Jusami Jurnal Sains Materi Indonesia
Homepage: http://jusami.batan.go.id
Akreditation No : 21/E/KPT/2018
Date 9 July 2018
ISSN 1411-1098
E-ISSN 2614-087X

MICROSTRUCTURE OF OXIDE DISPERSION STRENGTHENED STEEL WITH Cr CONTENT VARIATION

Marzuki Silalahi[1], Bandriyana. B[1], Dimyati. A[1], Bambang. S[1], Ahda. S[1] and Fitria. N[2]

[1] *Center for Science and Technology of Advanced Materials - BATAN*
Kawasan Puspiptek, Serpong 15312, Indonesia
[2]*Natural and Mathematic Faculty of Sumatera Utara University*
Jalan Doktor Mansyur No.9, Medan, North Sumatra 20155
E-mail: silalahimarzuki@gmail.com

Received: 13 September 2019 *Revised: 4 October 2019* *Accepted: 24 October 2019*

ABSTRACT

MICROSTRUCTURE OF OXIDE DISPERSION STRENGTHENED STEEL WITH Cr CONTENT VARIATION. Microstructure and phase distribution of innovative Oxide Dispersion Strengthened (ODS) steel based on Fe-Cr-ZrO_2 particularly for application at high temperature reactor with variation of Cr content was analysed. The alloy was synthesized with Cr composition variation of 15, 20 and 25 wt.% Cr, while zirconia dispersoid kept constant at 0.50 wt.%. The samples was synthesized by mechanical alloying comprising of high energy milling for 3 hours followed by vibrated compression with iso-static load at 20 ton. The final consolidation was performed via sintering process for 4 minutes using the Arc Plasma Sintering (APS) technique, a new method developed in BATAN especially for synthesizing high temperature materials. The samples were then characterized by means of scanning electron microscopy (SEM) with energy dispersed X-ray (EDX) analysis capability and X-ray diffraction. The mechanical property of hardness was measured using standard Vickers micro hardness tester to confirmed the microstructure analysis. The results show that the microstructure of the ODS alloy samples in all variation of Cr content consists generally of cubic Fe-Cr matrix phase with small of porosity and Zirconia particles distributed homogenously in and around the matrix grains. The achievable hardness was between 142 and 184 HVN dependent consistently on Cr content in which Cr element may cause grain refining that in turn increase the hardness.

Key words **:** ODS alloy, Zirconia, Arc Plasma Sintering APS, SEM, XRD

ABSTRAK

MIKROSTRUKTUR BAJA YANG DIPERKUAT DISPERSI OKSIDA DENGAN VARIASIKANDUNAGAN Cr. Telah dianalisis struktur mikro dan distribusi fasa dari Baja yang diperkuat dispersi Oksida (Baja Oxide Dispersion Stengthened-ODS) berbasis pada Fe-Cr-ZrO2 dengan variasi kandungan Cr untuk aplikasi pada temperatur tinggi. Variasi kandungan Cr dari paduan yang dianalisis adalahdengan komposisi 15, 20, dan 25 persen berat, sementara komposisi dari Zirconia ditetapkan konstan pada komposisi 0,5 persen berat. Sintesis bahan dengan pemaduan mekanis menggunakan milling energi tinggi selama 3 jam diikuti kompresi tervibrasi dengan pembebanan iso-statis 20 ton. Proses akhir adalah konsolidasi melalui proses sintering menggunakan teknik APS (Arc Plasma Sintering) selama 4 menit, sebuah metode baru yang dikembangkan di BATAN khususnya untuk sintesis material temperatur tinggi. Sampel-sampel kemudian dikarakterisasi menggunakan peralatan scanning electron microscopy (SEM) dengan analisis energy dispersed X-ray (EDX) dan difraksi sinar-X (X-ray diffraction). Sifat mekanik kekerasan diukur menggunakan alat ukur kekerasan mikro (microhardness) Vickers untuk mengkonfirmasi analisis struktur mikro. Hasil-hasil menunjukkan bahwa secara umum struktur mikro dari sampel-sampel paduan ODS dengan semua variasi komposisi kandungan Cr adalah fasa matriks Fe-Cr kubik dengan porositas kesil dan partikel-partikel Zirconia terdispersi secara homogen didalam dan sekitar butir dari matriks. Kekerasan dapat dicapai antara 145 dan 184 HVN secara konsisten bergantung pada kandungan Cr dimana ele-men Cr bisa mengakibatkan penghalusan butir yang pada gilirannya meningkatkan kekerasan.

Kata kunci : Paduan ODS, Zirconia, Arc Plasma Sintering APS, SEM, XRD

INTRODUCTION

Development of advanced materials take an important role for the design and operation of the High Temperature Reactor (HTR) which is widely accepted as the best nuclear facility for generating electricity with better inherent safety and higher efficiency as conventional ones [1,2]. Recently, nuclear scientists consider to use ODS alloy as structure and core materials in high temperature nuclear power plants hence replace conventional austenitic super alloys because of its good stress, creep and corrosion performance at high temperature [3,4]. ODS alloys are commonly produced via powder metallurgy routes involving mechanical alloying followed by a consolidation by means of sintering in an electrical furnace which is often very time and energy consuming. Therefore, sintering process currently becomes a critical issue in many countries. Since 1980's a new sintering technique based on the use of pulsed DC current, previously known as Field Assisted Sintering (FAS) Technology but well established as Spark Plasma Sintering (SPS) was invented and widely used that occupies a very different time-temperature-density space in powder consolidation maps compared with conventional methods [5,6]. The SPS technique, however, required high current to generate electrical field for heating the samples about 5000 Amps. In line with this program**,** a new method known as Arc Plasma Sintering (APS) has been developed in PSTBM-BATAN. The apparatus has been sucsessfully synthesized high strength and high temperature alloys using heat generated by low current plasma of maximum 80 Amps at 12 Volts which reduce time and energy consumption significantly [7, 8]. Due to its exceptionally high mechanical stability and strength at elevated temperature Y_2O_3 was usually used as dispersed oxide in ODS alloy manufacturing. However, zirconia which has low cross-section for neutron absorption is recognized to be suitable as dispersoids of ODS alloy and is now widely studied. Zirconium also may produce a pinning dispersoid against grain boundary migration that improve the strength significantly [9,10]. The microstructure and homogenizing of oxide dispersions in the ODS alloy is very important in improving of both high temperature strength and corrosion properties, however their characteristics have rarely been studied. In the ODS steel manufacturing process, Cr composition plays an important role in enhancing high temperature oxidation resistance by formation of chromium oxide as a protective layer. Cr also causes the grain refinement which gives additional strength [11]. Therefore, influence of Cr content to the microstructure of the alloy is necessary and widely investigated. In the following work the ODS steel of Fe-Cr based zirconia has been synthesized using powder metallurgy and consolidation in APS with special focus on the study the microstructure and hardness change in dependence to variation of Cr content.

EXPERIMENTAL METHOD

The Fe-Cr-ZrO_2 ODS alloy was synthesized with the composition 15, 20 and 25 wt.% Cr while ZrO_2 kept constant at 0.5 wt.%. The samples were prepared by mixing and milling of Fe, Cr and ZrO_2 powder for 3 hours. Observation using the SEM-EDS test was carried out for the powder after milling process showing the presence of Carbon and other elements which occurs due to the handling of the samples. The samples were then pressed by isostatic pressing machine with a compression load of 20 Ton to form sample coins. The samples were consolidated by sintering in the APS for 4 minutes, the duration reffered to the sintering process of ODS alloy with 12 Cr content [12]. The APS experimental set-up is shown in Figure 1 [7].

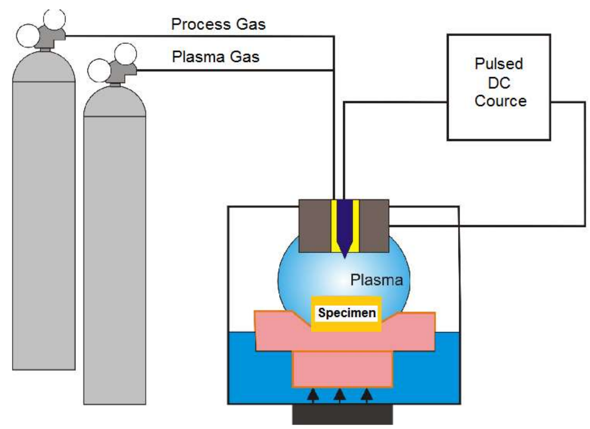

Figure 1. APS experimental set-up [7].

The main components of the APS is the arc plasma source that provide concentrated high temperature in a short time. This device allows fast consolidation process of pressed powder sample. The sintering was carried out in fully argon atmosphere in order to protect against oxidation during and after the process. The sample coin was placed on a copper cup and exposed by the plasma for 4 minutes at 25 Amps. The morphology and composition of the alloys were studied by means of Scanning Electron Microscopy (SEM) coupled to Energy Dispersive Spectroscopy (EDX). The EDX spectrums illustrate the chemical composition of the samples. The SEM area mapping was performed to observe the dispersion of the zircona in the alloy. XRD-diffraction analysis was carried out to evaluate the phase formation. Mechanical properties of the consolidated samples were studied using the Vickers microhardness (HV) measurement.

RESULTS AND DISCUSSIO

The ODS alloy before sintering observed by optical microscopy showed a relatively dense microstructure of grainy Fe and Cr particle with about 10 % porosity. After sintering by APS for 4 minutes, the general apperance revealed effective consolidation with high

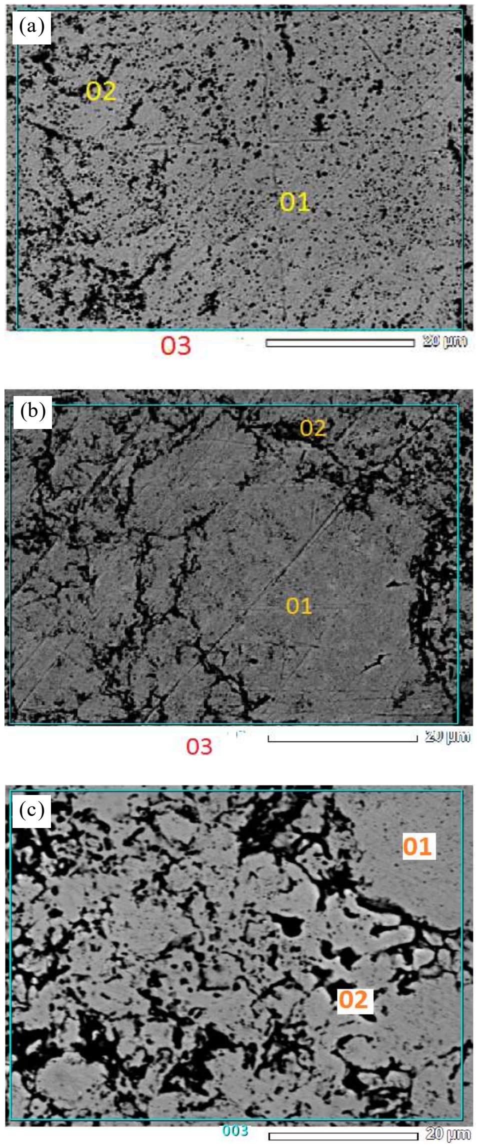

Figure 2. Microstructure of zirconia-ODS alloy with variation of Cr content (a). 15 wt.% Cr , (b). 20 wt.% Cr, (c). 25 wt.% Cr.

density and smaller porosity. The effect of Cr content to the alloy microstructure can be explained by the SEM-EDX test result as ilustrated in Figure 2. The elemental composition is presented in Table 1 as wt.%. The SEM examination on the consolidated materials shows the presence of particle with diffrent size and composition, randomly dispersed in the matric. It is obviously clear that structure of all ODS steel with some variation of Cr content were nearly the same with general apperance of small and equiaxed grains.

The structure consists of two phases, the Fe-Cr matrix phase and some Cr-rich particles. The elemental composition listed in Table 1 shows the composition of the consolidated materials is nearly close to the powder mix composition. Threfore, the sintering process with APS does not introduce significant changes in the composition of the powders. The SEM-EDS test showed a decrease in the composition of Cr element to around 21 wt%. This is due to the presence of Carbon element and increasing of the Fe element compositions which occurs during the milling and compacting process. Besides that, the oxygen element was also observed due to oxidation during the sintering process. The microstructure of the ODS alloy with increasing Cr content 15 to 25 wt.% showed finer grain size and more homogen distribution compared to those with 12 wt.% Cr from the previous study [12]. This elucidated that the Cr will influence the grain size of the alloy which may improve the mechanical properties.

Figure 3 and 4 illustrated the EDX mapping of ODS alloy that showed the distribution of the alloying element and the oxide dispersion. In general, the small equiaxed grain size of Fe and Cr were distributed in the alloy as confirmed by the SEM-EDX examination. The Zr and O, hence zirconia distribution is quite homogen. The grain size distribution of zirconia was similar to those typical found in ODS samples processed by Spark Plasma Sintered (SPS) [4].

The homogenous distribution of the zirconia oxide can increase the volume fraction of the small equiaxed grains in the matrix of the consolidated material that takes an important role in improving the mechanical properties. The XRD test was carried out to study the phase formation during alloying process. Figure 5 shows the diffraction pattern of sintered ODS alloy with 15, 20 and 25 wt.% Cr. Figure 6 shows the first peak of the diffraction pattern with 15, 20, 25 wt% Cr compare with the first peak of Fe, Cr and commercial ODS steel P91and the diffraction pattern for Fe base (labeled Fe B) and Cr base (labeled Cr B) elements having peaks close to Fe-Cr.

In general, the alloy was mainly dominated by the Fe-Cr phase as confirmed by the observation of the microstructure and measurement of elemental composition by the SEM-EDX. Analysis of the formation of this Fe-Cr phase was taken by the observation of the first and most

Table 1. Elemental compostion of ODS alloy with variation of Cr content

Element, wt.%	(a) 15 wt.% Cr			(b) 20 wt.% Cr			(c) 25 wt.% Cr		
	Area 1	Area 2	Area 3	Area 1	Area 2	Area 3	Area 1	Area 2	Area3
Fe	80.96	72.70	75.79	81.10	74.85	74.36	81.59	70.08	67.03
Cr	12.55	14.80	12.81	9.27	21.16	20.47	17.39	20.71	20.89
Zr	-	2.13	-	1.90	1.31	-	-	1.73	0.61
O	2.18	2.24	2.18	3.16	0.91	3.05	-	5.33	5.33

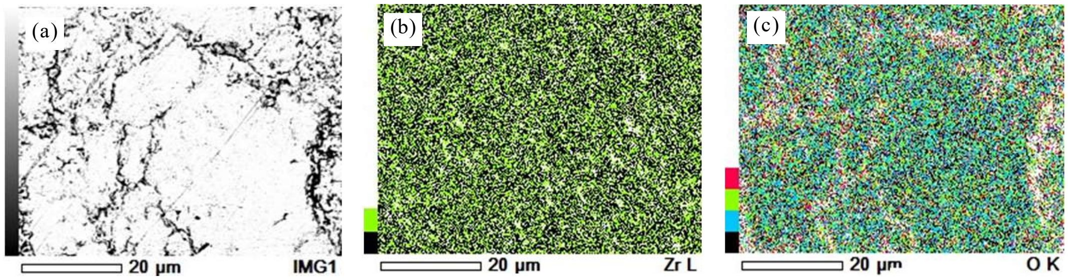

Figure 3. EDX mapping of Zr and O in ODS alloy with 20 wt.% Cr

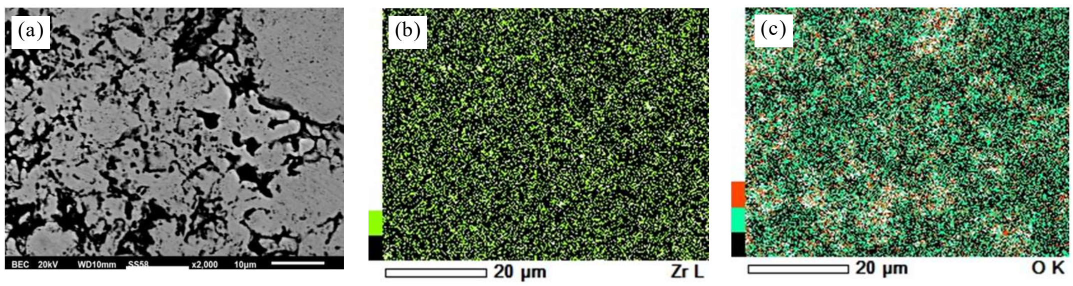

Figure 4. EDX mapping of Zr and O in ODS alloy with 25 wt.% Cr.

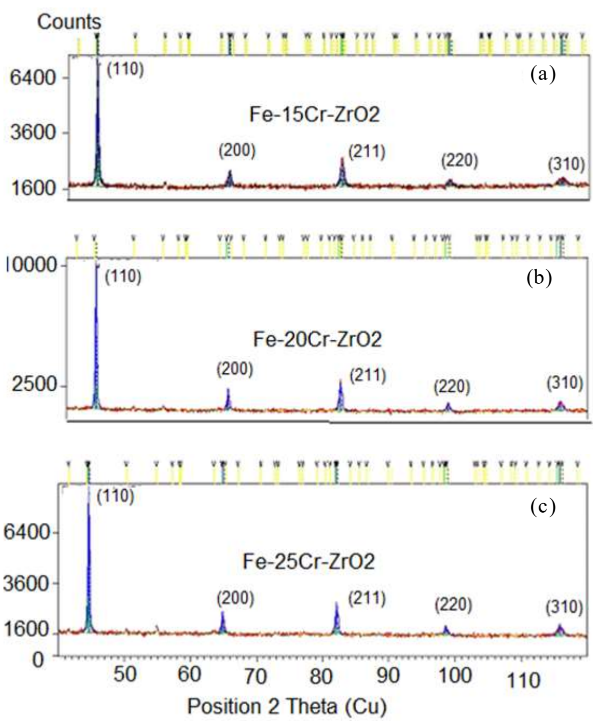

Figure 5. XRD pattern of Fe-Cr-ZrO_2 with (a). 15 w% Cr (b). 20 w% Cr, and (c). 25 w% Cr.

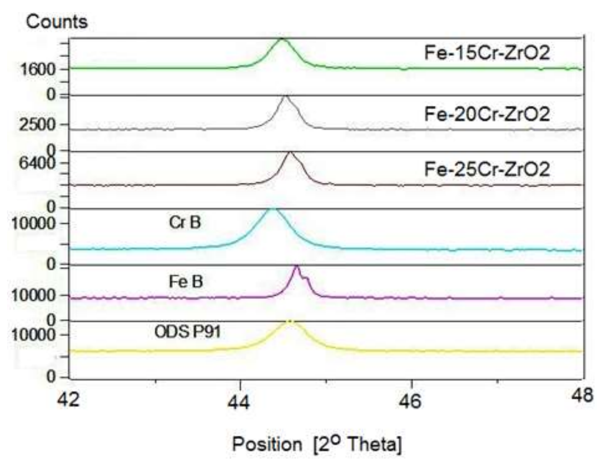

Figure 6. First peak XRD pattern of the ODS steel.

intense peak of the XRD pattern for FeCr-ZrO2. Figure 6 shows that increasing of the Cr content to 20 and 25 wt.%, will cause the peak of the full-width at half-maximum (FWHM) become wider which means the unit cel becomes smaller. This confirmed the grain refining effect caused by the Cr addition. Furthermore, the diffraction pattern of zirconia alloys does not look as perfect as compared to the diffraction pattern in commercial ODS P91 which has symitricaly peak form. The non symetricaly pattern of the zirconia ODS steel alloy was explained cause by the small peak of Fe and Cr due to the similarity of the crystal parameters of Fe, Cr and Fe-Cr. This data shows that the using of APS for sintering process has produced Fe-Cr alloys even though they have not been complete due to very short sintering time.

The hardness test was carried out to evaluate the mechanical characteristic of the alloy. The result of the hardness test with Cr variation is given in Figure 7. After sintering process for 4 minutes the ODS alloys have significant hardness 140 VHN to 180 VHN depend to the Cr content. It is obvious that increasing of Cr content will increase the hardnessIt is caused by theoxide dispersion and grain refinement as described in the observation of the microstructure.

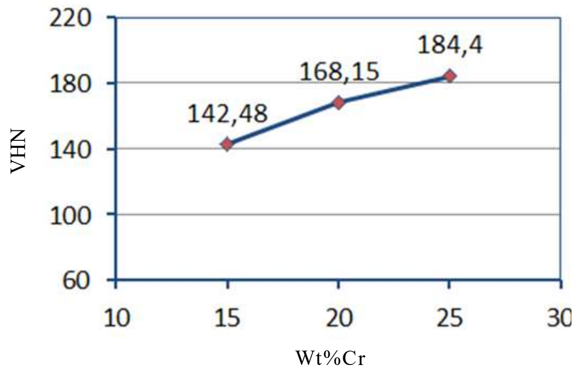

Figure 7. Hardness of ODS steel alloy in function of Cr content.

CONCLUSION

The structure of the ODS alloy sintered by the APS consists of mainly Fe-Cr phase with small grain and homogeneous zirconia oxide distribution. SEM investigation found that the sample with different Cr content exhibited some particle aglomeration and homogenized oxide dispersion that obviously improve the strength of the alloy. The XRD test confirmed the Fe-Cr phase formation even after 4 minute sintering process. The alloy showed exceptionally high Vickers Hardness of 180 VHR due to the grain refining and and homogeneous zirconia oxide distribution effect of Cr.

ACKNOWLEDGMENT

The authors thank to Dr. Muhammad Dani as Research and Development Coordinator for Nuclear Reactor Material, Dr. Abu Khalid Rivai as Divison Head of Advanced Material Science for their support, correction and contribution for publishing the paper.

REFFERENCES

[1]. A. García-Junceda, N. García-Rodríguez, M. Campos, M. Cartõn-Cordero, and J. M. Torralba, "Effect of Zirconium on the Microstructure and Mechanical Properties of an Al-Alloyed ODS Steel Consolidated by FAHP," *J. Am. Ceram. Soc.*, vol. 98, no. 11, pp. 3582–3587, 2015.

[2]. J. Bischof, A.T Motta, *J. Defence Science,* vol. 66, no. 4, pp. 316-322, 2016.

[3]. C. L. Chen, A. Richter, L. T. Wu, and Y. M. Dong, "Microstructural evolution and hardness of dissimilar lap joints of ODS/stainless steel by friction stir welding," *Mater. Trans.*, vol. 54, no. 2, pp. 215–221, 2013.

[4]. L. Raman, K. Gothandapani, and B. S. Murty, "Austenitic oxide dispersion strengthened steels: A review," *Def. Sci. J.*, vol. 66, no. 4, pp. 316–322, 2016.

[5]. R. Gao, T. Zhang, X. P. Wang, Q. F. Fang, and C. S. Liu, "Effect of zirconium addition on the microstructure and mechanical properties of ODS ferritic steels containing aluminum," *J. Nucl. Mater.*, vol. 444, no. 1–3, p. 4, 2014.

[6]. H. Zhang *et al.*, "Processing and microstructure characterisation of oxide dispersion strengthened Fe-14Cr-0.4Ti-0.25Y2O3 ferritic steels fabricated by spark plasma sintering," *J. Nucl. Mater.*, vol. 464, pp. 61–68, 2015.

[7]. A. Dimyati, *Proc. Asia Pacific Microscopy Conference*, vol. 11, 2016.

[8]. A. Dimyati, *Technical Report Insentif Riset Sistem Inovasi Nasional (InSINas)*, 2015.

[9]. M. Taguchi, H. Sumitomo, R. Ishibashi, and Y. Aono, "Effect of zirconium oxide addition on mechanical properties in ultrafine grained ferritic stainless steels," *Mater. Trans.*, vol. 49, no. 6, pp. 1303–1310, 2008.

[10]. T. Chuto, F. Nagase, and T. Fuketa, "High temperature oxidation of NB-containing ZR alloy cladding in LOCA conditions," *Nucl. Eng. Technol.*, vol. 41, no. 2, pp. 163–170, 2009.

[11]. N. Y. Iwata *et al.*, "Characterization of mechanically alloyed powders for high-Cr oxide dispersion strengthened ferritic steel," *ISIJ Int.*, vol. 49, no. 12, pp. 1914–1919, 2009.

[12]. Bandriyana, A. Sujatno, R. Salam, B. Sugeng, and A. Dimyati, "High temperature Oxidation of ODS alloy with zirconia dispersions synthesized using Arc Plasma Sintering," in *IOP Conference Series: Materials Science and Engineering*, 2017.

.