Microstructure development of ultra fine grained Mg-22 wt%Gd alloy prepared by high pressure torsion


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A hardenable lightweight Mg-22 wt%Gd alloy with ultra fine grained (UFG) structure was prepared by high pressure torsion (HPT) at ambient temperature. The development of microstructure during HPT processing was investigated. A homogeneous UFG structure with grain size of 300 nm was achieved after 15 HPT revolutions. The UFG alloy exhibits enhanced strength due to work strengthening by tangled dislocations forming a dense forest throughout grains. Dislocation density in the sample was determined by positron annihilation spectroscopy (PAS) and X-ray line profile analysis (XLPA). It was found that there is an additional source of X-ray profile broadening in addition to small crystallites and micro-strains caused by dislocations. The additional micro-strain component was attributed to lattice modulation by Gd-rich nano-wires formed by agglomeration of Gd solutes and to strains arising from boundaries of crystallite domains and inter-domain interactions. Analysis of the influence of the crystallite size on the strength of UFG Mg-22 wt%Gd alloy revealed a breakdown in the Hall-Petch relationship when the crystallite size decreased below a critical value of ≈ 30 nm.

1. Introduction

Lightweight Mg alloys are promising structural materials for automotive or aeronautical applications because of their low density and high specific strength. However, limited number of active slip systems in hexagonal close packed (hcp) structure leads to a poor formability of Mg alloys [1]. This disadvantage can be overcome by superplastic deformation at elevated temperatures which enables formation of complex shapes [2]. Such procedure requires good stability of mechanical properties of the material at elevated temperatures.

Mg-Gd alloys exhibit excellent thermal stability and good creep resistance at elevated temperatures above 300 °C [3–5]. The maximum solubility of Gd in Mg matrix was found to be 22.8 wt% at 550 °C [6]. At lower temperatures the solubility of Gd in Mg matrix dramatically decreases [7]. This allows for precipitation hardening of Mg-Gd alloys [8]. By quenching of Mg-Gd from elevated temperatures down to room temperature supersaturated solid solution (SSS) of Gd in Mg can be formed. Decomposition of SSS with increasing temperature takes place in a sequence of the following successive phases [3,9]: SSS → Gd clusters → β' (Mg3Gd, orthorhombic structure) → β (Mg46Gd9, cubic structure) [10,11]. The Gd clusters and β' phase are metastable while β is a stable phase. Note that previously it has been assumed that metastable β” phase (Mg7Gd, D019 structure) is formed at early stages of precipitation [3]. Recent high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observations however did not confirm particles with D019 structure but revealed that in early precipitation stages Gd atoms form a short-range order structure consisting of columns rich in Gd atoms aligned along the [0001]a direction in Mg matrix [9,12]. Formation of these clusters in early stages of precipitation was reported also in Mg-Y a Mg-Nd alloys [12–14].

Mechanical properties of Mg-Gd alloys can be further improved by grain refinement down to nano-scale [15–20]. Grain refinement down to nano-scale enables grain boundary sliding which improves the formability at elevated temperatures. HPT [21,22] is the most efficient technique for structure refinement by severe plastic deformation developed so far. A superplastic deformation occurring by grain boundary sliding mechanism has recently been reported for UFG Mg-Gd-Y-Zr and Mg-Gd-Zr alloys prepared by HPT [16,19] and equal channel angular pressing (ECAP) [20].
UFG Mg-Gd alloys with Gd content around 10 wt% or lower have been studied so far [15–20,23–27]. In the present work we chose Mg-Gd alloy with Gd concentration of 22 wt% (Mg22Gd) i.e. Gd content is close to the maximum Gd solubility in Mg matrix. HPT deformation was employed for fabrication of UFG structure. Severe plastic deformation introduces high density of lattice defects that are essential for extraordinary physical properties of UFG materials. Characterization of lattice defects in UFG materials is therefore very important task. This work presents detailed investigation of lattice defects introduced into Mg22Gd alloy by HPT processing. The evolution of lattice defects was correlated with development mechanical properties of the alloy. PAS [28,29] was employed for characterization of defects in HPT-deformed Mg22Gd alloy and study of defect evolution during HPT processing. PAS is a well developed non-destructive technique with a high sensitivity to open-volume defects, e.g. vacancies, dislocations and vacancy clusters, and has been successfully utilized for defects studies of UFG materials [30–34]. In the present work PAS was combined with microstructure observations by electron microscopy and line profile analysis of X-ray diffraction (XRD) patterns. The development of mechanical properties during HPT processing was monitored by micro hardness testing.

2. Experimental details

Mg22Gd alloy was prepared by squeeze casting in Ar + 1% SF6 atmosphere. Chemical analysis revealed that actual Gd concentration in the alloy is (22.4 ± 0.4) wt% and Gd is distributed uniformly within the whole cast ingot. The as cast alloy was solution treated at 530 °C for 5 h and the alloy is (22.4 ± 0.4) wt% and Gd is distributed uniformly within the matrix. Chemical analysis revealed that actual Gd concentration in the alloy is (22.4 ± 0.4) wt% and Gd is distributed uniformly within the whole cast ingot. The as cast alloy was solution treated at 530 °C for 5 h and the solution treatment was finished by quenching into water of room temperature.

UFG samples were prepared by HPT straining (quasi-constrained conditions) of the solution treated alloy under a pressure of 2 GPa and at room temperature. No slippage of samples took place during HPT straining. Samples subjected to various numbers of HPT rotations \( N = \tfrac{1}{4}, \tfrac{1}{2}, 1, 3, 5, 10, 15 \) were prepared in order to investigate the development of microstructure during HPT processing. A sample only compressed by the pressure of 2 GPa without any torsion deformation (\( N = 0 \)) was prepared as well. HPT-deformed samples were disk shaped with diameter of 20 mm and thickness which decreases with increasing number of HPT revolutions from \( h = 1.0 \text{ mm for } N = 0 \) to \( h = 0.8 \text{ mm for } N = 15 \). In torsion deformation the strain increases with increasing radial distance \( r \) from the center of the sample disk corresponding to the rotation axis. The equivalent von Misses strain in the distance \( r \) from the center of a sample subjected to \( N \) HPT revolutions is given by the relation [21]

\[
e_{\text{equiv}} = \frac{1}{\sqrt{3}} \frac{2\pi N r}{h}
\]

(1)

A \(^{22}\text{Na}\) positron source with activity of 1.5 MBq deposited on a 2 μm thick mylar foil was used in PAS measurements. A digital spectrometer described in Ref. [35] was employed for positron lifetime (LT) measurements. The spectrometer is equipped with BaF₂ scintillators and fast photomultipliers Hamamatsu H3378. Detector pulses are sampled using a couple of 8-bit ultrafast digitizers Acqiris DC 211 with sampling frequency of 4 GHz and stored in a personal computer. Analysis of sampled waveforms and construction of LT spectrum is performed using so-called integral true constant fraction technique [36]. The spectrometer exhibits excellent time resolution of 145 ps (full width at half maximum of the resolution function). LT spectra, which always contained at least \( 10^7 \) positron annihilation events, were decomposed using a maximum likelihood based procedure [37]. The source contribution to LT spectra was determined using a reference sample of pure Mg and its intensity was recalculated for Mg22Gd using a procedure described in Ref. [38]. The source contribution consisted of two components with lifetimes of \( \approx 368 \text{ ps and } \approx 1.5 \) ns and relative intensities of \( \approx 7 \) and \( \approx 1\% \), which come from positrons annihilating inside the \(^{22}\text{Na}\) source spot and the covering mylar foil, respectively.

Scanning (SEM) and transmission electron microscopy (TEM) were employed for the investigation of microstructure of individual specimens. Specimens for SEM investigations were first mechanically polished and finally polished was done using Leica™ EM RES120 ion mill. Thin foils for TEM observations were mechanically ground using emery papers and the final step was electro polishing. SEM observations were performed on the SEM Zeiss Auriga Cross Beam™ at the accelerating voltage of 20 kV. This microscope is equipped with electron backscatter diffraction (EBSD) and electron dispersive X-ray spectroscopy (EDX) system. TEM observations were carried out on the transmission electron microscope Jeol 2000FX at the accelerating voltage of 200 kV.

X-ray diffraction (XRD) measurements were carried out with the aid of Pananalytical X′Pert Pro powder diffractometer using filtered CuKα radiation. Variable divergence and anti-scatter slits were used for enhancing higher diffraction angle peak intensities, which are important for the line profile analysis. Diffracted X-rays were detected by a PIXCel position sensitive detector. The HPT processed specimens were measured at three different positions – in the sample center, in the half of the sample radius and in the sample periphery. The irradiated area was kept constant, \( 2 \times 2 \text{ mm}^2 \) for all measurements. X-ray line profile analysis was performed employing the whole powder pattern refinement method [39–43]. The computer program MStruct [43] was used for the fitting of the measured XRD patterns. Analysis of XRD patterns revealed the phase composition and the details of the real structure of investigated material i.e. the lattice parameters, size of coherently diffracted domains, dislocation density and microstrain.

Vickers microhardness (HV) testing was performed using an automatic microhardness tester Quen™ Q10. HV measurements were performed on a dense mesh containing more than 1000 indents for each HPT deformed sample. This enabled characterization of HV variations across the sample disk.

3. Results

3.1. Coarse grained alloy

The solution treated sample exhibits the mean grain size of \( \approx 400 \mu \text{m} \). Fig. 1a shows a SEM micrograph of the solution treated Mg22Gd alloy, i.e. prior to HPT straining. EDX analysis revealed that the concentration of Gd dissolved in Mg matrix is \( (21.0 \pm 0.6) \text{ wt\% } \) which is relatively close to the maximum Gd solubility in Mg. In addition to α-Mg grains the sample still contains particles of grain boundary β phase. A detail of these particles is shown in Fig. 1b. EDX analysis confirmed that chemical composition of these particles agrees with the composition of the β phase (Mg\(_{46}\)Gd\(_{9}\)). Furthermore the solution treated sample contains isolated rectangular shape particles which appear brighter in Z-contrast SEM images. Some of them are indicated by arrows in Fig. 1b. Only pure Gd signal was observed from the rectangular particles by selected area EDX. This indicates that the rectangular particles represent gadolinium di-hydride (GdH\(_2\)) phase. Note that hydrogen cannot be detected by EDX. The GdH\(_2\) phase was introduced high density of lattice defects that are essential for extra-
solution treated sample is around 3 wt%. The XRD phase analysis confirmed the presence of a small amount (a few wt%) of the GdH₂ phase with lattice parameter $a = (0.53001 \pm 0.00008)$ nm which corresponds well with results published in literature [49].

The solution treated Mg22Gd sample exhibits a single component LT spectrum with lifetime of $(226 \pm 1)$ ps which agrees well with the bulk positron lifetime for Mg, $\tau_B = 225$ ps [50]. Hence, density of defects in the solution treated alloy is very low (dislocation density <$10^{12}$ m$^{-2}$) and virtually all positrons are annihilated in the free state, i.e. not trapped at defects.

### 3.2. Ultra fine grained alloy

Fig. 3 shows an EBSD orientation map of the only pressed sample ($N = 0$). The sample exhibits average grain size of $\approx 350$ µm. Hence, compression by a high pressure of 2 GPa did not lead to a significant grain refinement. In Fig. 3b one can see that compression by high pressure introduced deformation twins into the sample. Twins are formed predominantly in grains with orientation unfavorable for deformation by basal slip and multiple twins contribute to fragmentation of grains.

An EBSD map of the sample subjected to $N = 1/4$ HPT revolution is shown in Fig. 4. The EBSD observations were performed at the half radius of the sample disk ($r = 5$ mm). From inspection of EBSD results it becomes clear that the sample exhibits bimodal structure: in some regions the grain size was refined down to nanoscale but in other regions coarse grains remain. Continuous change of orientation within coarse grains testifies to presence of high stress in the grains. Determination of EBSD orientation map in samples subjected to higher number of HPT revolutions was not possible because of high concentration of defects and stress in grains which prevent determination of orientation.

SEM micrographs of Mg22Gd alloy subjected to various numbers of HPT revolutions are shown in Fig. 5. SEM observations were performed at the half-radius of the sample ($r = 5$ mm). One can see in Fig. 5 that β phase particles were deformed and refined with increasing number of HPT revolutions. Bright field TEM micrographs in Fig. 6 document the development of microstructure during HPT straining. From inspection of Fig. 6 one can conclude that HPT deformation introduced high density of dislocations into the sample. Dislocations are distributed uniformly throughout grains forming a dense forest. Structure refinement with increasing number of HPT revolutions is clear in the micrographs. The mean grain size after $N = 15$ HPT revolutions decreased down to $\approx 300$ nm. This is remarkably smaller grain size than those reported for Mg alloys refined by top down approaches in Refs. [51–55]. However, it has to be noted that even smaller grain size below 100 nm was recently achieved by HPT processing of extruded Mg-Gd-Y-Zr alloy [19].

Selected area diffraction (SAED) patterns taken from the area of 6 µm are shown in the right panels in Fig. 6. The SAED patterns for samples subjected to $N = 1$ HPT consists of streaks indicating low angle miss-orientation of neighboring grains. The SEAD patterns for samples subjected $N = 5$ and 15 HPT revolutions became continuous rings testifying to a high angle miss-orientation of the majority of grains. Plastic deformation during HPT processing is realized not only by...
dislocation mechanism but also by twinning. Deformation twins were formed mainly in the beginning of HPT straining, see Fig. 7 which shows deformation twins in the sample subjected to $N = 1$ HPT revolution. Further HPT processing causes fragmentation of twins to smaller units.

The HV mapping of HPT deformed samples revealed that HV increases with the radial distance $r$ from the center of the sample disk and also with the number of HPT revolutions $N$. In both cases the increase of HV is caused by increasing strain which rises both with $r$ and $N$, see Eq. (1). This is demonstrated in Fig. 8 which presents HV as a function of the equivalent strain $\varepsilon_{\text{equiv}}$ calculated by Eq. (1). One can see in the figure that HV monotonically increases with $\varepsilon_{\text{equiv}}$ and becomes saturated at $\varepsilon_{\text{equiv}} \approx 146$.

PAS investigations of HPT deformed Mg22Gd samples were performed in the center of the sample ($r = 0.5$ mm), at the half-radius ($r = 3$ mm) and at the periphery ($r = 7$ mm). The lifetimes resolved in the LT spectra are plotted as a function of the equivalent strain in Fig. 9a.

All HPT deformed samples studied exhibited two-component LT spectrum. The shorter component with lifetime $\tau_1 < \tau_B$ represents a contribution of positrons annihilated in the free state. The longer component exhibits lifetime $\tau_2 \approx 250$ ps which agrees well with the lifetime reported for positrons trapped at dislocations in Mg [50]. The component with lifetime $\tau_2$ can be therefore attributed to positrons trapped at dislocations introduced by severe plastic deformation. The intensity $I_2$ of the dislocation component plotted in Fig. 9b increases with the equivalent strain and saturates at $\varepsilon_{\text{equiv}} \approx 500$.

The concentration of defects can be calculated from PAS data using the simple two state simple trapping model (STM) [56]. Within STM the quantity

$$\tau_f = \left( \frac{I_1}{\tau_1} + \frac{I_2}{\tau_2} \right)^{-1},$$

equals to the bulk positron lifetime $\tau_B$. For HPT-deformed Mg22Gd the quantity $\tau_f$ calculated by Eq. (2) agrees within experimental uncertainties to the bulk lifetime of 226 ps measured in the solution treated alloy. This testifies that prerequisite of STM, i.e. presence of single type of uniformly distributed positron traps, is fulfilled in the present case and STM can be used for determination of defect concentration. The mean dislocation density in the sample can be calculated from PAS data using the relation

$$\rho_D = \frac{1}{v_D} \left( \frac{1}{\tau_f} - \frac{1}{\tau_B} \right),$$

where $v_D$ is the specific positron trapping rate for dislocations. Here we used the value $v_D = 10^{-5}$ [52]. Fig. 10 shows the mean dislocation density calculated by Eq. (3) plotted as a function of the equivalent strain. Obviously $\rho_D$ monotonically increases with increasing strain. From TEM observations in Fig. 6 one can very roughly estimate that the order of magnitude of dislocation density in the sample subjected to $N = 15$ HPT revolutions is $\sim 10^{14}$ m$^{-2}$. This is in very reasonable agreement with the results of PAS investigations.

Uniform distribution of dislocations in HPT deformed Mg22Gd alloy can be seen also in TEM micrographs in Fig. 6. This seems to be typical of arrangement of dislocations in hcp metals subjected to severe plastic deformation. Similar arrangement was observed not only in Mg alloys [15,58] but also in HPT-deformed Hf [59] and Ti [60]. Because of limited number of active slip systems in hcp structure dislocations block each other and tangles of dislocations are formed. In contrast severely
Severe plastic deformation introduces not only dislocations but also vacancies created by non-conservative motion of dislocations [31,32,63]. In many metals vacancies are mobile at room temperature and agglomerate into small vacancy clusters which were observed in HPT deformed fcc metals (e.g. Cu [32], Ag [64], Ni [65]) or bcc metals (e.g. Fe [33]). In contrast no vacancy clusters were observed in the present work in HPT deformed Mg22Gd alloy. Dislocations facilitate diffusion of vacancies (pipe diffusion). Hence, a forest of closely spaced dislocations in HPT deformed Mg22Gd alloy enables efficient disappearance of deformation-induced vacancies by pipe diffusion to sinks at grain boundaries.

XRD phase analysis did not reveal any significant variations in phase composition of investigated samples with increasing HPT straining. The quantities of both minor phases Mg46Gd9 and GdH2 determined from the XRD measurements remain within experimental uncertainties same as for the solution treated sample. The lattice parameter $a$ of the α-Mg matrix phase also does not change during HPT processing and corresponds well to the lattice parameter determined for the only pressed sample ($N = 0$). The lattice parameter $c$ increases in the initial stages of the HPT straining between $N = 0$ and $N = 1$ from $c = (0.52173 \pm 0.00002)$ nm to $c = (0.5227 \pm 0.0001)$ nm and does not change with additional HPT straining.

The XRD diffraction pattern of the Mg22Gd alloy subjected to $N = 15$ HPT revolutions is plotted in Fig. 11. The XRD profiles of the HPT-deformed sample are obviously significantly broader compared to those for the solution treated sample (compare Figs. 2 and 11). Broadening of XRD profiles is, in general, caused by the effect of coherently diffracting domain size (crystallite size) and by the effect of lattice deformations (micro-strains) induced by lattice defects. XLPA was applied on XRD profiles and solid line in Fig. 11 shows the model function obtained by the whole powder pattern fitting method using the computer program MStruct [43].

The area weighted mean crystallite size $D$ calculated from the median and variance of log-normal size distribution obtained from fitting of XRD patterns is plotted in Fig. 12 as a function of the equivalent strain. It decreases with increasing strain from $D = (54.4 \pm 2.5)$ nm to $(17.3 \pm 1.9)$ nm.

The evaluation of angularly dependent diffraction profile broadening, caused by micro-strain is more complicated task. At first we assumed that the broadening by lattice deformation is caused exclusively by dislocations. Dislocation density was determined considering the most probable basal slip system for hcp Mg {0001} <1 1 -2 0> [66], and adopting the dislocation contrast factors parameterization given in Ref. [67]. The mean dislocation density determined by XLPA increases with the equivalent strain in similar manner as $\rho_D$ determined by PAS. This is demonstrated in Fig. 13 which compares dislocation densities determined by XRD and PAS normalized to their maximum values. However, the absolute values of $\rho_D$ determined by XRD were in the order of magnitude of $10^{15}$ m$^{-2}$. Such dislocation density is clearly too high (roughly 50 times higher) than those obtained by PAS and estimated by TEM. The explanation of this discrepancy is that in addition to dislocations the XRD profiles are broadened by other lattice distortions which cannot be detected by PAS. Possible candidates for sources of the additional broadening of XRD profiles are either (i) deformation twins or (ii) lattice modulation by short range ordered Gd-rich columns. Formation of short range ordered Gd-rich columns aligned in the [0001] direction was observed in solution treated Mg-Gd alloys artificially aged at relatively low temperatures (150–200 °C) [9,12]. The Gd-rich columns are formed by agglomeration of Gd solutes dissolved in the Mg matrix. Lattice defects (dislocations and vacancies) introduced by HPT deformation facilitate diffusion of Gd solutes. As a consequence the agglomeration of Gd solutes and formation of Gd-rich columns can
be accelerated in HPT-deformed Mg22Gd alloy and might occur already at room temperature. Note that in addition to the effects (i), (ii) there are also other possible sources of micro-strain in the materials subjected to severe plastic deformation: (iii) disclinations formed at junctions of grains contribute to elastic strain in UFG materials. Nevertheless their contribution to elastic strain was shown to be smaller than the contribution of disordered arrays of grain boundary dislocations [68]; (iv) based on comparison of XRD, high resolution TEM and molecular dynamic simulations of nanocrystalline FeMo powder Rebuffi et al. [69] suggested that micro-strain in nanocrystalline materials causing anisotropic broadening of XRD profiles stems not only from dislocations as described by Krivoglaz-Wilkens theory [70,71] but also from boundaries of crystallite domains (so called type II, inter-granular strain, which is homogeneous within a domain) and strains induced by interaction among different domains (so called type III, intra-granular strain, which vary across a domain) [69,72,73]. All these kinds of defects (i)-(iv) cause the broadening of XRD profiles in UFG materials but are “invisible” by PAS. Hence, the dislocation density obtained by means of the Krivoglaz-Wilkens theory is just an upper limit to the true value [69].

Fig. 6. Bright TEM micrographs showing microstructure development of Mg22Gd subjected to N = 1, 5 and 15 revolutions. SAED patterns, (0001) pole, taken from area of 6 µm are shown on the right panels. TEM observations were performed always at half-radius, i.e. in the radial distance from center $r = 5$ mm.
Hence, as a second step of analysis of X-ray line profile broadening the mean dislocation density was fixed at the values determined by PAS and an additional angular dependent diffraction profile broadening component was added. This additional broadening component accounts for the possible micro-strain sources (i)-(iv) described in the previous paragraph. This phenomenological micro-strain was modeled by a symmetric pseudo-Voigt function and Cagliotti polynomial with only $U$ and shape parameter $\eta$ non zero, which are directly connected to the micro-strain [43]. The additional micro-strain component obtained from fitting of XRD patterns is plotted in Fig. 14 as a function of the equivalent strain. From inspection of Fig. 14 it becomes clear that the additional micro-strain remains approximately constant in the beginning of HPT straining ($e_{\text{equiv}} < 10$), subsequently it increases with increasing equivalent strain and finally saturates at $e_{\text{equiv}}$ approaching 1000. Taking into account this development one can exclude deformation twins as possible source of the additional micro-strain because extensive twining occurs in the beginning of HPT processing and with increasing equivalent strain the twinning activity diminishes [74]. Since micro-strain caused by disclinations is too low to explain the observed broadening of XRD profiles, one can conclude that the additional micro-strain contribution stems most probably from the effect (ii) and (iv). It has to be noted that Mg22Gd alloy is not the only hcp material where XLPA yielded higher dislocation density than PAS [57]. For example the dislocation density determined by XLPA in UFG AZ31 alloy prepared by equal channel angular pressing was 5–6 times higher than that obtained by PAS [57]. On the other hand dislocation densities determined by XLPA in UFG metals with fcc or bcc structure where dislocations form a cellular structure were in excellent agreement with the values obtained by PAS [32,33]. This indicates that the discrepancy between XLPA and PAS likely occurs in materials where forests of tangled dislocations are formed because of the additional micro-strain component caused by the effect (iv). This could be a general phenomenon which requires a further systematic study. Nevertheless, the discrepancy between XLPA and PAS has never been as high as in the present UFG Mg22Gd alloy. This indicates that in UFG Mg22Gd alloy the short range ordered Gd-rich columns, i.e. the effect (ii), likely contributes to the broadening of XRD profiles in addition to the effect (iv).
4. Discussion

The yield strength estimated from measured hardness by the well known relation \( \sigma \approx \frac{HV}{3} \) is plotted in Fig. 15 as a function of the equivalent strain. Dislocations introduced by HPT straining lead to work hardening which is proportional to the square root of dislocation density. Hence, the yield strength of a plastically deformed sample can be expressed by the Taylor equation [75]

\[
\sigma = \sigma_0 + M\alpha G b \rho \sqrt{D}
\]

where \( \sigma_0 \) is the yield strength for solution treated Mg22Gd alloy with negligible density of dislocations, \( M \) is the Taylor factor [75], \( G \) is the shear modulus and \( b \) is the Burgers vector of dislocations. The parameter \( \alpha \) expresses the strength of dislocation-dislocation interaction [76].

From inspection of Fig. 15 it becomes clear that \( \sigma \) increases approximately linearly with the square root of dislocation density in accordance with the work hardening mechanism. Linear regression of data in Fig. 15 yielded \( \sigma_0 = (350 \pm 10) \) MPa which is close to the yield strength of \((300 \pm 10) \) MPa determined for the solution treated Mg22Gd alloy.
Hall-Petch relation\[83\] the basal slip system \{0001\} < 11 \overline{2}0 > prismatic \{10\overline{1}0\} < 11 \overline{2}0 > interaction of dislocations. This indicates that during HPT straining the distributed throughout the whole sample.

It is well known that grain refinement makes materials harder since grain boundaries represent obstacles for motion of dislocations and dislocations are piled-up at grain boundaries\[79,80\]. Moreover dislocations are generated at grain boundary ledges and move to grain interiors forming a dislocation forests there\[81\]. When dislocations generated at grain ledges are stopped inside grains at boundaries be-
tween crystallites leaving domains (crystallite interiors) dislocation-free then the dislocation density \(p_d\) is inversely proportional to the mean crystallite size \(D\)[82]. By inserting \(p_d \propto 1/D\) into Eq. (4) one obtains the relation

\[
\sigma = \sigma_0 + k_\text{HP} / \sqrt{D},
\]

where \(k\) is a material constant. Eq. (5) is very similar to the well known Hall-Petch relation [83]

\[
\sigma = \sigma_0 + k_\text{HP} / \sqrt{d},
\]

where \(d\) is the mean grain size and \(k_\text{HP}\) is the Hall-Petch coefficient. The Hall-Petch relation, however, contains the mean grain size \(d\) as a variable while Eq. (5) contains the mean crystallite size \(D\) (the mean size of coherently scattering domains) determined by XLPA.

Fig. 16 shows the yield strength estimated from HV measurements plotted as a function of the inverse square root of the mean crystallite size determined by XLPA. Interestingly linear relationship described by Eq. (5) can be observed in Fig. 16 for larger crystallites but when the crystallite size \(D\) decreased bellow a critical value \(D_{\text{crit}} \approx 30 \text{ nm}\) Eq. (5) does not hold anymore and \(\sigma\) becomes practically independent on the crystallite size. Breakdown in the Hall-Petch strengthening occurring on nano-scale has been reported by many authors in variety of materials\[84–87\]. Typically it occurs when grain size decreases to the range 10–30 nm which agrees very well with the behavior observed in Fig. 16.

Linear regression of the data in Fig. 16 in the region \(D > D_{\text{crit}}\) where Eq. (5) holds yielded \(k = (30 \pm 2) \text{ MPa} \mu\text{m}^{-1/2}\) and \(\sigma_0 = (320 \pm 10) \text{ MPa}\). The latter value is in good agreement with the yield strength of the solution treated alloy. The slope \(k\) of the strengthening Eq. (5) obviously cannot be compared with the Hall-Petch coefficients since the crystallite size \(D\) is usually substantially smaller than the grain size \(d\) used in the Hall-Petch relation. To get a very rough estimation of the Hall-Petch coefficient one can consider Mg22Gd sample deformed by 5 HPT revolutions which exhibits the mean grain size \(d = 450 \text{ nm}\) (estimated by TEM) and the mean crystallite size \(D \approx 30 \text{ nm}\) (determined by XLPA). Hence, \(k_\text{HP}\) should be roughly \((450/30)^{1/2} \approx 4\) times higher than \(k\). This results in \(k_\text{HP} \approx 120 \text{ MPa} \mu\text{m}^{-1/2}\), which falls to the range 100–300 MPa \(\mu\text{m}^{-1/2}\) commonly reported for the Hall-Petch coefficients in Mg alloys [88]. Hence, the present simple analysis indicates that breakdown in the Hall-Petch strengthening is determined by the crystallite size \(D\), i.e. the size of coherently diffracting domains, representing a measure of the average size of structural units of the material with lattice not distorted by defects. Similar result was obtained in Ref. [87] where the crystallite size \(D\) was also used as a variable in the Hall-Petch relation. This finding might also explain the Hall-Petch breakdown observed in extruded Mg already when grain size decreased below 5 \text{ µm}\ [89], i.e. for grains much coarser than 10–30 nm range found in fcc and bcc metals [87]. Although extruded Mg exhibited grain size of a few \(\mu\text{m}\) these grains likely consisted of domains (crystallites) with size in the nanocrystalline range.

5. Conclusions

The results obtained in the present work can be summarized as follows

(i) Structure of solution treated Mg22Gd alloy was refined by HPT at ambient temperature. A homogeneous UFG structure with the mean grain size of \(\approx 300 \text{ nm}\) was achieved after 15 HPT revolutions.

(ii) Enhanced strength of UFG Mg22Gd alloy can be explained by work strengthening by tangled dislocations forming a dense forest throughout grains.

(iii) In addition to dislocations there is an additional source of microstrain causing broadening of XRD profiles. This additional broadening can be attributed to lattice modulation by Gd-rich nano-rods formed by dislocation-assisted agglomeration of Gd solutes and to strains arising from boundaries of crystallite domains and induced by interaction among different domains.

(iv) A breakage of the Hall-Petch strengthening was observed when the crystallite size of UFG Mg22Gd alloy decreased below a critical value of \(\approx 30 \text{ nm}\).

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