Synthesis and microstructure evaluation of ODS steel 316L with zirconia dispersion

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Abstract. An Austenitic ODS steel was developed for reactor structural material by dispersed 0.5 wt % of nano powder zirconia (ZrO$_2$) to the AISI 316L steel. The synthesis was carried out by the powder metallurgy process with high energy milling and cooled compacting process. A new apparatus of APS (Arc Plasma Sintering) was used for consolidation the sample in the sintering process. Characterizations of the microstructure and elemental composition distribution were performed using the Scanning Electron Microscope (SEM) with X-ray Diffraction Spectroscopy (EDX) and area mapping. Identification for the change of phases and hardness were analyzed using the XRD-test and Vickers Hardness measurement. Austenitic phase with relatively equiaxed grain and homogeneity distribution of the ZrO$_2$ dispersoid were identified after the sintering process followed by the improvement of hardness due to the pinning effect of the grain boundaries.

1. Introduction
Currently ODS steels with Yttria (Y$_2$O$_3$) dispersion are candidate materials developed for applications in the high temperature of Nuclear Power Plant (NPP). Oxide dispersions in alloy steel matrices will act as a pinning and dislocation motion barriers thereby significantly increasing the mechanical properties at elevated temperature[1-3]. Excellent strength and mechanical properties are the main reason for the ODS steel to be the first choice as a high-temperature materials. Moreover, some investigations were explained that the ODS steels was widely designed for nuclear material due to their high creep and radiation resistance[4-5]. There are two types of the ODS steel that widely used as a nuclear material, namely ferritic and austenitic type of ODS steel. Ferritic ODS steel has been successfully characterized to be a prime candidate for advanced high temperature nuclear fuel cladding material. Saofu Li, et.all [6] has concluded that the ferritic ODS steel with 16 Cr content has excellent in mechanical strength and suitable used for advanced nuclear energy material.[6]. The austenitic ODS steels are still being developed in recent years, especially for advanced Nuclear Power Plant (NPP) structural materials. These steels are expected to be better in creep and swelling resistance compare with the ferritic steel type. The austenitic ODS steel was also developed due to the better of its micro structure stability and corrosion resistance in high temperature [7-8].

The yttria (Y$_2$O$_3$) which has a high melting point and a stable structure at high temperature is the main choice for oxide dispersoid in ODS steel synthesis[9-10]. However, several research showed that zirconia can replace the Yttria as a dispersoid and increased the high-temperature corrosion resistance [11-13]. Research conducted by Haijian Xu, et.all,[14] also showed that the addition of zirconium to the ODS steel of 9Cr-ODS steel enhanced the density and the mechanical properties.[14].
Zirconium also shows a great affinity for C that expected to form carbides which act as a pinning dispersoid against grain boundary migration[15-16].

The ODS alloy are usually produced by powder metallurgy (PM) routes involving mechanical alloying and followed by consolidation technique using the compaction and sintering process. Process of the PM requires a high cost due to the high time and energy consumption. However this method is better than the casting process for the superior to disperse the oxide which plays an important role in the ODS alloy manufacturing [17-18]. Synthesis of the austenitic ODS steel is currently being developed by dispersed the oxide to the steel of SS 304 and 316 and 316L in the PM method. Commercial steels of SS 316L with very low carbon contentless than 0.003 wt% was able to prevent sensitivity phenomenon and could formed a stable thin protective layer of Cr2O3 to increase the high temperature oxidation resistance[19-20]. Therefore, in this research dispersion the zirconia to the commercial steel of SS 316 L was investigated to obtain the ODS steel suitable for nuclear reactor structural materials. The ODS steel properties depend on the sintering process parameters that consolidate the material that improve the mechanical properties. However, the optimum of the sintering current resulted from the plasma source is necessary to be investigated to optimize the operating cost.

This paper discussed the microstructure of the austenitic ODS steel synthesized by the powder metallurgy method by dispersion the ZrO2 to the steel SS 316L. The morphology of samples and the oxide distribution were observed to evaluate the phase and grain size related to the mechanical properties of hardness. The relation between the sintering current of the APS with the microstructure and phase resulted during the synthesis process and the change of the hardness was also performed.

2. Experimental

The austenitic ODS steel was synthesized with the composition of 99.5 wt% of SS 316L powder and 0.5 wt.% of dispersion particles ZrO2. The samples were first prepared by mixing and milling all the powder material elements in the high energy milling with milling time of 20 hours. The milling was carried out in the stainless steel vial using the steel ball with compare ratio between the material and ball volume of 10:1. After milling, the samples were compressed in cold compression method using the isostatic compression machine with the compression load of 200 MPa to obtain samples in pellet or coin formed. Consolidation of samples were performed by a special sintering process using the experimental equipment of the APS (Arc Plasma Sintering) with the plasma heat generation. The device with the main component of arc plasma source provides a high temperature of space in a short time and allows fast process consolidation of powder metallurgy sample[21-23].

The sintering process was carried out in fully argon atmosphere to protect against oxidation. The sample was placed on a copper cup and exposed by the plasma heat for 4 minutes with the plasma current of 70 A. Morphology and composition of the alloys were studied by the Scanning Electron Microscopy (SEM) coupled with the Energy Dispersive Spectroscopy (EDX) to describe 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. Analysis of the XRD-diffraction pattern was carried out to evaluate the phase of the alloy. Physical and mechanical properties of the consolidated samples and the effect of the processing were also studied using the density and Vickers microhardness (HV) measurement.

3. Results and discussions

Observation by SEM-EDX test for pure SS 316L without zirconia dispersion after compaction and sintering process showed the microstructure and element composition as given in Figure 1. The SEM images of (a) shows an uneven topology with significantly large scratches and cracks, and consists of elemental of Fe, Cr, Ni, and Ti (b).
The microstructure of sample after sintering process using APS for 4 minutes with 60, 70, 80A observed by the SEM is illustrated in Figure 2. The samples showed good appearance with little porosity and good dense structure. The SEM-EDX examination revealed the presence of particle with different size and composition, randomly dispersed in the matrix. Addition of plasma current in the sintering process has not significant change for the microstructure, however in the 70 A current showed smaller grain size showing better consolidation for the sintering process.

The sintering current plasma will change the grain size of the structure where increasing of current produced finer grain size as obviously explained in Figure 2. It is obviously clear that zirconia dispersion in the ODS synthesis of powder metallurgy processing changed the microstructure of ODS steel to general appearance of small and equiaxe grains and some elongated grains. The change of microstructure was believed caused by the main process of ball milling due to the mixing, grain refining and pre alloying process. 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 as observed by the SEM-EDX measurement. The composition of elements showed nearly same with the pure SS 316L with the elements composition of wt% 80 Fe, 16 Cr and 9 Ni. The Zr element was observed in the SEM-EDX measurement in the sample with 70 A current with the wt% composition of around 0.3 wt%. 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 3.
Based on the Zr content observed in Figure 3 it can be explained that the zirconia distribution in the ODS steel was mainly homogeneously same. This homogeneity of distribution of the zirconia dispersion was reported as essential to prepare compact materials to enhance the strength of the ODS steel alloy.[23][24]. Analysis of the microstructure was also performed by identifying the phase formed on the alloy by the XRD test. Figure 4 showed the diffraction pattern of the ODS steels synthesized by dispersing the zirconia into the steel SS 316L with the variation of sintering current of 60, 70, and 80 A. Based on Figure 4, the zirconia phase for all sintering current conditions could not be identified with XRD test due to the composition of zirconia that was less than 1 % wt percent in the sample. The phase composition observed was the Austenite phase and the Ferritic Phase of the SS 316L, as from the beginning (powder precursor) SS316L already consisted of these 2 phases. From the literature, in general, SS316L usually contains a ferritic phase (3 to 20% ideally).[25][26]. Refinement of the X-ray pattern was performed using HighScore Plus program to fit the pattern, for all samples refinement gave the $R_{wp} < 4\%$ and Goodness of Fitting (GOF) value around 2.0, indicating a good refinement result. The plots of refinement result is shown in Figure 5, and the phase composition, lattice parameters obtained from this refinement is shown in Table 1.

![Figure 3. SEM-mapping area of Zr distribution for ODS 316L sintering with 60 A (a), 70 A (b) and 80 A (c)](image)

![Figure 4. XRD pattern of the ODS steel (from top to bottom) sintered by APS with sintering current variation of 60 A, 70A, 80 A, and SS316L powders as received](image)
After treated with milling, compaction and sintering process with the APS in variation of sintering current parameters as shown in Table 1, it can be seen that the composition of the Austenite and Ferrite phases changes. This composition confirmed the structure and composition of the element observed by the SEM-EDX. The lattice parameter value in the phases for each sample is different. This data can indicate that the elemental composition of each phase is different. However, to calculate and determine the elemental composition from these lattice parameter values is difficult for the alloy consists of more than 2 elements.

**Table 1. Phases composition, Lattice Parameters and Fitting**

| Sample     | Phase     | Lattice Parameters (Å) | Weight % | Rwp (%)   | GOF |
|------------|-----------|------------------------|----------|-----------|-----|
| Sintered 60 A | Austenite | a = 3.6031(4)          | 86(1)    | 3.41891   | 1.18400 |
|            | Ferrite   | a = 2.888(3)           | 14(1)    |           |     |
| Sintered 70 A | Austenite | a = 3.6063(4)          | 76(1)    | 3.29049   | 1.12558 |
|            | Ferrite   | a = 2.890(1)           | 24(1)    |           |     |
| Sintered 80 A | Austenite | a = 3.6049(4)          | 71(1)    | 3.47952   | 1.32281 |
|            | Ferrite   | a = 2.898(3)           | 29(2)    |           |     |
| SS316L powders | Austenite | a = 3.5979(4)          | 64(1)    | 3.15061   | 0.92915 |
|            | Ferrite   | a = 2.8773(3)          | 36.2(4)  |           |     |

Addition of current sintering that theoretically increase the sintering temperature change the full-width at half-maximum (FWHM) of the pattern as observed in Figure 5 that revealed the grain size finer with smaller of crystal size confirmed with the microstructure explained before. Figure 4
showed that XRD Pattern of SS316L as received is different with ODS SS316L after milling and sintering process. The evolution XRD peak is not totally disappeared. This phenomenon is affected by milling mechanism. This result is similar to that of P.P. Chattopadhyay et al. [27].

In this experiment, addition of current used in the sintering process by an APS showed a better level of consolidation and better of grain refining process that indicated by increasing of the hardness level and close with the explanation of the microstructure discussed before.

4. Conclusion
The synthesis of ODS steel by dispersing zirconia to SS 316L produced relatively equiaxed microstructure with fine grain. SEM mapping analysis showed a homogeneous dispersoid distribution that formed a dislocation motion barriers to improve the mechanical properties. The main austenitic and ferritic phases were identified to be the same as the previous phase of 316L. Addition of sintering currents for 50, 60 and 70 Ampere showed a better level of consolidation that formed the grain refining process close with the observation result of the microstructure test.

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![Figure 6](image-url)
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