Microstructure and phase analysis of Zirconia-ODS (Oxide Dispersion Strengthen) alloy sintered by APS with milling time variation

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Abstract. Investigation on the relationship between the process conditions of milling time and the microstructure on the synthesis of the zirconia-ODS steel alloy has been performed. The elemental composition of the alloy was determined on 20 wt% Cr and zirconia dispersoid of 0.50 wt%. The synthesis was carried out by powder metallurgy method with milling time of 3, 5 and 7 hours, static compression of 20 Ton and sintering process for 4 minutes using the APS (Arc Plasma Sintering) equipment. SEM-EDX and XRD test was carried out to characterize the phase and morphology of the alloy and the effect to the mechanical properties was evaluated by the Vickers Hardness testing. The synthesis produced sample of ODS steel with good dense and very little porous with the Fe-Cr phase that clearly observed in the XRD peak pattern. In addition, milling time increased the homogeneously of Fe-Cr phase formulation, enhanced the grain refinement of the structure and increase the hardness of the alloy.

1. Introduction
The Oxide Dispersion Strengthen (ODS) alloy was recently developed for high temperature material application because of their good on mechanical strength and creep resistance [1]. This alloy also showed significantly improvement on the high temperature irradiation resistance and is suitable for use as a nuclear facility material. The use of zirconia as a dispersoid oxide to replace the Ytria was carried out to enhance the nuclear and radiation properties of the ODS alloy. Zirconium also shows a great affinity for C that expected to form carbides which act as a pinning dispersoid against grain boundary migration [2]. The ODS alloy are usually produced by powder metallurgy (PM) routes involving mechanical alloying of the oxide and pre-alloyed followed by consolidation technique, such as hot isostatic pressing and consolidation process by sintering. This PM method is still superior to disperse the oxide which plays an important role in the ODS alloy manufacturing that is very difficult to conduct by the casting process because of the agglomeration problem. However, the PM process requires a high cost due to the high price of powder element and high time and energy consumption in the sintering process [3].

Some research has been conducted to enhance the sintering process by developing the plasma sintering method using the SPS device. This SPS is able to enhance the consolidation of the powder, however the SPS still need high energy consumption. The new method of Arc Plasma Sintering (APS) developed in PSTBM-BATAN uses plasma as heat source can synthesize some alloy and reduce process time and energy consumption significantly [4]. The performance of the ODS steel alloy synthesized by APS was depend on the operating process of the milling, compressing and sintering time. Basically, milling process was conducted to mix the alloying element and refiner the grain size.
of the powder. The longer time of milling process will produce the finer size of powder and predicted will refine the grain size and strengthened the alloy. However, the optimum of milling time is necessary to be investigated according to the highly cost for milling process.

Study and investigation for milling time optimization was performed by investigate the relation between the milling time and the microstructure. In this study, the relation between the milling time with the microstructure and phase resulted during the synthesis of ODS steel alloy and the change of the hardness was performed. The zirconia dispersion was used for the utilization of material in the nuclear facility to reduce the neutron absorption coefficient.

2. Experimental

The Fe-Cr ODS alloy was developed with the composition of 20 wt.% Cr and 0.5 wt.% of dispersion particles ZrO2. The samples were prepared by mixing and milling all the materials of Fe, Cr and ZrO2 powder with milling time of 3, 5 and 7 hours. After milling, the samples were pressed by isostatic pressing machine with the compression load of 20 Ton to form sample with coins formed. The samples were then consolidated by sintering process in the APS (Arc Plasma Sintering) for 4 minutes referred to the sintering time for processing the ODS steel with 12 Cr content [5]. APS is a new experimental sintering device developed at the PSTBM with schematic diagram as illustrated in Figure 1.

![Figure 1. Schematic diagram of APS](image)

The main component of the APS is arc plasma source that provide high temperature of space in a short time. This device allows fast process consolidation of powder metallurgy sample. The sintering process was carried out in fully argon atmosphere in order to protect against oxidation. The sample coin was placed on a copper cup and exposed by the plasma for 4 minutes with the power of 300 Watt with 25 A 12 V.

The morphology and composition of the alloys were studied by means of Optical Microscopy and Scanning Electron Microscopy (SEM) coupled to Energy Dispersive Spectroscopy (EDX). The EDX spectrums illustrate the chemical composition of the samples. The SEM- mapping for each element was performed to observe the homogeneity of alloying elements and the oxide dispersion in the matrix of the alloy. Analysis of the XRD-diffraction pattern was carried out to evaluate the phase of the alloy using the Match 3 program and was refined by Fullprof software. Mechanical properties of the consolidated samples and the effect of the processing and Cr composition were also studied using the Vickers micro hardness (HV) measurement.

3. Result and Discussion

The microstructure after sintering process using APS for 4 minutes observed by the optical microscopy showed good appearance with little porosity and good dense structure as showed in Figure
Figure 2. Morphology of ODS Steel Fe-20Cr-0.5ZrO$_2$ with Optical Microscopy P 500x with milling time of (a) 3 hours, (b)5 hours and (c) 7 hours

The SEM-EDX examination revealed the presence of particle with different size and composition, randomly dispersed in the ferritic matrix. It is obviously clear that structure of all ODS alloy with some variation of Cr content and milling time were nearly same with general appearance of small and equiaxial grains and some elongated grains. The structure consists of two phases of the matrix phase mainly consists of iron phase and precipitate which mainly consists of Cr as given in mark (1) and mark 2 in Figure 3.

Figure 3. Micro structure of zirconia-ODS alloy Fe-20Cr-0.5 ZrO$_2$ with of milling time process of (a) 3 hours, (b) 5 hours and (c) 7 hours.

The milling time will change the grain size of the structure where increasing of milling time produced finer grain size as obviously explained in Figure 3. The presence of zirconia in the alloy can be predicted by the wt% of Zr element which mainly observed in the diffusion zone of the matrix phase and the high Cr content phase. Observation on zirconia distribution in the alloy after consolidated by APS sintering process was carried out by SEM-area scanning test as resulted in the Zr distribution in Figure 4.

Figure 4. Mapping area of Zr in the ODS alloy Fe-20Cr-0.5ZrO$_2$ with milling time of 3 hours (a) and 5 hours (b)
Based on the Zr content observed in Figure 4, it can be explained that the zirconia was distributed homogeneously in the alloy and predicted that increasing of the milling time will influence the homogenizing of the zirconia dispersion which is very important for enhancing the mechanical properties of the ODS steel alloy. The grain size and typically of oxide distribution was similar with the typically grain size distribution found in Spark Plasma Sintered that was reported as essential to prepare compact materials with strength and good ductility [6].

**Figure 5.** XRD pattern of the ODS steel (a) Variation of 15, 20 25 wt% Cr, 3 hours milling and (b) Fe-20Cr-0.5ZrO₂ with 3, 5 and 7 hours milling
The XRD test was performed to analyse the alloying process of the ODS steel by identifying the phase formed on the alloy. Figure 5 showed the diffraction pattern of ODS steel alloy with variation of Cr content and milling time. The refine of the X-ray pattern was performed by Fullprof program to fit the pattern with the GOF result was less than 1.6. In general, the alloy was dominated with Fe-Cr phase confirmed the structure and composition of the element observed by the SEM-EDX. Analysis of the first peak of the XRD pattern was performed by more detail observation of the first peak (110) as illustrated in Figure 6.

![Figure 6. First peak analysis of XRD pattern of Fe 20Cr with milling time of (a) 3 hours, (b) 5 hours and (c) 7 hours](image-url)
Addition of milling time increase the full-width at half-maximum (FWHM) of the pattern as observed in Figure 6 that revealed the grain size finer confirmed with the micro structure explained before. More detailed analysis in the first peak of all samples showed the contribution of Fe-Cr peak contains of Fe-Cr and Fe peak that revealed the alloying process for Fe-Cr phase formation is not yet completed during the very small time sintering as also explained in the SEM-EDX observation.

The crystal size was also determined on the XRD examined and the calculation result of crystal size for several milling times was illustrated in Figure 7. Increasing the milling time on the alloying process showed the smaller of crystal size.

![Figure 7. Crystal size of the ODS steel Fe20Cr0.5ZrO2 on some milling time](image)

The hardness test was carried out to evaluate the mechanical characteristic of the alloy. The result of hardness test with variation Cr content and milling time of the ODS steel alloy was given in Figure 8.

![Figure 8. Hardness of ODS steel alloy for 3 and 5 hours milling time](image)

After sintering process for 4 minutes the ODS steel alloys have significant hardness number from around 140 VHN to 210 VHN depend on the milling time. Increasing of milling time will increase the hardness that was caused by the grain refinement produced by the milling time close with the explanation of the microstructure discussed before. The hardness numbers obtained by the very low milling time of 4 minutes and low energy consumption of APS-sintering are good enough compare with the commercial ODS steel hardness of Fe-15 Cr-0.5Y2O3 around of 200 VHN.

4. Conclusion
Sintering method using the APS has successfully generated microstructure of the ODS steel alloy with dense structure and little porosity. The structure consists of mainly Fe-Cr phase with small equiaxed grain, homogeneous zirconia oxide distribution and significant hardness number. In addition, milling time will finer the grain and increase the hardness of the alloy. The longer of milling time process will also result finer grain size and increase the hardness.
5. References

[1] Andrea Garcia-Junceda et al, 2015 J. Am. Ceramic Society, 2015 pp 1-6.

[2] Klueh R L, J P R Shingledecker, R.W. Swindeman, D.T. Hoelzer 2005 J. Nuclear Materials

[3] Lavanya Raman, Karthick Gothandapai, B.S. Murty 2016 Defence Science J 2016 Vol 66, Juky2016 pp316 – 322, Vol 66, No 4, July 2016

[4] Dimyati, “APS, New Challenge for low emission bio-waste treatment,” Proceeding of Asia-Pacific Microscopy Conference 11th, 2016

[5] Bandriyana B, et.all, 2017, IOP Conf. Materials Sci. and Eng. 176 1-6.

[6] Taguchi M, Sumitomo, Ishibashi R, Aono Y, 2008, Mat. Trans. 49 6 1303 – 1310.