Microstructure and oxidation resistance of spark plasma sintered Yttria-Zirconia ODS steels

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Abstract. In this experiment, the effect of Y₂O₃ and ZrO₂ additions on the microstructure and cyclic oxidation resistance of 17-Cr ODS steel containing Al consolidated using spark plasma sintering method were studied. In addition, density, porosity and hardness were also observed. Four compositions of ferritic steels as Fe-17Cr-3.5Al-Ti-Y ('FP'), Fe-17Cr-3.5Al-Ti-Y-0.4Y₂O₃ ('FY'), Fe-17Cr-3.5Al-Ti-Y-0.4ZrO₂ ('FZ'), and Fe-17Cr-3.5Al-Ti-Y-0.2Y₂O₃-0.2ZrO₂ ('FYZ') were prepared by mechanical alloying and followed by sintering at 1000 °C. Microstructure characteristics were observed for different aspect, viz. elemental distribution, composition, and phase identification. Cyclic oxidation tests were carried out at 800 °C for 8 cycles. The results show that ZrO₂ addition suppresses the formation of Y-Al-O clustering and promotes the formation of Y-Zr-O clustering and the enhancement of oxidation resistance of the alloy. However, in some condition it also has a deleterious effect on crack resistance. In contrast, the addition of Y₂O₃ decreases the oxidation resistance but increases the hardness.

1. Introduction

Ferritic-Martensitic Oxide Dispersion Strengthened (ODS) steel as material components of nuclear cladding has been developed for application at high corrosion and neutron irradiation environments of advanced nuclear reactor [1-4]. High temperature strength and resistance to swelling, thermal embrittlement, fatigue crack growth, and creep of ferritic/martensitic steel is superior compared to austenitic steel [5-8]. Moreover, the addition of oxide particle as dispersed materials (ferritic ODS steel) leads to increase in strength and resistance to thermally-induced creep [2]. Accordingly, the operation temperature of ferritic steel can be increased higher than 600ºC [2]. However, there are several aspects affecting the mechanical properties, physical properties, and corrosion-oxidation resistance of ferritic ODS steel, such as material composition, consolidation method and processing parameter.

The most common method used for consolidation of ODS alloy is extrusion and hot isostatic pressure (HIP). Comparatively, spark plasma sintering (SPS) is a relatively new consolidation method which has been developed. It utilizes pulsed direct electrical current to perform high-speed consolidation of powders. The properties of consolidated samples are improved because of intrinsic properties of nanoparticles maintained in their fully dense products by a very high heating and cooling rates during SPS [9]. Although SPS is widely studied, the effects of Zr (and its oxide form) on ODS steel consolidation are still rare.
A sufficient amount of aluminium addition into ferritic ODS steel is known to give advantage in increasing corrosion resistance. It was found that the addition of 4 wt.% Al into 16 wt.% Cr ODS steel increases corrosion resistance through the formation of thin alumina film on the surface of the steel. The exact effect does not show up in 19 wt. % Cr ODS steel with the addition of 4 wt.% Al because of a rather dense chromia film formed on the surface [10-12].

In contrast, the addition of aluminium is also capable of giving some deleterious effects into ODS steel. Those are oxide particle coarsening by the formation of Y-Al-O phase and the reduction of high temperature strength [12-13]. Zr addition into the alloy is one of the methods that can be used to prevent aforesaid deleterious effects. The first principle calculation results indicate that the binding energy of Y-Zr-O nanoparticle is more favourable and more stable than coarse Y-Al-O, resulting the increase of the strength of the steel [14]. However, there is still a lack of research concerning the effect of Zr addition in its oxide form (ZrO2) or in its stable form (Yttria-stabilized Zirconia) into ODS steel as dispersant on the oxidation resistance of the alloy.

In order to clarify the effects of Al-containing ferritic ODS steel with Y2O3 and/or ZrO2 additions and SPS consolidation method, several experiments were conducted in this study. This report presents and discusses the effects of Y2O3 and/or ZrO2 additions into 17Cr-3.5Al-ODS steel on microstructure, physical properties (density and porosity), mechanical property (hardness), and cyclic oxidation resistance.

2. Experimental Procedures

The alloys with nominal composition as 17Cr-3.5Al-Ti-Y (denoted as FP), 17Cr-3.5Al-Ti-Y-0.4Y2O3 (denoted as FY), 17Cr-3.5Al-Ti-Y-0.4ZrO2 (denoted as FZ), and 17Cr-3.5Al-Ti-Y-0.2Y2O3-0.4ZrO2 (denoted as FYZ) were prepared from high purity powders of Fe17Cr3.5AlTiY, Y2O3, and ZrO2. Each composition was mechanical alloyed (MA) using a high-energy planetary ball mill (SFM-1 Desk-Top). MA process was performed for 6 h with a rotation speed of 280 rpm, a ball to mass ratio of 10:1, and hexane as MA solution.

![Figure 1. Sintering configuration: (a) Dr. Sinter 515S, (b) carbon paper for top and bottom part, (c) graphite dies and punches, (d) carbon paper between powder and dies, (e) carbon cover and container configuration.](image)

The milled powders were consolidated into samples with a diameter of 15 mm using Dr. Sinter 515S Spark Plasma Sintering System at a constant axial pressure of 40 MPa and vacuum of 80 Pa. Carbon covers were used to increase the conductivity of samples (see Figure 1). Temperature was increased from a room temperature to 1000ºC with a constant rate of 100ºC/minute.

Density of sample was measured using Archimedes method. Porosity was calculated from optical microscopy data by ImageJ software analysis [15]. Micro-hardness (HV) was measured by a Vickers hardness tester Leco M-400-HI with 0.1 kgf load. High temperature cyclic oxidation test was performed...
at 800°C for 8 cycles. Microstructure observation was carried out using Hitachi SU3500 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectrometer (EDX Horiba). Phase identification was determined using Rigaku SmartLab X-ray diffractometer. Etching was carried out only for samples before oxidation using etchant solution standard for ferritic grade steel (aqua regia + acetic acid) [16]. The etchant composition was 5 mL HNO₃, 5 mL C₂H₄O₂, and 15 mL HCl.

3. Results and Discussion

3.1. Density and Porosity

The results show that samples with higher ZrO₂ content tend to yield lower density. This can be observed in Figure 2 (a). The density of FZ and FYZ are lower, 6.447 and 6.513 g/cm³, respectively compared to FP and FY, 6.619 and 6.637 g/cm³, respectively. The density of sample from highest to lowest is FY, FP, FYZ, FZ.

![Figure 2. (a) Density and (b) porosity of FP, FY, FZ and FYZ.](image)

![Figure 3. Hardness of FP, FY, FZ and FYZ sintered at 1000°C.](image)

It is well known that the greater porosity of the alloy is associated with lower density. This is in good agreement with the results of present study. This can be observed in Figure 2 (b). FZ and FYZ porosity are 0.864 and 0.684 %, respectively, which have greater value than FP and FY 0.476 and 0.400 %, respectively. Even though the density of ZrO₂ is higher than Y₂O₃ (5.68 compared to 5.01 g/cm³), samples with the addition of ZrO₂ show a slightly lower value compared to samples with the addition of Y₂O₃. This suggest that the microstructure of sintered alloy seems to affect the density and porosity of the ODS steel.

3.2. Hardness

Hardness test results as presented in Figure 3 show a slightly different pattern compared to density. The highest hardness of the sample is FY (246.9 HV) followed by FYZ (206.9 HV), FZ (190.13 HV), and then FP (183.43 HV) as the lowest one.
Although ZrO$_2$ hardness is higher compared to that of Y$_2$O$_3$, in accordance with the results as presented above, higher hardness of the samples seems to associate with its higher density and lower porosity. Since the size of starting material of ZrO$_2$ (10-15 μm) used in this study is higher than that of Y$_2$O$_3$ (5-10 μm) and also the effectiveness of particles size reduction may be lower due to high hardness of ZrO$_2$ (12.3 GPa) compared to Y$_2$O$_3$ (6 GPa) and steel milling ball (5 GPa), for ZrO$_2$ it can cause the distance between dispersed ZrO$_2$ particles becoming larger. Hence, it can reduce the strengthening effect.

3.3. Before Oxidation

3.3.1. Phase identification

The results of the XRD phase analysis after milling and after sintering (pre-oxidation) can be seen in Figure 4(a) and (b), respectively. According to the results, the phase detected for both conditions is α-Fe. This result is appropriate when compared with the Fe-Cr binary phase diagram. It indicates the homogeneity of Fe and Cr distribution. The similar results between these two conditions also indicate that a short sintering stage doesn’t lead any other phase formation.

![Figure 4. XRD patterns of FP, FY, FZ and FYZ: (a) after milling, and (b) after sintering.](image)

3.3.2. Microstructure

Figure 5 shows the optical microstructure images of FP, FY, FZ and FYZ after sintering at 1000°C. It can be seen that intergranular crack are observed in alloys with higher ZrO$_2$ content. These intergranular cracks contribute significantly to the increase in porosity and decrease in density for FZ and FYZ. While there is no intergranular crack observed in samples without ZrO$_2$ addition, i.e. FP and FY.

The presence of intergranular crack in alloys with the addition of ZrO$_2$ can be attributed to the accumulation of stress due to the change of ZrO$_2$ crystalline structure from monoclinic to tetragonal during sintering. The change in crystal structure leads to an increase in crystal volume by 9%[17]. This crystal structure transformation occurs in ZrO$_2$ which has not been completely stabilized by Y$_2$O$_3$ at sintering stage (at 18 mol.% of YO$_{1.5}$ or 9.47 mol.% Y$_2$O$_3$[18]). The stabilization will be reached after subsequent heat treatment.

![Figure 5. Microstructure images of FP, FY, FZ and FYZ before oxidation.](image)
3.3.3. Elemental distribution

Figure 6 shows the distribution of Fe and Cr elements in the etched samples of FP, FY, FZ and FYZ after sintering. There is no concentration/cluster of Fe or Cr in all samples. Fe and Cr elements are uniformly distributed in the alloy matrix. This indicates that Fe maintains its ratio with Cr and vice versa. The homogeneous distribution of Fe and Cr also proves that 17 wt. % Cr can be maintained in all sample. Hence, α-Fe is the only possible phase formed in the samples as XRD phase analysis results tell.

![Fe and Cr distribution in sample: (a) FP, (b) FY, (c) FZ, and (d) FYZ after sintering.](image)

3.4. Oxidation kinetic

The results of cyclic oxidation test show that the initial stage of oxidation contributes significantly to the rate of weight gain. The rate of weight gain from the lowest to the highest is FZ, FYZ, FP, FY, respectively. By looking at Figure 7, it can be seen that the rate of weight gain follows a logarithmic pattern. The logarithmic pattern of weight gain rate can generally be caused by two things, viz. the presence of surface reactions and the presence of rapid ionic transport paths [19].

The surface reaction occurs at temperatures below 400 °C. In the case of oxidation at higher temperatures (such as 800°C), alloys usually undergo a rapid surface reaction while in the initial heating stage. The surface reaction occurs when a high electric field is formed due to changes in electron concentration. This results in an increase in the rate of ion migration resulting in the formation of the oxide layer [20]. The rate of ion migration decreases to a very low value with the decrease of electron movement from the metal through the oxide to the adsorbed oxygen atom due to the thickening of the oxide layer [21].
In addition to surface reactions, the presence of rapid ionic transport paths (along grain boundary, dislocation pipes, surface of the pores, residual stress) can also affect the difference in the rate of weight gain when the oxidation step is carried out. The presence of rapid ionic transport paths scattered in alloys can be the path of oxidation movement. These pathways increase ionic flux and prevent the uniform oxidation. This path will be closed along with recrystallization, residual stress removal, grain growth, or pore closure due to the growth stress by the oxide [22].

Even though FZ has the highest porosity in comparison with the other samples, surprisingly its weight gain rate is the lowest followed by FYZ, FP, and then FY. It is clearly in contrast with rapid ionic transport paths theory, hence indicating the existence of other variable affecting the result. The cause of this result can be acquired by means of microstructural analysis which will be covered in the next section.

3.5. After Oxidation

3.5.1. Phase identification

Figure 8 shows X-ray diffraction patterns of FP, FY, FZ and FYZ after oxidation at 800°C for 8 cycles. In all samples, α-Fe, FeTiO$_3$, and α-Al$_2$O$_3$ phases are observed. Based on the calculation of the enthalpy of oxide formation by Chinnappan (2014) [23], FeTiO$_3$ phase is a less stable phase compared to Y-Al-O, Y-Ti-O, TiO$_3$, etc. Thus, the formation of more stable phase is still possible.

In FP, FZ, and FYZ samples, Cr$_2$O$_3$ phase is not detected. This is because even though based on the kinetics Cr$_2$O$_3$ formation is preferred (due to the much higher concentration of Cr content), but thermodynamically, Al$_2$O$_3$ is more stable. Hence, Cr$_2$O$_3$ may be formed only at the beginning of oxidation, and will be replaced by Al$_2$O$_3$ subsequently. In this study, XRD tests were performed after oxidation for 160 hours. Therefore, re-oxidation may be the main cause of Cr$_2$O$_3$ formation in FY.
Figure 8. XRD patterns of (a) FP, (b) FY, (c) FZ and (d) FYZ after oxidation at 800ºC for 8 cycles.

3.5.2. Microstructure
Figure 9 shows the cross-sectional SEM images of FP, FY, FZ and FYZ after oxidation at 800ºC for 8 cycles. The presence of crack in the oxide layer initiated at the oxide/metal interface area in FY and FYZ is observed. The worst condition is shown in FY where the formed Al₂O₃ layer is discontinuous. This can be attributed to the difference in thermal expansion coefficients between Al₂O₃, ZrO₂, Y₂O₃, and ferritic steel.

![Figure 9. Microstructure images of FP, FY, FZ and FYZ after oxidation at the oxide/metal.](image)

At the oxide/metal interface region, the high difference in thermal expansion coefficient between Al₂O₃ and substrate metal (8x10⁻⁶ : 13x10⁻⁶ /°C) may cause the spallation of the oxide layer when it was subjected to cyclic thermal loading. The same case is the most common cause of failure in coating applications in TGO interface (thermal-growth oxide) [24-26].

Moreover, the rise of Y₂O₃ content at the interface region of Al₂O₃ /substrate metal may induce crack initiation. This is because the coefficient of thermal expansion of Y₂O₃ which is almost similar to Al₂O₃ causes the stress to become stronger.

In contrast to Y₂O₃, the stabilized ZrO₂ (cubic crystal structure) has a thermal expansion coefficient closer to the substrate metal (ferritic steel), precisely between the substrate metal and the Al₂O₃ protective oxide layer, which is 10.5 x 10⁻⁶ /°C [27]. Therefore, the stress generation due to thermal expansion different becomes lower, hence lowering crack initiation and protective oxide layer discontinuity possibility. The difference in thermal expansion coefficient is what causes the highest Y₂O₃ content has the worst oxidation resistance. As for the FYZ sample (which has the second highest
Y$_2$O$_3$ content after FY), the initiated crack has not resulted in direct exposure of inner alloying elements yet. Accordingly, the oxidation rate is still well controlled.

3.5.3. Elemental distribution

Figure 10 shows the distribution of Cr and O elements near the surface of FY. The result indicates the formation of Cr$_2$O$_3$ cluster identified from XRD phase analysis. The formation of Cr$_2$O$_3$ may be caused by oxide layer discontinuity which enhances inward oxygen diffusion and promotes continuous oxidation of inner alloying elements.

![Figure 10. Clustering of: (a) Cr and (b) O in (c) FY sample after oxidation at 800°C for 8 cycles.](image)

Figure 11. Distribution of Al, Y, and O alloying elements from samples: (a) FP, (b) FY, (c) FZ, and (d) FYZ after oxidation at 800°C for 8 cycles.

![Figure 11. Distribution of Al, Y, and O alloying elements from samples:](image)
Figure 11 shows the Al, Y, and O distribution over all the samples after oxidation at 800°C for 8 cycles. In FP and FY, the presence of Al, Y, and O clustering is observed. This indicates the formation of minor phase of Al-Y-O. Although Y₂O₃ is not added into FP sample, the clustering of these three elements could be derived from Y reactive element of base material composition in the FP sample.

In the sample with ZrO₂ addition, the formation of Al-Y-O cluster does not occur. This shows that the ZrO₂ addition can also suppress the formation of minor phase Al-Y-O. This result is supported by the identification of Y, Zr, and O clustering elements on FZ and FYZ (see Figure 12). The existence of a finer Y-Zr-O cluster can reduce the formation of the coarser Al-Y-O cluster due to the higher Y-Zr-O bonding energy compared to Al-Y-O[28]. Hence, it prevents the depletion of Al for protective oxide scale formation.

4. Conclusions
Overall research showed that the addition of un-stabilized ZrO₂ to the alloy might cause cracking when sintering was done, thus increased porosity and decreased density of the alloy. The addition of ZrO₂ had a capability to decrease the tendency of the secondary phase Al-Y-O formation and increased the tendency of the more refined Y-Zr-O phase formation. Excessive addition of Y₂O₃ might cause discontinuity in the protective oxide layer. The substitution of the oxide of Y₂O₃ using ZrO₂ at the right level would increase the cyclic oxidation resistance.

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