Line profile analysis of ODS steels Fe$_{20}$Cr$_{5}$AlTiY milled powders at different Y$_2$O$_3$ concentrations

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Abstract. Mechanical properties of material are largely dictated by constituent microstructure parameters such as dislocation density, lattice microstrain, crystallite size and its distribution. To develop ultra-fine grain alloys such as Oxide Dispersion Strengthened (ODS) alloys, mechanical alloying is crucial step to introduce crystal defects, and refining the crystallite size. In this research the ODS sample powders were mechanically alloyed with different Y$_2$O$_3$ concentration respectively of 0.5, 1, 3, and 5 wt%. MA process was conducted with High Energy Milling (HEM) with the ball to powder ratio of 15:1. The vial and the ball were made of alumina, and the milling condition is set 200 r.p.m constant. The ODS powders were investigated by X-Ray Diffractions (XRD), Bragg-Brentano setup of SmartLab Rigaku with 40 KV, and 30 mA, step size using 0.02$^\circ$, with scanning speed of 4$^\circ$min$^{-1}$. Line Profile Analysis (LPA) of classical Williamson-Hall was carried out, with the aim to investigate the different crystallite size, and microstrain due to the selection of the full wide at half maximum (FWHM) and integral breadth.

1. Introduction
ODS steels have been considered as the structural materials future nuclear reactor Gen. IV [1-3]. Primary features of the ODS steels are high oxidation resistance at high temperature [4], high creep resistance [5], and resistance to high dose of particle irradiation [6]. ODS steels are commonly produced by mechanical alloying (MA) of the constituent metal powder. MA is preferred due to its ability to develop alloy with fine grain. It is generally accepted that the finer the grains or particles, the stronger the materials.

Additionally, MA could introduce microscopic features such as hard precipitates, dislocation density enhancement, micro plasticity, which contribute to the superior mechanical properties. However, there is a trade of between high oxidation resistance, and the mechanical performance. Thus, to accommodate the oxidation resistance, and mechanical properties, additional rare earth materials are needed. ODS steels are developed with small amount of Y$_2$O$_3$, normally between 0.5-3 wt%, but sometimes can be added between 5-15 wt% [7].

The role of rare earth materials such as Y$_2$O$_3$ has not been very well documented, especially during the process of MA. With high milling energy, and long period of milling time, there were many investigations showed the formation of Y-Ti-O nano-precipitate [8]. In this study, the role of different addition of Y$_2$O$_3$ is investigated. XRD line profile analysis (LPA) is valuable methods to evaluate the
crystallite size, and other crystal defects formation. Unlike Transmission Electron Microscopy (TEM) analysis, XRD could be carried out faster without sumptuous sample preparation. LPA based on XRD investigation takes into account the broadening of the diffraction peaks. The peak shape, the diffraction position, and the intensity of XRD profile give valuable information regarding the microstructure of materials and its feature.

The aim of this paper is investigating the crystallite size evolution, and lattice distortion using simple Williamson-Hall analysis. The LPA of XRD data was performed, and the determination of the peak shape was compared between Full-Width at half maximum (FWHM) and integral breadth.

2. Experimental Procedure

2.1. XRD measurement

The metal powder of Fe20Cr5AlTiY ODS steels was purchased from Sandvik Material Technology LTD, with the particle size of about 106 μm as received from manufacturer. The metal powder was manufactured by gas atomized process, with chemical composition as received shown at table 1 below.

| Element | Cr | Al | Ti | Ni | Mn | Y | Cu | Fe |
|---------|----|----|----|----|----|---|----|----|
| Mol%    | 17.2 | 6.6 | 0.58 | 0.47 | 0.36 | 0.097 | 0.097 | balanced |

MA process used planetary ball milled (PBM) of MTI Corp. There were 4 variances with different Y2O3 concentration, respectively of 0.5, 1, 3, and 5 wt%. The ball to powder ratio (BPR) was kept constant 15:1, using alumina ball of 10mm, and 20gr of mixed sample powder was placed inside tightly sealed alumina jars of 320 mL capacity. The MA was carried out for 24h, in which each cycle of MA took 4h, and 30 min paused to prevent excessive heating. After MA was finished, the ODS powder was examined by XRD using the machine of Smartlab, Rigaku operated at 40 KV, and 30 mA. Structural investigation used Bragg-Brentano setup, with Cu anode tube producing x-ray with λ=1.5419 Å. The scanning XRD covers 2θ from 20–120°, with scanning rate 4° min⁻¹ and step size 0.02°.

2.2. Line profile analysis

The first approach of LPA was introduced by Scherer [9] which characterize the apparent domain size that is a volume-weighted quantity,

\[
t = \frac{\gamma \lambda}{FWHM} \cos \theta
\]

where γ is constant close to unity, FWHM is full width at half maximum of the peak, θ is the Bragg angle at \([h k l]\) reflection. Though this formula was introduced in 1918, the Scherrer is still largely employed nowadays. Later, Wilson [10] defined the integral breadth of the apparent size:

\[
< D >_v = \frac{\gamma \lambda}{\beta} \cos \theta
\]

where the integral breadth \(\beta = \frac{A}{I_o}\), A is the peak area, \(I_o\) is the height of peak intensity. If the broadening due to sole strain effect, Stokes and Wilson [14] defined the relation between integral breadth and strain as

\[
\eta = \beta \cot \theta
\]

\[
e = \frac{\eta}{4} = \frac{\beta}{4} \tan \theta
\]
where $e$ is the maximum strain, and $\eta$ is the apparent strain. In many cases, line broadening is caused by simultaneous strain and crystallite size, therefore, those two effects has been combined by Williamson and Hall [11]. The Williamson-Hall (WH) plot proposed the correlation that sample broadening is the sum of the broadening due to crystallite size, and lattice strain.

$$\Delta K = \Delta K^s + \Delta K^D$$  \hspace{1cm} (5)

where $\Delta K^s$ and $\Delta K^D$ represent the broadenings affected by crystallite size, and lattice distortion respectively. If $\Delta K=\cos \theta(\Delta 2\theta)/\lambda$, and the diffraction vector $K = 2 \sin \theta/\lambda$, thus the linear plot between those value will have the intercept as the crystallite size ($\gamma /<Dv>$), and the slope represent the lattice distortion ($2\eta$). The expression of $\Delta 2\theta$ can be replaced by FHWM or $\beta$, which will influence the determination of $\gamma$, 0.94 for FWHM, and 1 for breadth $\beta$. Despite WH plot is very simple to obtain the crystallite size and the microstrain, the application is still widely used [12-14].

Calculation of the broadenings require two basic inputs for LPA analysis, first is the position of the peak and the second is the precise value of the FWHM, and $\beta$. In this paper, the determination of the peak position, FWHM or $\beta$ was done from the Rietveld analysis of the PDXL software. The phase found in the XRD profile from the ODS steels, are cubic Fe-Cr with space group number 229, Im-3m.

From the Rietveld analysis, the background was simulated with Chebyshev I, and the shape function of Pseudo-Voigt, which is combination of the Gauss and Lorentz.

3. Results

Each of the XRD profile was analysed with Rietveld refinement, and limited parameters were varied such as U, V, W for the description of the shape function. The result of the Rietveld analysis is shown in figure 1. The selection of the shape function is crucial, since it determines the best fitting that can be obtained for the XRD data. The Pseudo-Voigt function is generally preferred due to the combination of Gauss and Lorentz that can simulate the wide broadening and peak intensity.

![Figure 1. The Rietveld refinement of ODS Pure exhibiting 5 peaks, and the different shape functions.](image-url)
The broadening of each XRD profiles is shown in the figure 2, using Cagliotti function. This function is described as $FWHM = \sqrt{U \tan^2 \theta + V \tan \theta + W}$, which the U, V, and W parameters taken from Rietveld refinement, and the $\theta$ is the position of the peaks.

![Figure 2. The broadening of XRD profile described by Cagliotti Function](image)

The broadening can be firstly identified by the plot of $FWHM$ vs $2\theta$, which explain the trend of the broadening. The higher FWHM corresponds to the smaller crystallite sizes, and the larger microstratation. However, from figure 3 the most broadening is shown from the sample with 0.5 wt%, followed by 1 wt%, 3wt%, and 5 wt% of the $Y_2O_3$ concentration when subjected to the 24h mechanical alloying. It was generally accepted that applying the longer MA process, would result the smaller crystallite, and the larger microstrain [15].

Finally by applying the least square fitting of Eq. 5, it is obtained the WH plot as shown in figure 3 below.

![Figure 3. Williamson-Hall Plot for different $Y_2O_3$ concentration.](image)

4. Discussion

The description of WH plot shows that the intercept corresponds to the crystallite size $<D>$, while the slope corresponds to the microstrain ($\eta$). It was shown in the figure 1, the peak at $d_{hlh}(310)$ has the lowest, and almost indistinguishable between the peak and the background. Therefore, for the calculation of the crystallite size, and microstrain the peak at $d_{hlh}(310)$ was excluded. The calculation
of the sample broadening has to include the contribution of the instrument broadening. In this study the instrument broadening was assessed with the sample standard, and compared to the broadening of the ODS pure. The sample without any significant broadening due to small crystal size and microstrain will have horizontal linear fit according to figure 3. Finally, after the subtraction of the instrument broadening, it is obtained the value the crystallite size, and microstrain as shown figure 4 below.

![Figure 4. The trend of the \(<D>\), and \(\eta\) at different \(Y_2O_3\) concentration](image)

The lowest crystallite size was obtained at 0.5 wt% \(Y_2O_3\), followed by 1%, 3%, 5% and ODS pure. Both FWHM and \(\beta\) exhibited similar trend for crystallite. However, the figure of microstrain requires further analysis since the source is mainly the dislocation enrichment, and other crystal defects that may present after mechanical alloying. The result of the W-H plots for all samples finally shown in table 2.

| Sample (wt% \(Y_2O_3\)) | FWHM | \(<D>\) (nm) | \(\eta\) (%) | \(<D>\) (simple) | \(\eta\) (%) |
|--------------------------|-------|----------------|-----------|-----------------|-----------|
| 0                        | 146.15| 0.0349         | 102.96    | 0.0595          |
| 0.5%                     | 19.23 | 0.0281         | 14.53     | 0.0250          |
| 1%                       | 19.75 | 0.0177         | 15.17     | 0.0224          |
| 3%                       | 22.12 | 0.0427         | 16.62     | 0.0653          |
| 5%                       | 24.76 | 0.0252         | 18.76     | 0.0306          |

The correlation of the crystallite size and the broadening is shown in figure 5 using two primary peaks. In general the crystallite size from Breadth calculation is bigger while the microstrain is lower. The discrepancy shows that accurate determination of peak intensity and broadening is crucial, and in this case, FWHM term is more precise than simple Breadth.

The decreasing of the intensity is clearly visible at \(dhkl\) (110) especially the XRD profile with 1 wt% and 0.5 wt% \(Y_2O_3\) is at the lowest. The loss of the intensity is mainly correlated to the decreasing crystallite size which is confirmed from table 2 above. The intensity and broadening from 3 wt% \(Y_2O_3\) is significantly the largest, but the peak intensity of it is lower than 5 wt% \(Y_2O_3\) at \(dhkl\) (210). This particular behaviour explains the negative slope of WH plot in figure 3. Furthermore, the broadening of the sample after 24h, with various \(Y_2O_3\) concentrations shows small discrepancy. Thus, it can be concluded that different concentration of \(Y_2O_3\) influence the refinement of the crystallite, which hold the dominant source of the broadening.

The crystallite size is smaller with small amount of \(Y_2O_3\) concentration. This phenomenon could be explained that the \(Y_2O_3\) lattice does not stay intact during MA. During high energy milling, broken Y and O could possible interact with Ti, due to easy solubility to construct Y-Ti-O nanoclusters [16-17].
The critical concentration of $Y_2O_3$ might be limited to 1 wt%, which is adequate to possibility form Y-Ti-O nanocluster. The size of nanocluster is around 10 nm, so then when the excessive $Y_2O_3$ concentration will not produce Y-Ti-O due to limited amount of Ti atoms. The detection of the Y-Ti-O with XRD is very difficult due to the limited resolving power, thus further analysis is needed using TEM to detect the diffraction of Y-Ti-O phases.

5. Conclusions
Line Profile Analysis based on XRD is useful method to get insight of the microstructure especially for the determination of the crystallite size and crystal defects. WH plot is adequate to characterize the crystallite size of the ODS powder after high energy milling. The calculation of the crystallite size using FWHM with Pseudo-Voight model is more accurate than simple Breadth. However, the microstain is difficult to be investigated because the source of microstrain is not incorporated in the model.

References
[1] Ukai S, Harada M, Okada H, Inoue M, Nouruma S, Shikakura S, Asabe K, Nishida T and Fujiwara M 1993 J. Nucl. Mater. 204 65-73
[2] Baluc N, Gelles D S, Jitsukawa S, Kimura A, Klueh R L, Odette G R, van der Schaaf B and Yu J 2007 J. Nucl. Mater. 367-370 33
[3] Ukai S and Fujiwara M 2002 J. Nucl. Mater. 307-311 749-57
[4] Kaito T, Narita T, Ukai S and Matsuda S 2004 J. Nucl Mater. 329-333 1122-6
[5] Klueh R.L, Maziasz P.J, Kim I.S, Heatherly L, Hoelzer D.T, Hashimoto N, Kenik E.A and Miyahara K 2002 J. Nucl Mater. 307-311 773-7
[6] Ukai S, Kaito T, Seki M, Mayorshin A A and Shishalo O V 2005 J. Nucl. Sci. Technol. 42 109-22
[7] Kimura Y, Takaki S, Suejima S, Uemori R and Tamehiro H 1999 ISIJ Int. 39 176–82
[8] Yamashita S, Ohtsuka S, Akasaka N, Ukai S and Ohnuki S. 2004. Philos. Mag. Lett. 84 525-29
[9] Scherrer P. 1918 Nachr. Ges. Wiss. Gottinge. 98-100
[10] Wilson A C J 1963 Mathematical Theory of X-ray Powder Diffractometry (Eindhoven: Centrex Pub. Co.)
[11] Williamson G K and Hall W H 1953. Acta. Metall. 1 22-31
[12] Khorsand Zak A, Abd. Majid W H, Abirshami M E and Yousefi R 2011 Solid State Sci. 13(1) 251-56
[13] Prabhu Y T, Rao K V, Kumar V S S and Kumari B S 2014 World J. Nano Sci. Eng. 4 21-8
[14] Mote V D, Purushotham Y and Dole B N 2012 J. Theor. Appl. Phys. 6:6
[15] Longzhou Ma, Bruce S J K, Mary A A and Huang C C 2014 KONA Powder Part. J. 31 146
[16] Hirata A, Fujita T, Wen Y R, Schneibel J H, Liu C T and Chen M W 2011 Nat. Mater. 10 922
[17] Stoica G M, Stoica A D, Miller M K and Ma D 2014 Nat. Commun. 5 5178