}d_{110}^A$.

Again, these 125$_M$ reflections were present.

The intensity data for precipitates of this size and morphology are necessarily very poor compared with those required for precise crystal-structure determinations but, bearing this in mind, a fairly satisfactory fit to the data was found for the structure proposed. Hence we contend that the proposed $M'$ structure is basically correct.

References


J. Rietveld analysis of powder neutron diffraction data displaying anisotropic crystallite size broadening. By C. Greaves, Department of Chemistry, University of Birmingham, PO Box 363, Birmingham B15 2TT, England

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Abstract

In order to accommodate anisotropic crystallite-size broadening effects in the Rietveld refinement of constant-wavelength powder neutron diffraction data, a modified function for the peak full width at half maximum has been evaluated for polycrystalline Ni(OD)$_2$. The function resulted in significantly better agreement between observed and calculated profiles (the weighted residual $R_w$ decreased from 14.1 to 8.5%), and structural standard deviations were reduced by an average of 43%.

Introduction

The value of powder neutron diffraction has increased dramatically in recent years owing largely to the development of structure refinement techniques based on the total profile rather than integrated intensities (Rietveld, 1967, 1969). Of fundamental importance to the success of these methods is the fact that, at constant wavelength, the peaks are simple Gaussian provided their full widths at half-maximum height ($H$) are determined by instrumental factors alone. Variation of $H$ with $2\theta$ can be represented (Caglioti, Paolletti & Ricci, 1958) by

$$H = [U \tan^2 \theta + V \tan \theta + W]^{1/2},$$

where $U$, $V$, $W$ are parameters refined during the analysis. However, for high-resolution diffractometers, complexities have been encountered owing to non-instrumental contributions to the peak profile, in particular from crystallite-size broadening. Such broadening results in a departure from a Gaussian shape, and more flexible peak-shape functions have therefore been proposed (Young & Wiles, 1982). With respect to changes in $H$, although (1) has satisfactorily accommodated broadening effects for some samples (Santoro, D'Antonio & Caulder, 1983), a serious difficulty