Mechanosynthesis of A Ferritic ODS (Oxide Dispersion Strengthened) Steel Containing 14% Chromium and Its Characterization

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Abstract. One of the advanced materials for application at high temperatures which is aggressively developed in the world is ODS (Oxide Dispersion strengthened) steel. ODS ferritic steels are one of the candidate materials for future nuclear reactors in the world (Generation IV reactors) because it is able to be used in the reactor above 600 °C. ODS ferritic steels have also been developed for the interconnect material of SOFC (Solid Oxide Fuel Cell) which will be exposed to about 800 °C of temperature. The steel is strengthened by dispersing homogeneously of oxide particles (ceramic) in nano-meter sized in the matrix of the steel. Synthesis of a ferritic ODS steel by dispersion of nano-particles of yttrium oxide (yttria: Y$_2$O$_3$) as the dispersion particles, and containing high-chromium i.e. 14% has been conducted. Synthesis of the ODS steels was done mechanically (mechanosynthesis) using HEM (High Energy ball Milling) technique for 40 and 100 hours. The resulted samples were characterized using SEM-EDS (Scanning Electron Microscope-Energy Dispersive Spectroscope), and XRD (X-ray diffraction) to analyze the microstructure characteristics. The results showed that the crystal grains of the sample with 100 hours milling time was much smaller than the sample with 40 hours milling time, and some amount of alloy was formed during the milling process even for 40 hours milling time. Furthermore, the structure analysis revealed that some amount of iron atom substituted by a slight amount of chromium atom as a solid solution. The quantitative analysis showed that the phase mostly consisted of FeCr solid-solution with the structure was BCC (body-centered cubic).

Keywords: Mechanosynthesis, Ferritic, ODS, Chromium, HEM

1. Introduction

High chromium steels are one type of steel-based materials for high-temperature service operation of many power plants such as nuclear reactors [1-2]. However, the conventional high chromium steels are limited to about 600 °C of service temperature. Therefore, development of advanced steel-based materials for higher temperature service operation is needed. Oxide dispersion strengthened (ODS) steels are one type of steel-based high-temperature material candidates which are mostly developed for advanced nuclear fission reactors (so-called Generation IV reactors) and nuclear fusion reactors because of the promising materials to be utilized at high temperature under severe irradiation exposure environment [2-11]. Development of ODS steels with the addition of several significant elementals has been done by several researchers. Development of Al added high-Cr ODS steels had been reported in order to improve the corrosion resistance at elevated temperature [9-10]. Furthermore, it has been
reported that the Al addition to ODS ferritic steel considerably improves the compatibility between U–Zr fuel and the ODS steel [11].

ODS steels have been developed by powder metallurgy method using mechanical alloying technique so-called mechanosynthesis to obtain a dispersion of oxide particles in a steel matrix [2-11]. Mechanical alloying is a technique to acquire homogeneous materials from elemental powder materials. Welding, breaking, and re-welding processes of the powder particles were performed in a milling machine during mechanical alloying. Finally, fine dispersion of oxide particles (mostly Y$_2$O$_3$ nano-particles) inside the matrix of the steel will be obtained. Therefore, the optimum amount of Y$_2$O$_3$ in the steel is significantly important. It has been reported that the tensile strength and hardness of ODS steel increases as the content of Y$_2$O$_3$ increases, but it should be noted that the content of Y$_2$O$_3$ needs to be controlled within a range [12]. A novel route for synthesizing of ODS steels has also been developed using a sol–gel method combining with hydrogen reduction [13]. Furthermore, it has been reported about mechanically alloyed of ODS ferritic steels in different atmospheres which give an effect of the mechanical and microstructural properties [14].

In this paper, the study of mechanosynthesis of a ferritic ODS steel containing 14% chromium is presented. The amount of nano-sized ceramic Y$_2$O$_3$ powder was 0.25 wt%. The ferritic ODS steel was synthesized using HEM (High Energy ball Milling).

2. Experimental Method
Iron (Fe), chromium (Cr), titanium (Ti), molybdenum (Mo) elemental powders were mixed with nano-sized Y$_2$O$_3$ powder for the mechanosynthesis of a ferritic ODS steel. The powders of Fe, Cr, Ti, Mo, and Y$_2$O$_3$ were bought from a chemical company without any further treatment. The ratio of Fe:Cr:Ti:Mo:Y$_2$O$_3$ was 84.45:14:1:0.3:0.25 as the composition in weight percentage.

The ratio of BPR (ball-to-powder mass ratio) of the samples was 5:1. In order to avoid or to minimize oxidation and impurities during milling, a toluene solution was added as process control agent in the vial which has already inserted the powders and the balls. The mixed powders were milled using HEM (High Energy ball Milling) for 40 and 100 hours. The speed of the vial during milling was 1,000 rpm (rotation per minute). The characterizations were done using SEM (Scanning Electron Microscope) - EDS (Energy Dispersive X-Ray Spectroscope) and XRD (X-Ray Diffraction) for microstructure analyses.

3. Results
The SEM-EDS analysis of ODS powders after milling for 40 and 100 hours are shown in Figures 1-4. Figure 1 of SEM micrograph with 500 times magnification of the sample after milling for 40 hours shows the various morphology i.e. small, medium and big chunks. However, the powder was dominated by small chunks. During mechanical alloying, welding, breaking, re-welding, and re-breaking processes of the powder particles occurred in a vial in the milling machine. Therefore, some of the powders were still in welding or re-welding stage, and some of the powders were in breaking or re-breaking stage. Figures 2 show SEM-EDS analysis with 2,000 times magnification of the sample after milling for 40 hours, (a) SEM micrograph, (b) EDS analysis at position-1, (c) EDS analysis at position-2, (d) EDS analysis at position-3. The EDS analysis was presented in quantitative of elemental percentages as shown in Table 1. The results showed that the chromium content slightly decreases from the original composition. It might occur because some percentage of impurity from the vial and toluene such as carbon was unexpected added during the milling process.
Figure 1. SEM micrograph with 500 times magnification of the sample after milling for 40 hours

Figure 2. SEM-EDS analysis with 2,000 times magnification of the sample after milling for 40 hours
(a) SEM micrograph (b) EDS analysis at position-1 (c) EDS analysis at position-2 (d) EDS analysis at position-3

Table 1. Chemical compositions of the sample after milling for 40 hours

| Element/area | Original (mass%) | Area-1 (mass%) | Area-2 (mass%) | Area-3 (mass%) |
|-------------|-----------------|----------------|----------------|----------------|
| Cr          | 14              | 12.63          | 13.32          | 13.66          |
| Ti          | 1               | 0.94           | 1.3            | 0.96           |

Figure 3 of SEM micrograph with 500 times magnification of the sample after milling for 100 hours shows that the powder was dominated by small chunks. In general, from SEM micrograph of morphology, it is able to be analyzed that the sample after milling for 100 hours was smaller than the sample after milling for 40 hours. Therefore, most of the powders were in breaking or re-breaking stage and a small amount of the powders welding or re-welding stage. Figures 4 show SEM-EDS analysis with 2,000 times magnification of the sample after milling for 10 hours, (a) SEM micrograph,
(b) EDS analysis at position-1, (c) EDS analysis at position-2, (d) EDS analysis at position-3. The EDS analysis was presented in quantitative of elemental percentages as shown in Table 2. The results showed that the chromium content slightly decreases from the original composition. It is able to be analyzed that the content of chromium in the sample after milling for 100 hours was more decrease than the sample after milling for 40 hours. It might occur because some percentage of impurity from the vial and toluene such as carbon was unexpected added during the milling process. Therefore, more milling time more impurity increases.

| Table 2. Chemical Compositions of the sample after milling for 100 hours |
|--------------------------|-----------------|-----------------|-----------------|-----------------|
| Element/area            | Original (mass%) | Area-1 (mass%)  | Area-2 (mass%)  | Area-3 (mass%)  |
| Cr                      | 14              | 11.93           | 12.02           | 12.63           |
| Ti                      | 1               | 0.86            | 0.97            | 0.94            |
Figure 5 showed XRD pattern of the samples after milling for 40 and 100 hours. For the sample after milling 40 hours, the peaks of 2θ diffraction pattern are at 44.51°, 65.13°, 82.14°, 98.57° which is FeCr phase as in the JCPDS 34-0396. For the sample, after milling for 100 hours, the XRD pattern tend to grow as an amorphous structure. The phenomenon occurred because of a milling time. The results also showed that the XRD pattern of the sample after milling 100 hours was broader than the sample after milling 40 hours. It happened because the longer the milling time make a reduction of crystal particle size. Therefore, it is found that the grain size was decreased with the increasing of the milling time which is shown by the decreasing and broadening of the spectrum.

![Figure 5. XRD patterns of the samples after milling for 40 and 100 hours](image)

Figure 6 shows XRD pattern analysis of the sample after milling for 40 hours in more detail with refinement. The results showed that the XRD pattern consists of 3 phases i.e. FeCr alloy, FeCr solid solution, and FeO₂. The quantitative analysis showed that content of the phases were 1.3%; 92.2%; 6.5% for FeCr alloy, FeCr solid-solution and FeO₂ phases, respectively. It is able to investigate that the structure of the sample was BCC (body-centered cubic) as shown in Figure 6. The structure analysis revealed that some amount of iron atom substituted by a slight amount of chromium atom as a solid solution. Therefore, the formation of the solid solution might occur during milling process beside of homogeneous composition process of the powder. This process of solid solution reaction might occur due to diffusion through interfaces and grain/subgrain boundaries of the metals during the milling process.

![Figure 6. XRD pattern analysis with refinement of the sample after milling for 40 hours](image)
It showed that some of the oxygen from environment reacted with iron to form FeO₂ during the milling process. Furthermore, the phase of the sample after milling for 40 hours was dominated by FeCr solid solution phase. The phenomenon of this kind of process has also been reported [16]. However, some amount of alloy was formed even for the 40 hours milling process.

4. Conclusion
Mechanosynthesis of a ferritic ODS steel containing 14% chromium using high energy ball milling for 40 and 100 hours and its characterization have been done. The results showed that the grain size was decreased with the increasing of the milling time. The structure of the sample was BCC (body-centered cubic) with some amount of iron atom was substituted by a slight amount of chromium atom as a solid solution. Some of the oxygen from environment reacted with iron to form FeO₂ during the milling process. Nevertheless, some amount of alloy was formed during the milling process. It is able to analyze that to improve the quality of the synthesis process at least two factors should be done i.e. first, increasing the BPR (ball to powder mass ratio) to increase the mechanical impact that will increase the alloy phase and second, more protect the vial and machine environment to avoid or to minimize the impurities.

5. References
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