

Correlation between strength and microstructure of ball-milled Al–Mg alloys determined by X-ray diffraction

G. Ribárik, J. Gubicza, T. Ungár*

Department of General Physics, Eötvös University, Budapest, P.O. Box 32, H-1518, Hungary

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Abstract

The microstructure of ball-milled Al base Al–Mg alloys is determined by the “Convolutional Multiple Whole Profile” fitting procedure proposed for the evaluation of X-ray diffraction peak profiles. The whole measured powder diffraction pattern is fitted by the sum of a polynomial background and physically well-established theoretical profile functions. The procedure provides the size distribution function of crystallites and the characteristic parameters of the dislocation structure. The mechanical strength of the specimens is correlated to the parameters of the microstructure by the Hall–Petch and the Taylor models. Both models show that the critical resolved shear stress saturates at a Mg-solute concentration of about 2 wt.% probably due to the clustering of the Mg-solute atoms.

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1. Introduction

X-ray diffraction peak profile analysis is a powerful method for determining the microstructural properties of ultrafine-grained materials. The effects of crystallite size and lattice strain on peak broadening can be separated on the basis of their different diffraction order dependence. The standard methods of X-ray diffraction profile analysis based on the full width at half-maximum (FWHM), the integral breadths and on the Fourier coefficients of the profiles provide the apparent crystallite size and the mean-square of lattice strains [1–3]. In metals and alloys, the anisotropic strain field of dislocations results in non-monotonic order dependence of strain broadening of diffraction peaks (strain anisotropy) [4–6]. This effect can be well accounted for by the dislocation model of the mean-square strain by introducing the contrast (or orientation) factors of dislocations [7–13]. Since the values of the dislocation contrast factors depend on the dislocation slip systems present in the crystal, the evaluation of X-ray peak profiles for the contrast factors permits the determination of the dislocation structure [14–16].

In the last few years, considerable efforts have been made to develop procedures that can determine the parameters of the microstructure by fitting whole diffraction patterns [17–22]. A few years ago the Multiple Whole Profile (MWP) fitting method was developed, where the crystallite size distribution and the parameters of the dislocation structure were determined by fitting physically well-established profile functions of size and strain profiles to the measured physical profiles [18,19]. The procedure is working either on the Fourier transforms or on the intensities of the measured physical profiles and is available to any user through a front end on the web: <http://www.renyi.hu/mwp/> [19]. Scardi and coworkers [20,21] elaborated a Whole Powder Pattern Fitting (WPPF) method in which the experimental profiles are fitted by Voigt functions. This method has been developed further by introducing the Whole Powder Pattern Modelling (WPPM) procedure where more realistic, however, simplified theoretical profile functions are used [22]. In the present paper, the Convolutional Multiple Whole Profile (CMWP) fitting procedure is presented for the determination of crystallite size distribution and the dislocation structure of materials. The profile functions are calculated as the convolution of the theoretical size and strain profiles and the measured instrumental profiles. The procedure is available to any user through a front

* Corresponding author. Tel.: +36-1-372-2801; fax: +36-1-372-2811.
E-mail address: ungar@ludens.elte.hu (T. Ungár).

end on the web: <http://www.renyi.hu/cmwp/>, in a similar way as the earlier MWP method. The parameters of the microstructure determined by the CMWP method are compared with the results obtained by the earlier MWP fitting procedure for ball-milled Al–Mg alloys. The microstructure parameters provided by the X-ray method are discussed in terms of the mechanical behaviour of the severely deformed alloys. The analysis of the hardness and X-ray data shows that solution hardening in this alloy saturates at room temperature at the solute Mg concentration of about 2 wt.%.

2. Experimental

Al base Al–Mg samples were prepared from high-purity Al (99.9%) powder and 0, 3 and 6 wt.% high-purity Mg chips (less than 2 mm thick and 5 mm long) by mechanical alloying. The powder mixture was milled for 3 h using a Spex8000 shaker miller at room temperature. The charge was loaded into a steel vial in a glove box with a purified argon (<3 ppm oxygen) atmosphere. Martensitic stainless steel (440C) balls with diameters of 6.4 and 7.9 mm were used for milling with a ball-to-powder ratio of 10:1. Stearic acid (2%) was used as a control agent to prevent severe cold welding. Since both, the balls and the vial of the mill are made of hardened steel, the iron contamination in the soft Al alloy is very small, below 0.02 at.%.

The X-ray diffraction patterns were measured by a Philips X'pert powder diffractometer using CuK α radiation ($\lambda = 0.15418$ nm) and pyrolytic graphite secondary monochromator. Step size and step time were 0.03° and 22 s per step. The measured powder pattern of the Al–3 wt.% Mg specimen is shown in Fig. 1. The instrumental pattern was measured on a NIST SRM660a LaB $_6$ peak profile standard material.

3. Brief summary of the evaluation of X-ray data

In the methods used in this paper, we assume that: (i) both, size and strain effects are present, (ii) the crystallites have spherical shape with log-normal size distribution, (iii) strain is caused by dislocations with restrictedly random distribution [7–9] and (iv) the sample is either an untextured bulk polycrystal or a fine powdered material, where the dislocation contrast factors can be averaged over the permutations of the hkl indices [15]. In this case, the Fourier transform, $A(L)$, of the peak profile function can be written as [2,7,8]:

$$A(L) = A^S(L, m, \sigma) \exp \left[\frac{1}{2} (-\pi b^2) \rho L^2 (g^2 \bar{C}) f(\eta) \right], \quad (1)$$

where A^S are the size Fourier coefficients in which m and σ are the median and the variance of the crystallite size distribution function. A detailed description of the A^S Fourier coefficients can be found in [19]. The exponential expres-

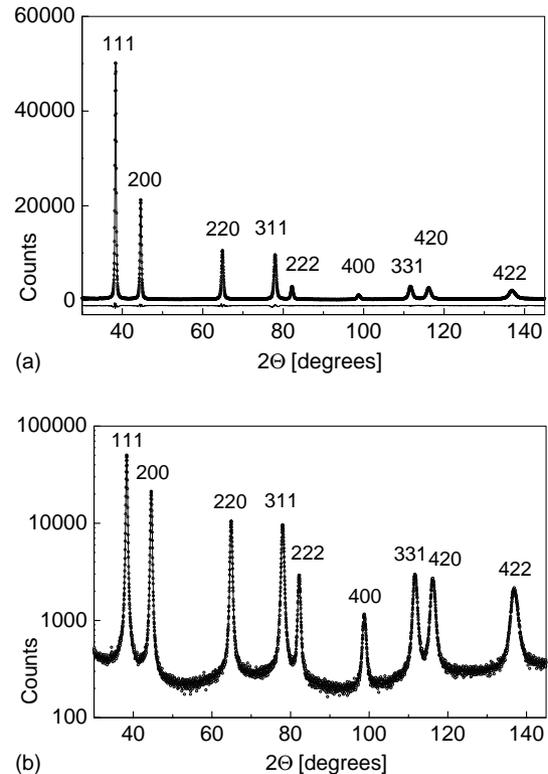


Fig. 1. X-ray diffraction pattern of Al–3 wt.% Mg powder mixture milled for 3 h in (a) linear and (b) logarithmic intensity scales. The measured data and the function fitted by the CMWP method are shown by open circles and a solid line, respectively. The difference between the measured and fitted data is plotted at the bottom of (a).

sion is the strain Fourier coefficients, where g is the magnitude of the diffraction vector, b the Burgers vector of dislocations, ρ the average dislocation density, \bar{C} the average dislocation contrast factor, cf. [14], $\eta = L/R_e$, L the Fourier length and R_e is the effective outer cut-off radius of dislocations. Following the notations of Wilkens [7,8], instead of R_e we prefer to use the dimensionless parameter $M = R_e \sqrt{\rho}$, which is a measure of the dipole character of dislocations: a small or large M value indicates strong or weak dipole character, respectively. The $f(\eta)$ function, called Wilkens' strain function, is valid for dislocations in the entire L range from zero to infinity, see Eqs. (A.6)–(A.8) in ref. [8]. The size profile with the simplest crystallite shape and size distribution function requires at least two parameters, here m and σ . The strain profile (except for the contrast effect of dislocations) needs at least two parameters for the dislocation structure: the density and the arrangement parameter, ρ and M . In the simplest case of cubic crystals, the contrast effect of dislocations can be taken into account by one fitting parameter: q [18,19]. The value of \bar{C}_{h00} and ρ appear as a product in Eq. (1), see also Eq. (10) in ref. [18], therefore it has to be determined separately [14]. This means that in the simplest case, the numerical procedure is operating with five independent parameters: m , σ , ρ , M and q . It is noted that, due to the physical nature of the microstructure,

this is the minimum number of parameters which have to be used.

4. Convolutional Multiple Whole Profile fitting method

In the MWP method, the measured powder pattern has to be corrected for (i) overlapping peaks, (ii) instrumental broadening and (iii) background [19]. The normalised Fourier transforms of the measured peaks corrected for background and instrumental effects are fitted simultaneously by the theoretical Fourier transforms. The numerical procedure enables also the fitting of the intensities by using the inverses of the Fourier transforms. Mathematically, the two different approaches mean different weighting of the central and the outermost parts of the profiles. In order to avoid the uncertainties and errors introduced by the correction procedures in (i)–(iii), the method of Convolutional Multiple Whole Profile fitting has been elaborated. The whole measured diffraction pattern is fitted directly by the sum of the background and the theoretically constructed profile functions. These profile functions are calculated for each reflection as the convolution of the inverse Fourier transforms of the theoretically well-established size and strain Fourier coefficients (see Eq. (1)) and the corresponding measured instrumental profiles. The background is determined as a spline going through intensity values defined interactively by the user, or as a fitted sum of Legendre polynomials. However, in the present procedure, the crystal structure is not refined, the intensity maxima and the peak positions of the theoretical profiles are allowed to be adjusted to the measured ones by the least-squares method. The fitting procedure is carried out by the same non-linear least-squares algorithm as in the MWP procedure and the microstructural parameters used in the fitting were also the same [19]. By using the appropriate instrumental diffraction pattern the procedure can be used in a straightforward manner, either when the data are collected with monochromatic or with conventional $K\alpha$ doublet radiation. A typical example of the fitted pattern, corresponding to the Al–Mg alloy containing nominally 3 wt.% Mg, is shown in Fig. 1. The difference plot between the measured and fitted patterns is given at the bottom of Fig. 1(a).

5. Results and discussion

The average dislocation densities and arrangement parameters, ρ and M , the q parameter values for the dislocation contrast factors and the median and the variance of the log-normal size distribution functions, m and σ , determined by the CMWP method and the MWP method applied on the Fourier coefficients and on the intensities, respectively, are listed for the three specimens in Table 1. A relatively good correlation can be seen between the size and dislocation density values provided by the CMWP procedure and the MWP method applied on the intensities. The only discrepancy is between the m and σ values corresponding to the pure aluminium specimen, which is probably due to the instrumental correction used in the MWP method. In the Stokes method, the measured Fourier transform is divided by the instrumental one and if the measured profile is relatively narrow, the tail part of the physical Fourier transform is obtained by dividing small numbers by each other. This might result in the uncertainty of the calculated physical Fourier transform. The correlation between the values obtained by the MWP method applied on the Fourier coefficients and the other two procedures is somewhat poorer. This is probably due to the different weighting of the profiles in the two different approaches. In the case when the intensities are fitted, the tail region of the profiles have more weight. Whereas, when the Fourier coefficients are fitted, the central parts of the intensity profiles, corresponding to the tail region of the Fourier spectrum, have more weight. The discrepancies between the values of the q parameters determined by the different fitting methods are due to the same reasons as in the case of the other parameters. Since the MWP method contains intrinsic deficiencies compared to the CMWP procedure, especially because of the separation of overlapping peaks and the Stokes' correction of instrumental effects, at the discussion of the results, we shall use the microstructure parameters provided by the CMWP procedure.

The lattice constants of the three samples were determined by the standard Nelson–Riley method [23]. The Mg concentration in the solid solution was determined by using the slope in Vegard's law given for Al–Mg by Pool and Axon [24]. The nominal and measured Mg contents for the three

Table 1

The dislocation density, ρ , the dislocation arrangement parameter, M , the q parameter in the dislocation contrast factor and the median and the variance, m and σ , of the size distribution function for the three Al–Mg specimen obtained by the three different whole profile fitting methods

Nominal Mg (wt.%)	Method of evaluation	ρ ($\times 10^{14}$ m $^{-2}$)	M	q	m (nm)	σ	R_{wp} (%)
0	CMWP	12 (2)	1.1 (2)	1.3 (1)	73 (7)	0.10 (2)	6.4
3		44 (4)	1.2 (2)	1.1 (1)	29 (3)	0.29 (3)	4.0
6		100 (15)	1.3 (2)	0.7 (1)	26 (3)	0.13 (3)	5.2
0	MWP Fourier	19 (2)	1.0 (2)	0.7 (1)	60 (6)	0.18 (2)	8.9
3		40 (4)	1.2 (2)	0.5 (1)	33 (3)	0.21 (3)	2.4
6		72 (6)	1.0 (2)	0.4 (1)	19 (2)	0.40 (3)	4.6
0	MWP intensity	7 (2)	1.2 (2)	0.9 (1)	43 (5)	0.29 (2)	13.0
3		45 (4)	1.3 (2)	0.6 (1)	31 (3)	0.26 (3)	11.0
6		91 (9)	1.3 (2)	0.4 (1)	23 (3)	0.15 (2)	7.0

Table 2

The nominal and the measured solute Mg concentrations, the hardness and the area weighted mean crystallite size of the three Al–Mg alloys

Nominal Mg (wt.%)	Solute Mg (wt.%)	H (GPa)	$\langle x \rangle_{\text{area}}$ (nm)
0	0.00 (7)	1.1 (1)	75 (8)
3	2.26 (8)	2.3 (1)	36 (4)
6	5.52 (6)	2.7 (1)	27 (3)

specimen are given in Table 2. The hardness, H , was measured by depth-sensing indentation tests in a Shimadzu dynamic ultra-micro hardness tester (DUH 202) on compacted samples [25]. The X-ray analysis has shown that the compaction did not alter the microstructure of the specimens [25]. The hardness data are also listed in Table 2.

The strengthening of our submicron grain size specimen can be modelled either by the Hall–Petch [26,27] or by the Taylor [28] model, respectively:

$$\frac{H}{3} = \frac{H_0(c)}{3} + \frac{K}{\sqrt{d}} \quad (2)$$

$$\frac{H}{3} = \frac{H_0(c)}{3} + \alpha G b M^T \sqrt{\rho} \quad (3)$$

where the denominator, 3, stands for transforming the hardness into stress values [29], $H_0/3$ the friction stress, K the constant in the Hall–Petch relation, d the average grain or crystallite size, c the solute Mg concentration, α the constant between zero and unity ($\alpha = 0.3$ is taken here), G the shear modulus (26 GPa) and M^T is the Taylor factor, $M^T = 3$. The area averaged mean crystallite diameters, $\langle x \rangle_{\text{area}}$, listed in Table 2 are used as the d values in Eq. (2). The $H_0(c)/3$ values, calculated according to Eqs. (2) and (3) are plotted as a function of the solute Mg contents in Fig. 2. The value of $K = 3.7 \text{ GPa nm}^{1/2}$ in Eq. (2) for Al–Mg alloys is taken from [30]. In the case of the pure Al specimen, $H_0(c)/3 = 0.02 \text{ GPa}$ [31]. In Fig. 2, it can be seen that $H_0(c)/3$ increases up to about 2 wt.% Mg and saturates above that.

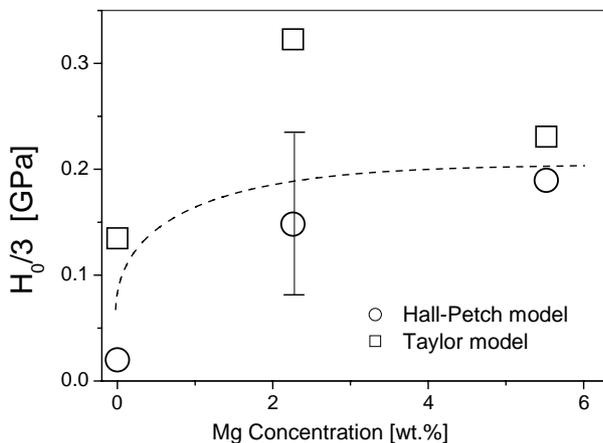


Fig. 2. The friction stress as a function of the solute Mg content of the Al–Mg alloys, obtained by the Hall–Petch or the Taylor model given in Eqs. (2) and (3), respectively.

The X-ray diffraction patterns indicate single phase solid solutions for all three specimens. From this and from the saturation of the concentration dependent friction stress, it is concluded that the Mg atoms, most probably, form small clusters when the Mg concentration is larger than about 2 wt.%. These small clusters neither give individual diffraction peaks in the diffraction pattern nor increase the friction stress beyond 2 wt.% Mg. Clustering in Al alloys is well known, especially in ternary alloys [32,33], where Mg with Si or Cu forms co-clusters. The observation of Mg clustering in Al is rather difficult due to the small difference in the X-ray or electron scattering factors. The mechanical properties provided an indirect indication of clustering of Mg atoms in Al. The analysis of the strength of the three specimens in terms of crystallite size or dislocation density, in the present case, does not enable to distinguish between the mechanisms operating according to the Hall–Petch or the Taylor model. This is probably due to the small crystallite size whose diameter is comparable to the average dislocation distance. Since the two length scales are close to each other the strength of the specimens is scaling with both in a similar way.

It has to be stressed here that the fortuitous quantitative agreement of the crystallite size and the average dislocation distance in the present case does not mean that the two parameters are correlated to each other in terms of the evaluation procedure of the broadened diffraction peaks. The two parameters are provided independently, since one is related to the order independent and the other to the order dependent part of peak broadening, cf. [1,2]. The similar magnitude of the two parameters has purely physical reasons enabling conclusion on the physical nature of the microstructure. It is very likely that the crystallites or grains are not subdivided by subgrains or dislocation cells, and that most of the dislocations reside in or near the crystallite or grain boundaries, in accordance with the submicron grain size of the specimens.

6. Conclusions

A numerical fitting procedure (the Convolutional Multiple Whole Profile fitting method) has been developed for determining the microstructure in terms of crystallite size distribution and the dislocation structure from X-ray diffraction patterns. In the procedure, the sum of a polynomial or spline background and the convolution of theoretical profile functions with measured instrumental profiles are fitted to the measured pattern. The hardness of ball-milled pure Al and two Al–Mg alloys have been discussed in terms of the crystallite size and dislocation densities. The friction stress obtained from either the Hall–Petch or the Taylor model shows saturation at around 2 wt.% of the solute Mg concentration, which might be due to clustering of Mg atoms in the supersaturated solid solution state at room temperature.

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