Synthesis and Phases Characterization of Fe-Cr ODS (Oxide Dispersion Strengthened) Steel Using X-ray Diffraction Technique

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Abstract. The formation of Fe-Cr alloy phase was analyzed using X-Ray Diffraction (XRD) technique to improve the synthesis process of the Oxide Dispersion Strengthened (ODS) steel. Synthesis of the ODS steel was performed using powder metallurgy method with a difference milling time of 3 hours, 5 hours and 7 hours. The phase composition and structure parameters of the Fe-Cr phase was analyzed by processing the diffraction data using the software of Rietveld refinement HighScore Plus. The crystallite size and micro-strain of the alloy was calculated by the Williamson-Hall equation plot method. Results of the refinement analysis showed that the Fe-Cr alloying process has been successful for samples with milling time of 3 and 7 minutes. The milling time in the synthesis process change the crystallite size and micro-strain of the Fe-Cr alloys formed.

1. Introduction
Research for high temperature material was successfully conducted to develop the manufacturing of advanced material ODS steel. This advanced material was now developed to be a prime candidate for the fourth generation of the Nuclear Power Plant (NPP) reactor structure material [1-4]. Development of the research has also successfully produced some commercial ODS steel to be used in the field of some high temperature industry. The ODS steel has some advantages on strength, corrosion resistance and creep resistance in high temperature due to its process technology [5,6]. ODS steels are developed by dispersing oxides to the matrix and grain boundaries of the steel during the synthesis process. The dispersed oxide will inhibit the movement of the dislocation that increased the strength significantly [7]. The oxide of Yttria which has a high melting point and a stable structure is commonly used as a dispersoid so that the degradation of strength in high temperature can be minimized [8]. The ODS steel was successfully synthesized by powder metallurgy method which can disperse oxides homogeneously during the process [7]. The raw materials of Fe, Cr, Ni powder and several elements are mixed and alloyed in a mechanical process by milling and compacting then consolidated by the sintering process. Alloying process of Fe-Cr or Fe-Cr-Ni takes an important role in the manufacturing process to improve the ODS steel properties. This optimal and perfect alloying process were determined by the operating parameters in the milling, compacting and sintering processes. Identify the alloy phase formation and the quantity of alloying achieved during the process is an important method to produce a perfect alloy.

The XRD technique is an accurate method for identifying the alloy phase formation to complement of the metallographic analysis in the optimization of the ODS steel synthesis process. The challenge of using XRD technique in the analysis of ODS steel samples is caused by the special phase formed during the synthesis process. The process involved two alloy elements, namely α-Fe and α-Cr have the same crystal structure of bcc and almost have the same lattice constant value, namely α-Fe = (0.28662 ± 0.00002) nm and α-Cr = (0.2884 ± 0.0001) nm (9)(10). Otherwise, the Fe-Cr alloy formed in the synthesis process will have a lattice constant whose value is between the α-Fe and α-Cr lattice constants [11]. This parameter causes the position of the 2θ diffraction peaks of the three phases to be almost the same and if there are two or three of these phases in the sample, the 2θ diffraction peaks of the phases coincide with each other, especially for the first diffraction peaks of these phases. As for the very low
composition of oxide phase, the ZrO$_2$ phase can not be identified by X-ray diffraction technique due to the very low detection limit of XRD (1% w.t in general). Therefore, it requires an accurate data processing and analysis by determining some information to overcome the phase identification problem caused by overlapping diffraction peaks. In addition, more accurate data and information related to the phase formation in the Fe-Cr alloying process are also needed for optimization of the ODS steel synthesis process.

In this paper, application of the XRD technique with data processing using the Rietveld method for Phase Analysis and Crystal Structure of Fe-Cr alloys is discussed. The characterization results are expected to be used as input to optimize the synthetic parameters of ODS steel manufacturing.

2. Experimental

In this study, three samples of ODS steel with element compositions of Fe (balanced), 20 wt% Cr and 0.5 wt% zirconia were synthesized by powder metallurgy methods through the processes of milling, compaction and sintering. The 3 samples were classified by the milling time process with the sample code of S-3, S-5 and S-7 for the milling time of 3 hours, 5 hours and 7 hours respectively. All samples were then compacted with the same treatment by the compaction process with static pressure load of 200 MPa and sintering process using an APS (Arc Plasma Sintering) apparatus with a sintering time of 30 minutes. The samples were then characterized by XRD to identify and analyze the phase of alloy formed in the synthesis process.

To identify the phase of Fe-Cr alloy and other phase formed in the synthesis process, the diffraction pattern from the XRD test was further analyzed. The diffraction pattern of the sample was taken using PANalytical-Empyrean X-rays Diffractometer with data collection parameters of continuous scan mode ($2\theta = 40^\circ$ - $120^\circ$), step size = 0.0260 ($^\circ$2$\theta$). Goniometer = Theta / Theta, the radiation used is CuK$_\alpha$, ($\lambda = 1.5406$ Å) at room temperature (25$^\circ$C). The processing of diffraction patterns using Rietveld Analysis (Refinement)(14)(15) was carried out using the HighScore Plus software version 3.0 from PANalytical [14]. Refinement begins with refining the global parameters, namely the background parameter, sample displacement and zero point shift. The sample displacement and zero point shift parameters are refined using the Eskolaite phase, by first keeping the phase lattice parameter values fixed, and after getting a value that is close to it, then the phase lattice parameter value is refined. Then, the parameter values of the sample displacement and zero point shift are kept fixed in the refining of the next phases. The Profile function used is Pseudo Voigt and the parameters to be refined included of unit cell parameters, profile parameters (W's, V's, and U's), asymmetric parameters, and peak shape parameters. The full width at half maximum of the diffraction peaks (FWHM) of the Fe-Cr phase from the Rietveld refinement were used to calculate the crystallite size and micro-strain using the Williamson and Hall, W-H Plot method after being corrected from instrument FWHM contribution that was measured using Si standard sample.

3. Results and discussion

X-ray diffraction test for ODS steel sample of Fe-20Cr-0.5ZrO$_2$ with a variation of milling time of 3 hours, 5 hours, and 7 hours produced diffraction patterns as shown in Figure 1. Qualitative analysis for the three diffraction patterns showed that all samples consist of 2 phases, namely the Fe, Cr alloy phase which is shown by a diffraction pattern with high intensity (with the same crystal structure as the α-Fe phase) and the Cr$_2$O$_3$ phase which is shown by the pattern with low intensity. In the three samples, the diffraction pattern of the zirconia phase was not visible, because the composition (% wt) of this phase was lower than the detection limit of the XRD method. Rietveld analysis was carried out to more carefully find out the phase composition of each sample and the crystal structure of the Fe, Cr phases formed. The Rietveld refinement was performed by matching the diffraction pattern of the sample with the diffraction pattern from the ICSD database. The result indicated that the phase identified is the Chromium Iron alloy phase (0.2/0.8) with Reference Code: ICSD 98-010-2752 and Eskolaite Cr$_2$O$_3$ phase with Reference code: ICSD 98-016-7270. The refinement process starts by using three phases, namely the two phases and added with the Chromium - Alpha Cr phase with the Reference code: ICSD 98-004-4731. However, the S-3 and S-7 samples showed better results for refinement with 2 phases.
Figure 1. XRD Pattern of all ODS steel with milling time of 3 hours (top), 5 hours (middle) and 7 hours (bottom)

The plot of the refinement results is shown in Figure 2, while the Refinement Agreement Indices of the three samples is shown in Table 1, as follows.
Figure 2. The refinement plot of the entire pattern (left) and the first peak (right), for sample with milling time 3 hours (a), 5 hours (b), and 7 hours (c).

Table 1. Refinement Agreement Indices

| Sample | Weighted R factor, Rwp (%) | Goodness of Fit, GOF |
|--------|---------------------------|---------------------|
| S-3    | 2.28411                   | 0.87786             |
| S-5    | 2.39292                   | 0.92706             |
| S-7    | 2.31534                   | 0.87397             |

The phase composition, lattice parameters and Cr composition of the Fe-Cr alloy calculated using the equation from Sutton and Hume-Rothery [9] are shown in Table 2 as follows:

Table 2. Phase composition, lattice parameters and Cr composition of the Fe-Cr alloy

| Sample | Phases | Lattice parameters (Å) | Weight % | Cr Composition (atomic %) |
|--------|--------|------------------------|----------|---------------------------|
| S-3    | Iron Rich (Fe,Cr) | a : 2.8761(1) | 89(11) | 18.3333                  |
|        | Eskolaite, Cr₂O₃   | a : 4.954(3) | 11(1)  |                           |
| S-5    | Iron Rich (Fe,Cr) | a : 2.8744(2) | 66(2)  | 15.1852                  |
|        | Chromium Rich (Cr,Fe) | a : 2.8832(6) | 27(2)  | 31.4814                  |
|        | Eskolaite, Cr₂O₃   | a : 4.95700 | 7(1)   |                           |
|        |                   | c : 13.594000 |         |                           |
| S-7    | Iron Rich (Fe,Cr) | a : 2.8765(2) | 80.5(5) | 19.0741                  |
|        | Eskolaite, Cr₂O₃   | a : 4.959(1) | 20(1)  |                           |
|        |                   | c : 13.634(5) |         |                           |

Rietveld refinement analysis of the three diffraction patterns showed a fairly good agreement indices, namely the Weighted R factor, Rwp (%) which is less than 3% and the Goodness of Fit value, GOF which closed to 1. From the sample observation of refinement, especially the zoom plot for the first peak, it can be seen that the diffraction data of S-3 and S-7 were suitable to be fitted with a single-phase Fe-Cr alloy, while for the diffraction pattern of the S-5 sample was more suitable for the 2-phase Fe-Cr alloy. The results of the refinement analysis showed that for the S-3 and S-7 samples the Fe-Cr alloying process has been successful. The alloy composition for the S-3 sample was Fe-18.33 at% Cr or Fe-17 wt% Cr, approaching the intended value, namely Fe-20 wt% Cr as well as for the S-7 sample with an alloy composition is Fe-19.07 at% Cr or Fe-18 wt% Cr. The deficiency of the Cr composition form the Fe-Cr alloy was due to oxidation of Cr that formed Cr₂O₃ eskolaite phase, that are 11 wt% in the S-3 sample, 7 wt% in the S-5 sample and 20 wt% in the S-7 sample. In sample S-5, two phases of the Fe-Cr alloy were formed, namely Fe-15.1852 at% or Cr Fe-14 wt% Cr and Fe-31.48 wt% or Cr Fe-29 wt% Cr, respectively. It is necessary to study further why the alloying process in the S-5 sample has not produced a single Fe-Cr alloy phase, whether the inconsistency of the synthesis process is in the milling, compacting or sintering process. However, in the S-5 sample, the oxidation process was
smaller, indicated by the quantity of 7 wt% of the Eskolaite Cr$_2$O$_3$ phase formed. Crystallite size and micro strain, calculated using the Williamson-Hall equation and plot method, were shown in Figure 3 and Table 3. Crystallite size and micro strain, calculated using the Williamson-Hall equation / plot method, are shown in Figure 4 and Table 3. It can be seen that the milling process change crystallite size and micro strain of the Fe-Cr phase.

![W-H Plot of Fe-Cr Phase for Sample S-3](image)

![W-H Plot of Fe-Cr Phase for Sample S-5](image)

![W-H Plot of Cr rich Fe-Cr Phase for Sample S-5](image)

![W-H Plot of Fe-Cr Phase for Sample S-7](image)

Figure 3. Williamson-Hall Plot of the Fe-Cr Phase in ODS steel (Fe-20% Cr).5%ZrO2

| Sample | Phase          | Crystallite size (nm) | Micro Strain $<\varepsilon>$       |
|--------|----------------|-----------------------|------------------------------------|
| S-3    | Fe-18 at% Cr   | 232                   | $6.44196E-4 \pm 1.14906E-4$         |
| S-5    | Fe-15 at% Cr   | 113                   | $3.20657E-4 \pm 1.92566E-4$         |
| S-5    | Fe-31 at% Cr   | -                     | -                                  |
| S-7    | Fe-19 at% Cr   | 412                   | $5.9016E-4 \pm 1.0956E-4$           |

Table 3. Crystallite Size and Micro Strain of Fe-Cr phase

4. Conclusion
X-ray diffraction measurement with diffraction data processing using Rietveld-Refinement provide accurate information on the phase composition and structural parameters of Fe-Cr phase. The diffraction peaks of the Fe and Cr phases as well as the overlapping Fe-Cr phases can be accurately identified. The results of the refinement analysis showed that the Fe-Cr alloying process has been successful for samples with milling time of 3 and 7 minutes with the alloy composition of Fe-17 wt% Cr, and Fe-18 wt% Cr. The calculation results of crystallite size and micro-strain values for all samples, showed that
the difference in milling time in the synthesis process gave a significant difference in the values of crystallite size and micro-strain of the Fe-Cr phase.

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