Synthesis and characterization of high chromium zirconia-oxide dispersion strengthened (ODS) steel

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Abstract. High Chromium ODS ferritic steel dispersed by zirconia was synthesized by the Mechanical Alloying process for application as high-temperature nuclear reactor structure material. The zirconia was chosen as dispersoid to increase the oxidation resistance of the steel. The powders of Fe and Cr with composition of Fe-25 wt.% Cr and 0.5 wt.% ZrO$_2$ were processed by milling and isostatic compaction then continued with the sintering process for consolidation. The process of sintering was performed by the plasma-based heating using the new apparatus of APS (Arc Plasma Sintering). The sintering was processed with 40 A current and 22 minutes sintering time to result in the optimal Fe-Cr alloy formation. A microscopy technique with scanning electron microscopy (SEM), and X-ray diffraction (XRD) were applied to analyze the mechanism of the alloying process. The Vickers hardness measurement and the oxidation test were carried out to evaluate the mechanical and high-temperature oxidation behavior. The alloying process was considered by the Fe-Cr interdiffusion with Cr the faster one. The distribution of zirconia observed by SEM-mapping showed the homogeneity distribution in the matrix of the alloy. The Vicker hardness of 142.8 VHN was believed caused by the oxide strengthen and fining the grain. The parabolic oxidation curve obtains from the MSB oxidation test showed good oxidation resistance caused by the formation of the protective layer of Fe$_2$O$_3$ and some metastable of ZrO.

1. Introduction
Recently, the advanced materials of Oxide Dispersion Strengthened (ODS) steel have been developed and widely used for high-temperature reactor structure materials [1,2]. The ODS steel has a unique structure with a Fe-Cr alloy matrix containing homogeneously dispersed stable oxides. This structure improved the mechanical properties of the alloy by obtaining high strength and good resistance to corrosion, creep as well as high neutron irradiation resistance and thermomechanical stability at high temperatures [3,2]. The problem of oxidation is an important thing to be considered for high-temperature reactor structure material, besides the irradiation damage. Therefore some researchers were conducted to enhanced the oxidation resistance of the ODS alloy. The corrosion and oxidation resistance of steel and some iron-based alloys in high temperatures are influenced by the chromium content in alloys. Some research has resulted that the uses of ODS ferritic steels with low chromium content as the structural material for supercritical water reactor (SCWR) are not suitable for insufficient corrosion resistance of the materials [4]. The ODS steel with a composition of 9 Cr and 12 Cr developed by Japan Atomic Energy Agency (JAEA) has obtained good strength and radiation resistance, however the corrosion and oxidation resistance is necessary to be improved for use as the cladding material. The content of Cr takes...
an important role in increasing the high corrosion resistance of the ODS steel which has been successfully developed by the National Institute for Materials Science (NIMS) [5]. Therefore, the high oxidation rate of ODS steel can be effectively prevented by determining the high Cr content in the synthesis and manufacturing process. However, it should be noted that too much Cr content in ODS steel will cause embrittlement material due to the formation of chromium precipitation [6].

Currently most commercial ODS steels in the market were synthesized with Fe-Cr based alloys dispersed with Yttria (Y₂O₃) which have a high melting point and are stable at high temperatures [7]. Besides Yttria, zirconia is now being investigated as a candidate for disperzoid in ODS steel making especially for the application of nuclear materials to improve high-temperature oxidation resistance and to prevent radiation damage to materials. Zirconia also has a higher melting temperature and greater thermal stability than Yttria and has several advantages [2, 7, 8]. In addition zirconia is predicted to increase oxidation resistance due to the zirconium property which can produce zirconium-oxide due to the large affinity of zirconium to oxygen. Increasing of the alloy strength and grain boundary migration can be achieved by addition zirconium in the synthesis of ODS Steel [1]. Dispersion and homogeneity of oxides in the matrix and grain boundaries will influence the strength and oxidation resistance of ODS steel. This level of oxide homogeneity depends on the synthesis, especially in the sintering process [9]. Research shows that ODS steels achieve their superior properties because they are homogeneously distributed in nanometer-sized particles of second-phase oxides in ferritic/martensite steel matrices [10, 11]. The method of sintering process that takes an important role in the ODS steel fabrication was now developed and investigated in some research.

The commercial ODS steel was mainly produced by the powder metallurgical technique with mechanical alloying process using the ball-milling. After alloying, the process was then followed by various consolidation techniques, such as hot-isostatic pressing and continued with some sintering process and various thermomechanical treatments technique. The Mechanical Alloying (MA) technique was effectively used to produce a uniform dispersion of nano-sized oxides in the metal matrix and prevent the grain growth [10, 11]. However, the MA is a complex and high costly process for utilization in industrial applications. One improvement of the sintering process was performed by developing the plasma sintering method to enhance the consolidation of the powder. The SPS (Spark Plasma Sinter) device was successfully used for the sintering process of some ODS alloys with very fast heating, cooling rates and short hold times. However, the SPS processing the powder to be consolidated is loaded into an electrically and thermally conductive graphite mold and a large DC pulsed current (1000–5000 A) is applied under uniaxial pressure. This process, still needs high energy consumption for the sintering process and difficult for homogenizing the sample product with complex form. The new device called SPS (Spark Plasma Sinter) was developed and successfully used for the sintering process of some ODS alloys with fast heating and short operating times. However, the sample to be sintered by SPS was loaded into an electrically and thermally conductive graphite mold and difficult for homogenizing the sample product with complex form. The sintering process then performed by a large DC pulsed current (1000–5000 A) applied under a uniaxial pressure that needs high energy consumption [10].

A new method and device of Arc Plasma Sintering (APS) have been developed for the sintering process based on the heating plasma method. The main component of APS is a torch that generates a plasma heat source in the localized spot from the argon gas and electric arc. This apparatus has successfully synthesized some ODS alloys with excellent sintering and significantly reduce the processing time and energy [12].

In this study, the ferritic high Chromium ODS steel with zirconia dispersoid was synthesized by using the APS for the sintering process. The mechanism of the alloying process, the influence of sintering time and current to the morphology and hardness of the ODS steel were investigated. Furthermore the oxidation characteristic of high Cr amount and the oxidation mechanism of the ODS alloy was studied.
2. Experiment setup

2.1. Mechanical alloying and consolidation

Samples of high Chromium content for ferritic ODS steel dispersed by the zirconia were synthesized with the composition of 25 wt.% Cr and 0.5 wt.% of ZrO₂. Mechanical Alloying method with the main step of milling, compaction and sintering process was developed to synthesize the sample. Investigation of the ball-milling time and compression load have been carried out which achieved optimal results for 8 hours for milling time and 200 kN for compression load. A vibration process is carried out on samples in a die before compaction to reduce the porous of the sample. The compression process is carried out using an isostatic pressing machine with a compression load of 200 kN to produce samples in the form of coins with a diameter of 15 mm and a thickness of 3 mm. To improve the quality of milling results the grain size of Cr was first reduced through the milling process for 5 hours to make it closer to the grain size of Fe. The sample was then consolidated through the sintering process using the APS (Arc Plasma Sintering) to result in optimally alloying of Fe-Cr.

APS is new experimental sintering equipment based on plasma as a heat source. The schematic diagram and image were illustrated in Figure 1.

![Figure 1. System of sintering process using APS][12]

The main component of APS (Arc Plasma Sintering) equipment consists of the torch with the nozzle for plasma generator, DC voltage source, and sample stage. The torch consists of 3 parts which function as an anode, cathode and an insulator placed between the cathode and anode. During the sintering process, the DC voltage jumps at a high frequency in the torch which is supplied by argon gas. In the electric arc environment on the torch nozzle, argon gas turns into plasma as a heat source for the sintering process. The plasma heat can reach high temperatures until around 2000 °C and the sintering process runs very quickly with relatively small energy. In this investigation, the sintering process of the ODS steel sample was carried out in some combination of sintering times and plasma currents to study the process mechanism and optimize the alloying results. The sample was placed on a copper cup and exposed by the plasma sintering times from 6 to 22 minutes with the power of 300 Watt, 12 V and the current from 25 to 40 A. After sintering process some samples were heat treated by annealing process at 800 °C for 8 hours in the argon as atmosphere for homogenization process.

2.2. Characterization

Scanning Electron Microscopy (SEM) was used to study the morphology of the microstructure of the alloy. For chemical composition analysis of the sample, the SEM is combined with Energy Dispersive Spectroscopy (EDX) equipment. The SEM-mapping is performed to study the alloying process and the
homogeneity of the oxide by observe the alloying elements area mapping. Analysis of the XRD-diffraction pattern was carried out to evaluate the formation and the mechanism of the alloying process. Mechanical properties of samples were tested using a Vickers microhardness method to study the effect of the steel ODS alloying process. The oxidation test was carried out to evaluate the oxidation rate of ODS steel at high temperatures. The test was carried out using MSB (Magnetic Suspension Balance) equipment at the temperature of 700 °C for 6 hours to evaluate the character of ODS steel oxidation in the initial conditions of the oxidation process.

3. Results and discussion

3.1. Microstructural

Based on the investigation of the Fe-Cr alloying process, it can be explained that the alloying process on ODS steel manufacturing is the formation of the Fe-Cr phase following the interdiffusion process between Fe and Cr [13]. The sintering process takes an important role to form the Fe-Cr phase that depends on time and plasma current during sintering using APS. Figure 2 showed the microstructural of the alloy Fe-25Cr 0.5ZrO2 observed on the sample with different sintering time. Figure 2a shows the microstructure for 6 minutes sintering which consists of the Fe-Cr phase matrix and the dark area which Cr content dominant. This structure shows that the sintering time of 6 minutes has not resulted in the complete of Fe-Cr phase. For 16 minutes of sintering time as illustrated in Figure 2b, the microstructure shows the relatively homogeneous formation of the Fe-Cr ferritic phase. Only a small part is still seen in the Fe-Cr interdiffusion zone. Figure 2c showed microstructure with 22 minutes sintering time, almost all samples consist of Fe-Cr phase with relatively fine grain and homogenous with low porosity.

Identify the element composition of the alloy was performed by the SEM-EDX test for some area in the SEM microscopy for samples with the variation of the sintering process.

Figure 2. The microstructure of Fe-25Cr-0.5 ZrO2 after sintered by using APS, with sintering time of 6 minutes (a), 16 minutes (b) and 22 minutes (c).
Figure 3 showed the element composition of Fe-20Cr-0.5ZrO2 ODS steel sintered for 22 minutes with APS current of 40A observed in SEM-EDX. The composition of all areas was 78.16 wt.% Fe and 21.84 wt.% Cr. Overall, the total chemical composition of the consolidated material for Fe-25Cr-0.5ZrO2 sintered by the APS is kept unchanged during and after milling, press forming and sintering. Therefore, the sintering process with APS does not introduce significant changes in the composition of the powders. This test explained that the alloying process for ODS alloy with 22 minutes of sintering gives the nearly complete alloying process.

Figure 3. SEM-EDX test of Fe-25Cr-0.5ZrO2 with 22 minutes sintering time.

The homogeneity distribution of zirconium oxide dispersoid was very important to the performance of ODS alloy steel. Evaluation and analysis of the homogeneity of the zirconia were carried out by observed the result of SEM EDX mapping. SEM-EDX mapping area for elements of Fe and Cr for the ODS steel sintered by the APS for 22 minutes was illustrated in Figure 4.

Figure 4. SEM-EDX mapping element of Zr and O sintered by APS for 22 minutes.

The elements distribution of Zr and O in Figure 4 showed homogeneity distribution in the matrix of the alloy steel that explained the homogeneity of zirconia dispersoid in a matrix of Fe-Cr. The homogenously level of the zirconia oxide can increase the volume fraction of the small equiaxed grains in the matrix of the consolidated material and play an important role in improving the mechanical properties. Otherwise, the SEM EDX mapping element for Cr in Figure 5 explained and confirmed the process for Fe-Cr phase formation during plasma exposure for 6 and 22 minutes. After 6 minutes sintering process using APS the Cr elements are distributed in the matrix and some areas which rich in
Cr atoms. The addition of sintering time to 22 minutes showed the process of Cr element dispersion in the matrix. This process showed and confirmed the diffusion of Cr during the Fe-Cr alloying process.

![Figure 5. SEM-EDX mapping of Cr element for Fe-Cr-ZrO$_2$ synthesis for sintering time of 6 minutes (a) and 22 minutes (b).](image)

3.2. XRD measurement
The microstructure characteristics results using XRD are shown in Figure 6 which showed diffraction pattern of ODS alloy after sintered for 22 minutes. The XRD pattern identified one peak of Fe-Cr which means that after 22 minutes sintering using the APS, the alloying process has been completed by forming a 100% Fe-Cr phase. Microstructure analysis for different sintering times was carried out on the first peak of the highest of the XRD pattern. The results showed that the Fe-Cr phase was performed for a sintering time of 16 and 22 minutes shown in Figure 7.

![Figure 6. The first peak of XRD of Fe-25Cr-0.5ZrO$_2$ sintered for 16 minutes (a) and 22 minutes (b).](image)
XRD measurement confirmed the presence of both Fe and Cr with typical BCC structure up to 16 minutes of sintering with lattice parameters of 2.866637 Å for Fe and 2.88453 Å for Cr respectively. After 22 minutes sintering a single crystal occurs having the lattice parameter of \( a = 2.87522 \) Å. This explains the process of FeCr phase formation driven by the Fe-Cr inter diffusion which more complete for longer of sintering time. Analysis of the Fe-Cr phase formation on the ODS steel synthesis for Cr variation content performed in the past research explained that the higher Cr content would increase the grain refining and increase the hardness and strength. Furthermore the Fe-Cr phase formation on the sintering process by APS has not been completed due to a very short sintering time. In general, increasing of sintering time from 16 to 22 minutes will increase the formation of the Fe-Cr phase as confirmed with the microstructure analysis.

3.3. Hardness and oxidation behavior

The performance of ODS Fe-25Cr-0.5ZrO\(_2\) steel sintered by the APS was investigated by evaluating the hardness and high-temperature oxidation resistance. The hardness of Fe-25Cr-0.5ZrO\(_2\) was measured by the Vickers Hardness number. The results were 116.3 VHN for 16 minutes sintering time and increased to 142.8 VHN for 22 minutes. This explains that the hardness increase with increasing the sintering time. Increasing the hardness was also explain the change of the microstructure by the finer grain and also the more homogenous of the oxide dispersed in the matrix.

Figure 7 shows oxidation characteristics of Fe-25Cr-0.5ZrO\(_2\) sintered for 22 minutes after and before the annealing process which showed the weight gains resulted from the oxidation in the air as a function of the oxidation time. The sample is ODS steels Fe-25Cr-0.5 ZrO\(_2\) sintered for 22 minutes before and after treated by the annealing process. The oxidation curve of ODS steel Fe-12Cr-0.5 ZrO\(_2\) performed in the past research was also added to observe the effect of Cr element addition to the oxidation performance. Analyzing the oxidation behavior was performed by observed and analyze the curve characteristic in the early and important oxidation test for 6 hours.
Figure 7 showed the oxidation characteristic of Fe-25Cr-0.5ZrO$_2$ follows a parabolic curve for time heating treatment until 200 minutes. This phenomenon explained that mass gain is proportional to the square root of time, and indicated the formation of the protective oxide layer. The protective oxide layer is formed from the diffusion of oxygen anions through the iron oxide lattice. The metal cations transport however is fully inhibited. In general, this parabolic curve is similar to the high-temperature oxidation characteristic of Fe-Cr alloy. The annealing process is likely to affect the weight gain, however the oxidation curve showed a higher corrosion rate. The 25 Cr composition also explains better corrosion rate compare with the 12 Cr composition. Furthermore, the high composition Cr showed the more stable of parabolic grow kinetics form that means the better on the thin film protection formation. Based on some of the data experiments of Fe-Cr alloy and the ODS steel with 12 Cr composition [14], the thin protection layer formed after the oxidation test of ODS steel with 25 Cr composition is predicted as a stable Cr$_2$O$_3$ and Fe$_2$O$_3$. This oxide was good enough as a thin protected for corrosion of oxidation.

4. Conclusion
The high chrome ODS alloy Fe-25Cr-0.5 ZrO$_2$ was successfully synthesized by the Mechanical Alloying method using the new apparatus of APS for the sintering process. The alloying process was known as interdiffusion of Fe and Cr process which obtained the complete of Fe-Cr phase formation on the sintering time around 16 to 22 minutes with 40 A 25 V using APS. The zirconia homogeneously distributed in the matrix of the alloy. The sintering time of 22 minutes has almost all samples consist of the Fe-Cr phase with relatively fine grain and homogenous. The increased hardness was caused by the oxide strengthen and fining the grain. The good oxidation resistance caused by the formation of the protective layer of Fe$_2$O$_3$ and some metastable of ZrO$_2$.

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