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Microstructural Characterization of Cold-Worked Lead (Pb) Powder by X-Ray Diffraction Line Profile Modelling

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ABSTRACT

Microstructural parameters for plastically deformed (hand-filed) and annealed lead (Pb) powders are investigated in terms of X-ray diffraction profile fitting analysis. Like the case of Pb-Bi binary alloy systems in α-phase the net deformation stacking fault probability is very small. The values of area averaged crystallite size and dislocation density is comparable with vapour deposited Pb film [3]. From modified W-A analysis the value of dislocation density (ρ) is found out to be of the order of 10^{15} m^{-2} and that from multiple whole profile (MWP) analysis is of the order of 10^{13} m^{-2}. A disagreement in case of cold-worked powders between MWP fitting of Fourier coefficients and modified W-A analysis is observed. Comparable to MWP procedure the modified W-A analysis provides a better result indicating the importance of dislocation microstructure in the analysis procedure. The type of dislocation is found to be predominantly of screw, $\langle 100 \rangle$ type dipoles for cold-worked and edge type in annealed powders respectively. The dislocation arrangement found to be more correlated in cold-worked powders compared to annealed powders.

Keywords: X-ray line profile analysis, Anisotropic Strain Broadening, Dislocation induced strain broadening, Dislocation contrast factor.

1. Introduction

The interpretation of X-ray diffraction pattern from deformed metals and alloys is the subject of research for the last few decades. The shift and broadening of X-ray diffraction lines has been related to changes in lattice parameter, presence of stacking and twin faults probabilities, residual stresses, small coherent domains, micro strains, compositional inhomogenieties, dislocations, etc. in the sample. The above parameters are generally related to some X-ray line profile parameters like peak FWHM (full width at half maxima), integral breadth, asymmetry, variance, centroid, Fourier transform, etc. Methods frequently used for analysis such as conventional Warren-Averbach (W-A) [18], Williamson-Hall (W-H) [20] method and peak-shift analysis method [17] provide information regarding one or more defect related parameters as described earlier [2,6]. But, all these methods suffer from certain simplifying assumptions. However, any interpretation about the microstructure of deformed materials is difficult from those

methods. For example, the shape of strain-broadened profile for dislocated crystal depends on the extent of inhomogeneity of dislocation distribution [19]. Recent theoretical formulation of X-ray diffraction line profile based on theoretical functions is more amenable to practice [8, 11, 9]. The method of Whole Pattern Fitting provides a more direct interpretation of material microstructure which may be complementary to the direct imaging techniques (such as TEM). However, a comparison with conventional methods (W-A and W-H) should be encouraged in order to investigate the discrepancies in such methods. In such cases analysis based on modified W-H and/or modified W-A which more rigorous can be advantageous. In the present communication we investigated cold-worked Pb using all the available methodologies to assess the extent of their applicability.

2. Experiment and data analysis

Cold-worked and annealed Lead powder was prepared from spectroscopically pure Lead bar of (99.99 % of purity) from Sigma-Aldrich, U.K. [4]. The cold-worked powder was annealed at ~ 250^0C ($\pm$ 10^0C) for 10 hours. Specially prepared poly-crystalline Si powder was used to eliminate the effect of instrumental broadening [1]. Data collection process in step scan mode for both the cold-worked and annealed powders was done by a highly stabilized Philips 1130 X-ray generator attached to a PW 1710 diffractometer and the procedure of data collection and method of analysis can be found else-where and the references therein [4].

3. Results and discussion

3.1. X-ray diffractogram

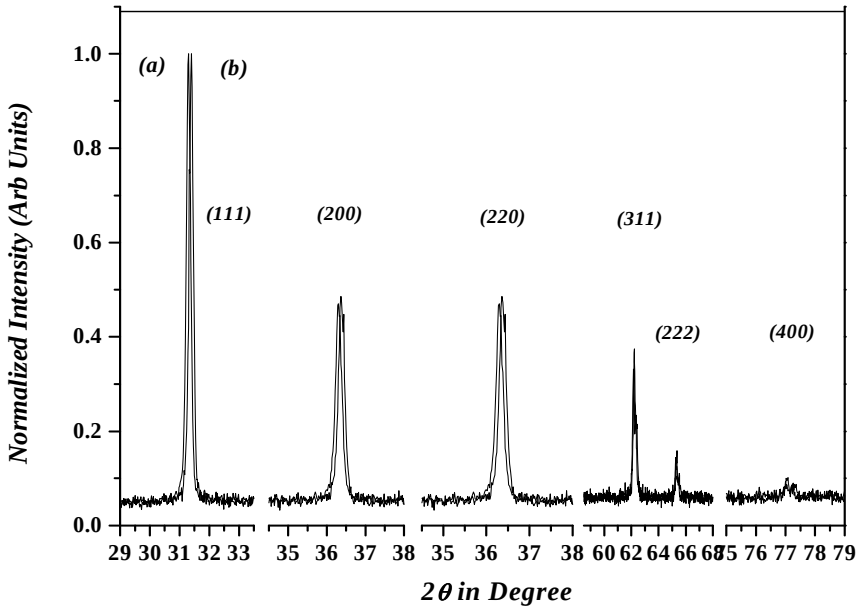

Figure 1: Normalized X-ray diffraction pattern for (a) cold-worked and (b) annealed Pb powder specimen for first six Bragg reflections.

Figure 1 shows the normalized X-ray diffraction pattern for both cold-worked and annealed lead powder. It is observed that the peaks remain unaltered for both the cold-worked and annealed samples indicating that the effect of cold-working is very small and significant recovery takes place immediately after cold-working. Similar phenomenon was observed in case of Pb-Bi binary alloy systems in α-phase [5]. Further the peaks are shifted towards higher diffraction angle due to annealing.

The result of peak shift analysis as described in [17] shows very small presence of deformation stacking fault probability (α=2.0×10^{-4}) and complete absence of residual stress in the powder sample. The lattice parameter is calculated from the respective peak positions of both the cold-worked and annealed samples. The extrapolated values of the lattice parameter obtained from the $\cos\theta\cot\theta$ plot reveals that there is no significant change in lattice parameter upon cold-working (a_{cw}=0.495 nm (±8.27×10^{-5}nm)), a_{ann}=0.495nm (±6.12×10^{-5}nm)).

3.2. Conventional Williamson-Hall analysis

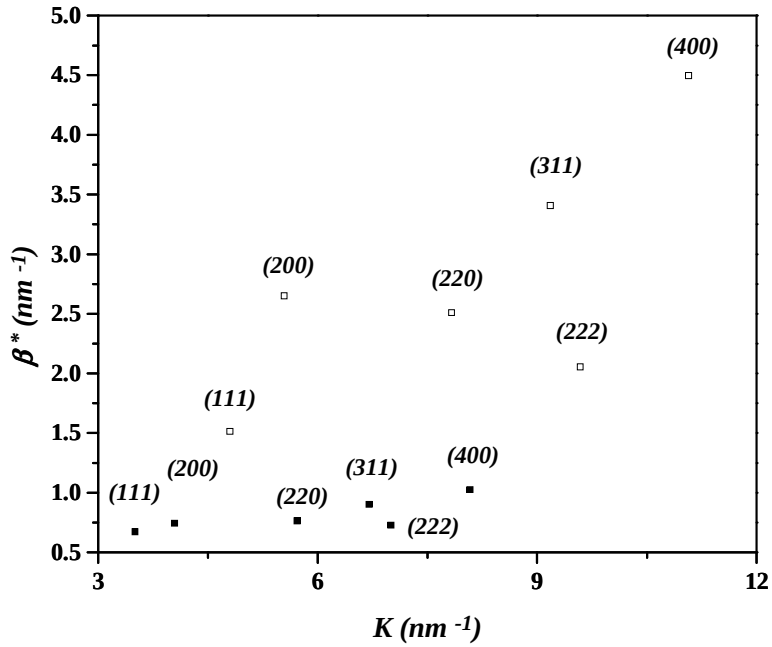

Figure 2:

Conventional Williamson-Hall plot for ■ cold-worked lead and □ cold-worked copper powder

The conventional Williamson-Hall plot corresponding to integral breadth for both cold-worked and annealed lead powders is shown in figur.2. The plot shows prominent anisotropic peak broadening in cold-worked lead. Further, the global increase of integral breadth with diffraction vector (*K*) indicates the presence of lattice distortion.

It is noticed in the conventional W-H plot that the integral breadths shows more anisotropic nature in cold-worked copper than in cold-worked lead powder indicating that the dislocation induced anisotropic line broadening in lead is much smaller than that of copper powder, lead *(A_i =3.910)* is elastically more anisotropic than copper *(A_i =2.207)*.

The progression of broadening is indicative of dislocation induced line broadening in accordance with earlier studies on different materials [9, 4, 12, 13, 14, 15, 10]. A preliminary idea about the type of dislocation present in the samples can be estimated from the value of the parameter *q* obtained from integral breadths and Miller indices [12]. For lead powders the value of *q* was obtained to be 2.024 and 1.460 for annealed lead samples. The theoretical values of *q* are 2.47 for pure screw and 1.64 for pure edge dislocation in lead respectively. This signifies that in cold-worked samples the dislocation may have a mixed character with equal screw and edge component where as for annealed samples it may be predominately edge type. The present result differs from cold-worked copper where a more screw character has been observed [4].

3.3. Modified Williamson-Hall analysis

The modified W-H analysis for both the samples was done according to the method suggested by Ungar and Borbely [16]. Due to negligible presence of deformation stacking fault probability (α) correction due additional broadening is not taken into account. The modified W-H plot for cold-worked and annealed samples are shown in figure 3. It is observed from the plot that integral breadths follow a smooth quadratic behavior for both the cold-worked and annealed samples with the new scaling parameter $K^2\overline{C}$. For a dislocated crystal the integral breadths is expressed according to the relation [19],

$$\beta = \frac{1}{\langle L \rangle_v} + A(K^2\overline{C}) + B(K^2\overline{C})^2 \tag{1}$$

where *A* and *B* are constants which depends on burgers' vector, dislocation density, dislocation dipole polarization and effective outer cut-off radii of dislocation distribution. For dislocated crystals with weak defect correlation the integral breadth can be written in the form [3].

$$\beta = \frac{1}{\langle L \rangle_v} + \frac{1}{2}(\rho\xi^2 b^2 \ln P)K^2\overline{C} \tag{2}$$

where, $\xi = \left[1 + \frac{\ln(\ln P)}{4\ln P}\right]^{-1}$ and $P \approx 3M \approx \frac{3}{\sqrt{\pi \ln 2}}(\beta_G/\beta_C)$

and M is the dislocation arrangement parameter. Equation (2) reveals a nearly linear dependence.

The non-linearity in the plot of β with $K^2\overline{C}$ indicates the non-randomness of dislocation structure and possible dipole polarization. Fig 3 indicates that this may be the case in the present sample. The average volume weighted crystallite size $\langle L \rangle_V$ is obtained by extrapolating the curve to $K^2\overline{C}$ = 0 and comes out to be 87 nm for the cold-worked and 157 nm for the annealed sample.

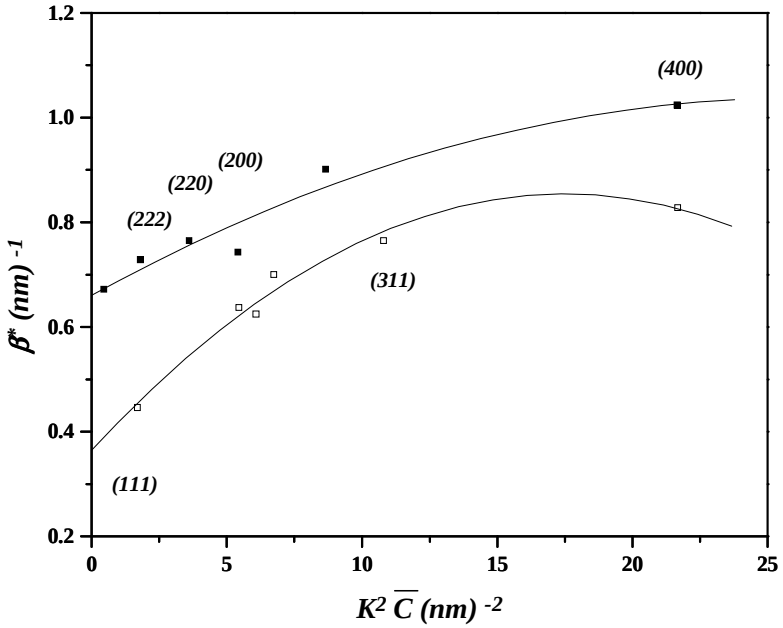

Figure 3: Modified Williamson-Hall plot for ■ cold-worked and □ for annealed lead powder.

The dislocation density can be calculated from equation (2) if the Cauchy and Gaussion components of the integral breadth for each profile is known. In the present case it is observed that the profile shape is of Cauchy type indicating some correlation in the dislocation distribution may exist in the present study. So value of ξ could not be determined as described and is obtained by setting the dislocation arrangement parameter (M) to be 1 signifying a non-correlated random dislocation distribution. The dislocation density was obtained to be 5.34 X 10^{16} m^{-2} according to equation (2). Such a high value of dislocation density obtained from modified W-H analysis may be due to the inadequacy of restrictedly random dislocation distribution model assumed in the method.

3.4. Multiple whole pattern fitting analysis

A more physically based process for evaluation of microstructure of materials is multiple whole pattern (MWP) fitting of Fourier coefficients [7]. The model involves *ab*-initio size and strain functions for the assumed dislocation distribution. The normalized Fourier coefficients for the first six Bragg reflections were fitted simultaneously using the software MWP [7]. Figure (4) shows the fitting results. The dislocation density (ρ), effective outer-cut-off radius of dislocation distribution (R_e) where, $R_e = (exp2)R_e^*$, the median (m) and the variance (σ) of log-normal size distribution of spherical crystallites and the dislocation type factor (q) are refined through the program. The results are shown in table 1. It is observed from figure 4 that in case of cold-worked lead the true specimen broadening is underestimated indicating that restrictedly random distribution may not be

a proper choice. This is also reflected in the refined value of *(q)* and dislocation density *(ρ)*. A much better fit is observed in case of annealed lead sample. It is observed that the value of the parameter *q* obtained from the MWP fit is 2.67 for cold-worked and 1.76 for annealed lead powder specimens respectively which differs significantly from the result of modified W-H analysis.

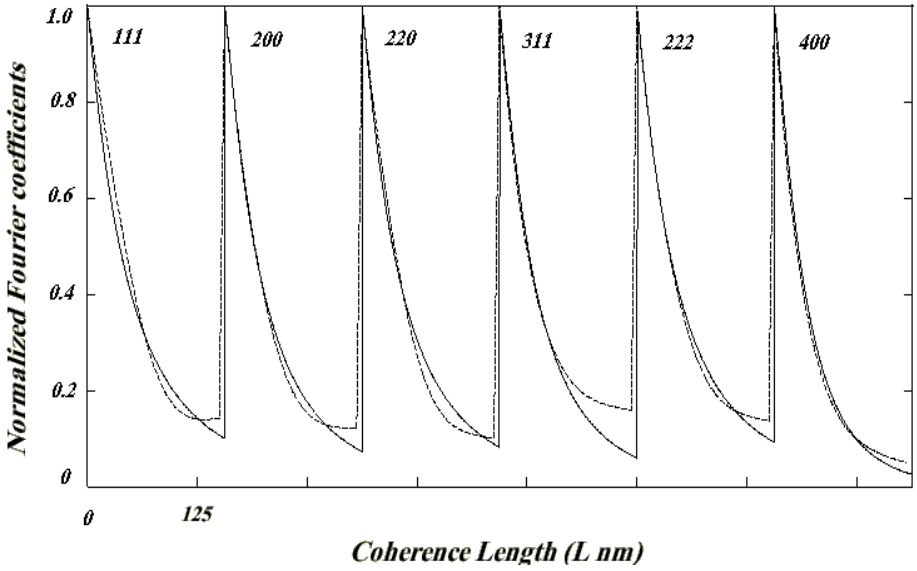

Figure 4: (a)

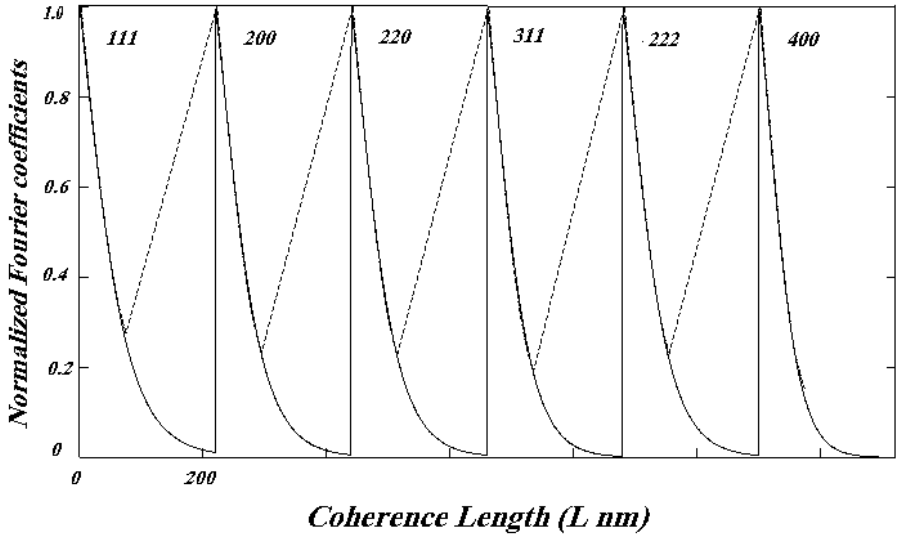

Figure 4: (b)

MWP fitting of 4(a) cold-worked and 4(b) annealed lead powder. Dotted line represents experimentally calculated and solid line represents theoretically obtained Fourier

transforms. Maximum fitting range $|L|_{max}$ = 125 nm for cold-worked and $|L|_{max}$ = 200 nm for annealed lead powders.

Table 1: Microstructural Parameters from MWP-fit of Fourier coefficients

Parameters	*Cold-worked Pb*	*Annealed Pb*
m (nm)	8.93	65
σ	0.89	0.5
q	2.67	1.76
ρ $10^{13}\,m^{-2}$	8.0	1.22
R_e (nm)	183.4	952.3
μ	1.64	3.33
Reliability Factors (Final SSR)	0.638	0.023
$\langle L \rangle_A$ (nm)	44	80
$\langle L \rangle_V$ (nm)	109	115

This nature of dislocations produced during cold-working is quite similar to that of cold-worked copper [4]. However, the dislocation microstructure of cold-worked lead and copper may differ significantly as is evident from MWP fitting results.

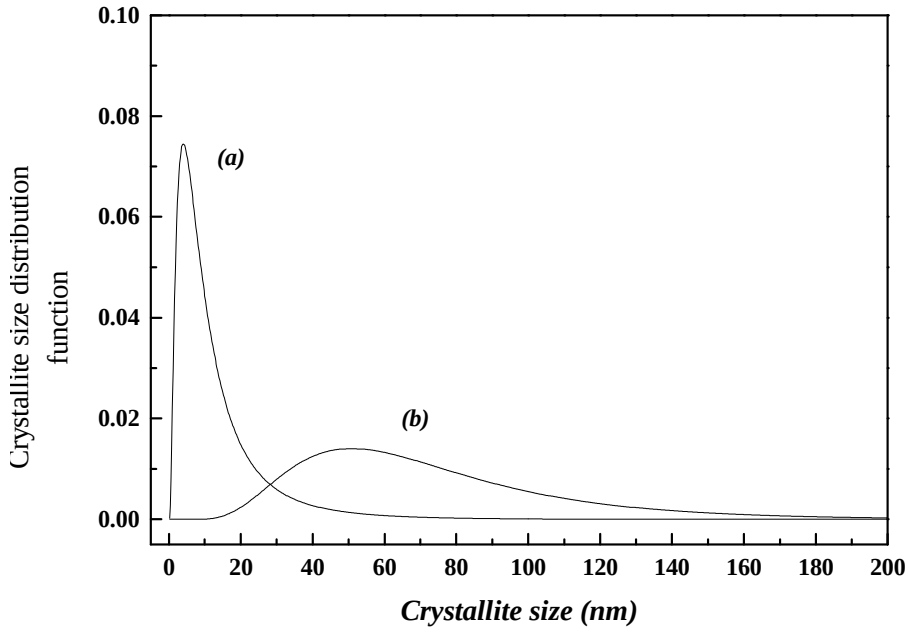

Figure 5: Crystallite size distribution for (a) cold-worked and (b) annealed lead powder sampled

The dislocation density is of the order of 10^{13} m^{-2} for cold-worked lead specimen and decreases with annealing. The average dislocation separation $\rho^{-1/2}$ is 111 nm for cold-worked sample and is equivalent to the volume averaged crystallite size indicating that crystallites possibly represent sub-grains. Further the dislocation arrangement parameter (μ) is 1.64 and 3.3 for cold-worked and annealed sample respectively. Table 1 further lists the parameters defining the crystallite size distribution. Both the median and the variance of size distribution for cold-worked lead is smaller than that for annealed lead sample showing a narrow size distribution for cold-worked sample compared to the annealed one. It has been shown [11] that the size values obtained from X-ray are comparable to the sub-grain size obtained from TEM. Similar explanation may be possible in our case also.

Figure 5 shows the crystallite size distribution obtained for both cold-worked and annealed lead specimen. The volume and surface weighted crystallite size $\langle L \rangle_V$ and $\langle L \rangle_A$ respectively are also shown in table 1. The value of $\langle L \rangle_V$ differs considerably from the value as obtained from modified W-H analysis.

3.5. Modified Warren Averbach analysis

The integral breadths (β^*) in modified W-H analysis follow a smooth quadratic behavior with the scaling parameter $K^2\overline{C}$. But the dislocation density as obtained from there shows a large difference with that obtained from MWP procedure.

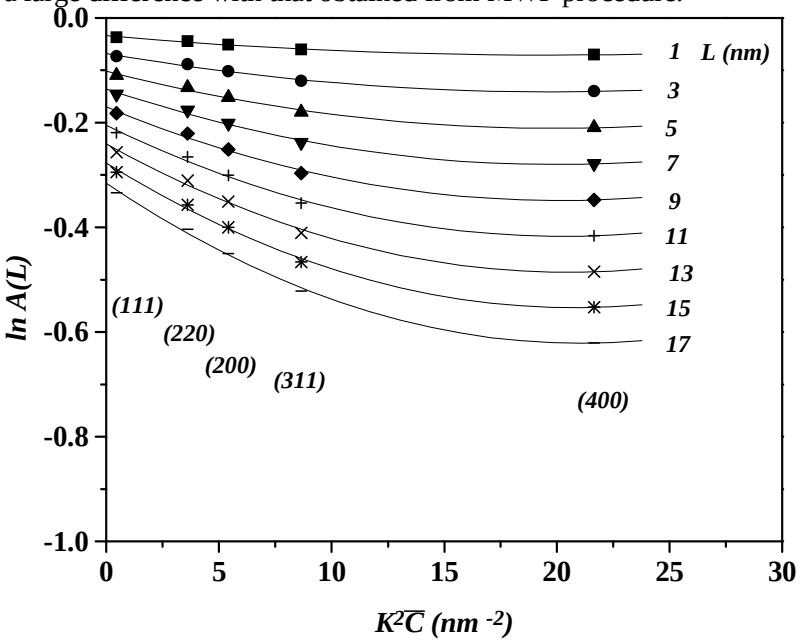

Figure 6: A typical modified Warren-Averbach plot of cold-worked lead powders

This may be due to difference in assumptions involved. In order to investigate it a detail modified Warren-Averbach analysis has been done according to the following relation,

$$\ln A(L) \cong \ln A^S(L) - \frac{\pi a^2}{4}\rho L^2 \ln\left(R_e/L\right)K^2\overline{C} + O(K^2\overline{C})^2 \quad (3)$$

A typical modified W-A plot for the cold-worked lead powder is shown in figure 6. The values of area averaged crystallite size $\langle L \rangle_A$, effective outer cut-off radius of dislocations (R_e), dislocation density (ρ) and dislocation arrangement parameter (μ) are obtained from the plot. The value of $\langle L \rangle_A$ obtained for cold-worked sample is 57.6 nm and the value of dislocation density is obtained as 2.4 x 10^{15} m^{-2} which is in close agreement with that obtained for vapour deposited lead-film [3] and are listed in table 2. Also the dislocation arrangement parameter becomes 6.26 in the case if cold-worked sample.

Table 2: Microstructural parameters obtained from modified Warren-Averbach procedure for cold-worked lead powders

$\langle L \rangle_A$ (nm)	$\rho\ 10^{15}$ m^{-2}	R_e (nm)	μ
57.6	2.43	12.69	6.26

A disagreement with the earlier observation of nonlinear W-H analysis and MWP analysis is noticed. The plot of MWP fitting for cold-worked sample shows a notable misfit between the experimentally obtained and theoretical Fourier coefficients and also the rate of decrease of theoretical Fourier coefficients is faster than calculated ones signifying that the theoretical broadening is smaller than the actual observed broadening which in-turns indicates a less dislocation density. However, a better agreement in modified W-A analysis indicates the importance of dislocation microstructure in the analysis procedure.

4. Conclusion

Plastically deformed (hand filed) and annealed lead powder specimen was studied in terms of theoretical physical microstructural-model of spherical crystallites (having a log-normal size distribution) and a restrictedly random dislocation distribution. A high value of q factor indicates that the type of dislocations may be predominantly of screw type present in the cold-worked sample whereas, edge type dislocation prevails in the annealed specimens. Annealing produces a decrease in dislocation density. It is observed that modified Warren-Averbach analysis yields much acceptable results compared to Multiple Whole Pattern fitting using a restrictedly random dislocation distribution.

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