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# Microstructural characterization and strengthening mechanisms of a 15Cr-ODS steel produced by mechanical alloying and Spark Plasma Sintering

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ABSTRACT

The microstructure of the oxide dispersion strengthened (ODS) Fe-15Cr ferritic steel with Ti and Zr additions was characterized using transmission electron microscopy (TEM), elemental mapping, synchrotron small angle X-ray scattering (SAXS) and electron backscatter diffraction (EBSD) techniques. The results showed that bimodal grain size distribution in the matrix was observed, which is attributed to the heterogeneous recrystallization process during the Spark Plasma Sintering (SPS).

TEM and SAXS results showed that very high density nanoscale oxides are formed in 15Cr-ODS steel. Large concentration of nm-scale trigonal-phase $Y_4Zr_3O_{12}$ oxides and some large oxides of monoclinic $CrTi_2O_5$ are observed in specimen by high resolution TEM (HRTEM) and Energy-dispersive X-ray spectroscopy (EDS) mapping. Finally, the yield stress was experimentally measured and quantitatively estimated. The findings indicated that theoretical calculation was in accordance with the experimental results, and strengthening contributions from solute atoms, grains boundaries, dislocations and oxides was presented.

## 1. Introduction

Oxide dispersion strengthened (ODS) ferritic steels are amongst the most promising candidates for large scale structural materials in fast breeder reactors and blanket applications for fusion reactors. The steels that exhibit remarkable irradiation swelling resistance and excellent tensile, creep strength are being developed by powder metallurgy, well-known to produce nanostructure and ultrafine grained materials [1–5]. The superior performance of ODS ferritic steels over their conventional heat resistance steels and austenitic steels is attributed to the high number density of nano-sized oxides within the matrix [6–9].

To do so, powder metallurgy is the main manufacture process of ODS steels [10]. Hot Isostatic Pressing (HIP) and/or Hot Extrusion (HE) are classic, almost unique, methods to consolidate the ODS steels for controlling the microstructures and mechanical properties of ODS steels [5,11]. However, abnormal grain growth and precipitation coarsening are often observed since these processes require exposure for several hours at high temperatures over 1273 K (1000 °C) [12,13]. Compared to HIP and/or HE methods, Spark Plasma Sintering (SPS) is a novel powder consolidation technology [14]. The advantages of SPS spend much less time in both heating and cooling during sintering process. SPS has been widely used because of its ability to heat up the materials very quickly, providing a powerful tool to retain the original nano-grains. Recently SPS has been employed to prepare ODS steels. Bimodal microstructures were obtained in ODS steels after consolidation (SPS), which are different from the ODS steels microstructure produced by HIP and HE [15–18]. Grain structures composed of ultrafine grains with coarse grains improve ductility when compared to monomodal nanostructure materials [19–22]. Some groups have found that the Y—O and Y-Ti-O nano-sized oxides were observed in Ti-free and Ti-containing ODS steels produced by SPS, respectively [23,24]. The advantage of those nanoscale oxides is described as follows: (1) to inhibit the migration of dislocations and grain boundaries to enhance high temperature strength; (2) to provide sinks for the irradiation induced defects; and (3) to supply a great number of nucleation sites for small helium bubbles and promote radiation-induced vacancy-interstitial recombination [25–27]. All of the above attribute to high microstructural stability in retardation of loss of toughness at lower irradiation

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temperatures and to potential degradation of creep strength at higher temperatures. Some research groups have also reported the benefit of Ti addition in refining oxide particles ($Y_2O_3$) sizes, and increasing their number densities, through changing their chemical composition [28,29]. According to the first principle calculation results, the binding energy of Y-Zr-O phase is higher than that of Y-Ti-O phase in Fe matrix, which means that the Y-Zr-O phase is easier to form and more stable than Y-Ti-O phase [30]. Some researchers have found that the addition of element Zr can refine the oxides due to smaller oxide formation energy [31]. For this, some researchers have suggested utilizing of Zr rather than Ti in Al-ODS steel which promoted formation of finer Y-Zr-O particles compared to coarse Y-Al-O particles [32]. So it was expected that the addition of Zr elements in ODS steels without Al addition would refine the oxide particles and increase the number density of oxide particles by forming Y-Zr-O phase instead of Y-Ti-O and/or Y-O phase, which can improve the high temperature strength with a good corrosion resistance ability.

In the present research, we aimed at investigating the 15Cr-ODS steel with Ti and Zr additions fabricated by MA and SPS. The grain morphologies and the nano-sized oxides were observed by means of EBSD, SAXS, TEM and HRTEM. The yield strengths of 15Cr-ODS steel were measured at room temperature, 550 ℃ and 650 ℃. The strengthening mechanisms were estimated based on the comparison between the theoretical calculation and experimental measurements.

## 2. Experimental

A 15Cr-ODS steel with nominal chemical composition of Fe-15Cr-2W-0.3Ti- 0.3Zr-0.3$Y_2O_3$ (wt. %) was manufactured by using high-purity elemental powders and nanoscale $Y_2O_3$ powders. The mixed powders were mechanically alloyed (MA) in a FRITSCH Pulverisette 5 planetary mill for 50 h with a rotation speed of 260 rpm and ball-to-powder weight ratio of 10:1 under high-purity Ar atmosphere at room temperature. The stainless steel ball was applied as milling media. Its actual composition after MA was measured by inert gas pulse infrared thermal conductive method (ASTME1019-2003) and is listed in Table 1.

The MA powders were then consolidated by SPS to form a dense cylindrical pellet of 30 mm diameter and 6 mm height. SPS device was a Sumitomo graphite SPS-1050 sintering system (Japan). Sintering cycles were performed under 50 MPa average pressure, with a heating rate of 400 K $min^{-1}$ up to the holding temperature for a soaking time of 5 min. The soaking temperature was chosen at 950 ℃. The cooling was ensured by direct contact with water-cooled punches, which induced a cooling rate of 200 K $min^{-1}$. Relative density of SPS compacts was measured using the Archimedes' principle where the mass of the sample emerged and immersed in water is measured using a very precise weighing scale, and the density of ferritic steel (7.82 g/$cm^3$) was chosen as the theoretical density. The relative density of 15Cr-ODS steel fabricated by SPS is reaches to 97.7%.

X-ray diffraction (XRD) was carried out on the specimen to analyze the crystal structure, using a Rigaku Smartlab, using Cu $K_\alpha$ radiation, at a voltage of 40 kV, a current of 40 mA and a speed of 2 (°)/min. The diffraction angle ($2\theta$) range of all the measurement was restricted to 15–120°. The lattice parameter a was calculated by the Cohen-Wagner extrapolation plot ($a_{hkl}$ vs. $\cos^2\theta/\sin\theta$) [33], the lattice strain ($\varepsilon$) of specimen was determined by means of Williamson-Hall equation from XRD patterns according to Scherrer formula after subtracting the widths due to instrumental broadening and strain effects using the equation [34]:

**Table 1**
The actual composition of ODS steel (wt. %).

| Fe | Cr | W | Ti | Zr | Y | O | N | C |
|---|---|---|---|---|---|---|---|---|
| Bal. | 14.8 | 1.9 | 0.29 | 0.27 | 0.25 | 0.21 | 0.03 | 0.08 |

$$B\cos\theta/\lambda = 0.9D + 2\varepsilon\sin\theta/\lambda \quad (1)$$

Where $B$ is the integral widths that were attained by eliminating the instrumental broadening, $\theta$ is the diffraction angle, λ is the wavelength of X-ray (1.541 Å), $D$ is the grain size, and $\varepsilon$ is the strain in matrix. Hence, the dislocation density ρ was derived as [35]:

$$\rho = 14.4\varepsilon^2/b^2 \quad (2)$$

Where $b$ is the Burgers vector (0.248 nm) [36].

FIB lift-out method was employed to prepare transparent electron microscopy (TEM) specimens by using JEOL JIB-4601 F FIB system. Low-energy Ga beam (5 kV and 1 kV) was used to remove the higher energy ion damage. Finally, those micro-samples were electro-polished using flash electropolishing at 20 V in a solution of 80%$C_2H_5OH$ + 20% $H_2SO_4$ at about 0 ℃ for 0.02 s. The microstructure was characterized using a JEOL JEM-2100 TEM with an acceleration voltage of 200 kV. To determine the number density of oxide particles, the local TEM foil thicknesses were measured by convergent beam electron diffraction method (CBED) 34 [34,37]. High angle annual dark field (HAADF) and scanning transmission electron microscopy (STEM) images were taken in an aberration corrected FEI Titan$^3$ G2 60–300 microscope operated at 300 kV. EDS characterization was done in STEM mode at 300 keV to obtain elemental mapping. The EBSD samples with dimension 3 × 5 × 5 $mm^3$ for grain morphologies and size analyzing were mechanical polished and then electro-polished in order to remove the deformation layer introduced during mechanical milling. The grain morphologies and size were analyzed by EBSD, which EBSD experiment was carried out on JEOL JSM6500 F Scanning Electron Microscopy (SEM) in step length of 50 nm in Hokkaido University.

Synchrotron radiation SAXS experiments were performed in transmission mode using two systems at the National Institute for Materials Science (NIMS). To obtain a reasonable transmission rate, the samples were mechanically thinning to less than 30 μm A two-dimensional imaging detector was used to collect the scattering patterns. The distance between the samples and the detector was 2 m. After correction (using cowhells as standard sample), the two-dimensional scattering rings were transformed into one-dimensional scattering curves by using Fit 2D software [38]. The scattering vector $q$ is defined as:

$$q = \frac{4\pi \sin\theta}{\lambda} \quad (3)$$

Where λ is the X-ray wavelength, $2\theta$ is the scattering angle.

The IRENA package developed by Argonne National Laboratory was used to fit the SAXS curves [39]. The fitting equation used in IRENA package is given below [40]:

$$I(q) \approx G\exp\left(\frac{-q^2R_g^2}{3}\right) + B\left[\frac{erf\left(qR_g/\sqrt{6}\right)}{q}\right]^p \quad (4)$$

Where $G$ is a constant defined by the specifics of composition and concentration of the oxides. For dilute oxides, $G = N_p n_p^2$, where $N_p$ is the number of oxides in the scattering volume and $n_p$ is the number of excess electrons in an oxide compared to Fe matrix. Thus, $G = N_p(\rho_e V_p)^2$, where $V_p$ is the volume of an oxide and $\rho_e$ is the electron-density difference between the oxide and Fe matrix. $R_g$ is radius of gyration. $B = N_p 2\rho\pi_e^2 S_p$, where $S_p$ is the oxide surface area.

The number density distribution $N(r)$ of oxides with radius $r$ is assumed to have a log normal distribution, which is defined as follows:

$$N(r) = \frac{1}{\sqrt{2\pi}}\frac{1}{r\sigma}\exp\left\{-\frac{[\ln(r/R_0)^2]}{2\sigma^2}\right\} \quad (5)$$

Where $R_0$ is the radius at the peak position of number density, and the standard deviation $\sigma$ is the width of log normal distribution of $N(r)$. The average diameter $d_{ave}$ and standard deviation $\sigma$ in this study were obtained from IRENA package directly.

The tensile tests were carried out using Shimadzu AG-Xplus electro-