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Microstructure and Mechanical Properties of 14Cr-ODS Steels with Zr Addition

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Abstract: In this study, oxide dispersion strengthened (ODS) ferritic steels with nominal composition of Fe–14Cr–2W–0.35Y₂O₃ (14Cr non Zr-ODS) and Fe–14Cr–2W–0.3Zr–0.35Y₂O₃ (14Cr–Zr-ODS) were fabricated by mechanical alloying (MA) and hot isostatic pressing (HIP) technique to explore the impact of Zr addition on the microstructure and mechanical properties of 14Cr-ODS steels. Microstructure characterization revealed that Zr addition led to the formation of finer oxides, which was identified as Y₄Zr₃O₁₂, with denser dispersion in the matrix. The ultimate tensile strength (UTS) of the non Zr-ODS steel is about 1201 MPa, but UTS of the Zr-ODS steel increases to 1372 MPa, indicating the enhancement of mechanical properties by Zr addition.

Keywords: ODS ferritic steel, Microstructure, Mechanical properties

Introduction

In a future environmental friendly energy scenario, the aim of decreasing reliance on fossil fuels has motivated a worldwide interest in advanced nuclear energy [1, 2]. To meet the higher standard of material performance in generation IV fission reactors and future fusion reactors, it is necessary to develop new structural materials with excellent properties

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including irradiation resistance, corrosion resistance and good high temperature strength [1, 3]. Recently, oxide dispersion strengthened (ODS) ferritic steels have been developed as fuel cladding for next generation nuclear systems. Compared with conventional ferritic/martensitic steels, ODS steels have better tensile and creep strength, radiation resistance and oxidation resistance due to the high number density of nano-sized oxide particles with good thermal stability [4–11]. Cr can improve the corrosion resistance of ODS steels, but the Cr content can be balanced between a merit of corrosion resistance and a demerit of aging embrittlement at high temperature [12]. Therefore, the Cr content in ODS steels was usually controlled to less than 16 wt%. Some research groups have also reported the benefit of Ti addition in refining oxide particles (Y₂O₃) sizes, and increasing their number densities, through changing their chemical composition [13–15]. 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 [16]. Some researchers have found that the addition of element Zr can refine the oxides due to smaller oxide formation energy [17]. 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 [18]. 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–O phase, which can improve the high temperature strength with a good corrosion resistance ability. In this research, we report a new alloy system based on conventional ODS steels with Zr addition which were fabricated by mechanical alloying (MA) and hot isostatic pressing (HIP). The grain size, size and phase composition of oxide particles, and mechanical properties of the 14Cr-ODS steels were characterized.

Experimental

The ODS ferritic steel with the nominal composition of Fe–14Cr–2W–0.35Y₂O₃ (wt%) was prepared by MA, using high-purity metal powders of Fe, Cr, W and Ti in

size about 10 μm and Y_2O_3 particles sized between 30 and 50 nm. In order to investigate effects of Zr addition on the microstructure and mechanical properties of ODS ferritic steels, Zr powders (0.3 wt%) in size of micrometer were used. The MA was performed in a high purity Ar (99.99 wt%) atmosphere by using a planetary ball mill. The ball-to-powder weight ratio of 10:1 and a rotation speed of 260 rpm were conducted with milling time up to 50 h [19]. Subsequently, the milled powders were then sealed into a mild steel can, degassed at 400°C for 4 h in vacuum ($<10^{-4}$ Pa) and then consolidated by HIP at 1100°C under a pressure of 150 MPa for 2 h. The relative density of specimen was measured by means of the Archimedes method and compared to a calculated, theoretical density of the ferritic steel 7.82 g/cm³. To investigate the effect of Zr addition on the grain size, the Electron backscatter diffraction (EBSD) specimens from HIPed bars with dimension $3 \times 5 \times 10 \text{ mm}^3$ was carried out on a JEOL JSM7001F SEM after electro polishing in step length of 0.1 $\mu\text{m/s}$. The oxide particles size and composition of the specimens were investigated by transmission electron microscopy (TEM) using a JEM-2010 with an Energy Dispersive Spectroscopy (EDS). The TEM samples were prepared by using a replica method. The procedures for the preparation are as follows: mechanically polished $5 \times 10 \text{ mm}^2$ of the ODS steels were pre-etched in a dilute acid solution (hydrochloric acid (10%), ethanol (90%)) for 10 min. The chemically etched surfaces were then coated with an amorphous carbon film to a thickness of about 1500 Å with a JEOL 560 fine carbon coater, and subsequently chemical etched again in a similar acid solution to make the separation of carbon films from the substrate of the alloys. The carbon films can be cleaned carefully in an ethanol solution (10% pure ethanol: 90% distilled water), were finally put on copper meshes. Extraction replicas can give us more coherent information about oxide particles analysis without a matrix. The SAXS measurements were performed in transmission mode at Shanghai Synchrotron Radiation Facility (SSRF) in BL16B1 beamline to analysis the size and number density distribution of nano-sized oxides in ODS steels. The photon energy and wavelength were 10 KeV and 1.24 Å, respectively. In order to obtain a good transmission rate, the ODS samples were finally mechanically ground to 30 μm in thickness. A two-dimensional imaging detector was used to collect the scattering patterns. After corrections (using a cowhells standard), the two-dimensional diffraction rings were transformed into one-dimensional SAXS intensity (I)-scattering vector (q) curves. The scattering vector q is

defined as: $q = 4\pi \sin \theta / \lambda$, λ is the X-ray wavelength, θ is the scattering angle. After correction (using cowhells as standard specimen), the two-dimensional scattering rings were transformed into one-dimensional scattering curves by using Fit 2D software produced by Andy Hammersley on V 10.132. [20].

In this study, SAXS data were fitted by software package IRENA package [21]. The oxides were assumed to be spherical [22]. The unified equation summarized by Beaucage is an approximate form that describes a complex morphology over a wide range of q in terms of structural levels. The fitting of SAXS data was based on the maximum entropy algorithm [22, 23], so that the size distribution of oxides could be assessed. The unified equation is given below:

$$I(q) \approx G \exp\left(\frac{-q^2 R_g^2}{3}\right) + B \left[\frac{\text{erf}(q R_g / \sqrt{6})}{q} \right]^3 \quad (1)$$

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 ρ_e is the electron-density difference between the oxide and Fe matrix. R_g is radius of gyration. B is a prefactor specific to the type of power-law scattering and defined according to the regime in which the exponent P falls.

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

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

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

Vickers microhardness tests were performed by using 401MVDTM Vickers hardness tester at a load of 100 g. The hardness values were determined based on the average of 10 points. Tensile tests were carried out at constant strain rate of $2 \times 10^{-3} \text{ mm s}^{-1}$ at room temperature (RT) and 650°C, respectively with the dimensions of 1 mm thick, 3 mm wide and 13 mm gauge length. Tension tests were performed three times at each temperature.

Result and discussion

Microstructure characterization

The relative density (the ratio of real density and theoretical density) of the two kinds of 14Cr-ODS ferritic steels produced by MA and HIP is greater than 99%. EBSD method was exploited to evaluate the change of grain size by Zr addition. Results are shown in Figure 1. It can be seen from the inverse pole figure (IPF) maps that no obvious anisotropies were observed in the specimens. The grain size can be refined by Zr addition. The mean grain sizes were around $1.3 \pm 0.4 \mu\text{m}$ and $0.7 \pm 0.3 \mu\text{m}$, respectively which can be determined from the EBSD images. Based on Hall–Petch relation, the smaller grain size means higher yield strength. The histograms of grain size distribution were presented in Figure 2. It shows that the distribution of the grain size becomes narrower by Zr addition and that the grain size is mainly distributed in the range of 0.2–6.8 μm and 0.1–3.8 μm in non Zr-ODS steel and Zr-ODS steel, respectively. The statistical EBSD results, seen in Figure 2, indicate that Zr addition has significant effect on the grain size and distribution.

After a long time milling, the alloy elements go on a complete dissolution at the atomic scale and matrix which form a supersaturated solid solution within the matrix and the grains of powders are refined and high-density defects and dislocations are produced due to severe and repeated plastic deformation, resulting in high stored energy [19, 24]. Nano-scale grains in MA powders grow or recrystallize during HIP due to high temperature. However, the formation of high density of rich nano-oxides can impede the growth of grains during HIP. Some researchers also reported that Fe–Zr and Fe–Ni–Zr alloys which were produced by MA are resistant to grain growth due to the amount of Zr available for segregation in a large grain-boundary area [25, 26]. According to the first principle calculation results, the Y–Zr–O phase is easier to form

Figure 2: Grain size distribution of the ODS steels by EBSD analysis.

and more stable [16]. The grains may grow very slowly due to Zr addition.

Typical morphologies of oxides in the specimens of the two kinds of ODS steels are shown in Figure 3(a) and 3(b). The image taken from carbon replica specimens indicated that oxides with a size less than 10 nm were relatively uniformly distributed. Significant difference in the size distribution of oxides in the two kinds of specimens was found. The mean particle sizes were measured to be 5.4 ± 1.9 and 3.3 ± 1.1 nm as estimated by counting more than 1000 particles in the TEM images taken in different regions of the specimens in the non Zr-ODS steel and the Zr-ODS steels, respectively, as given in Figure 4(a) and 4(b). It is found that selected-area diffraction (SAD) patterns from oxides fit the cubic structure Y_2O_3 compounds in non Zr-ODS steel. In Zr-ODS steel, the nano-sized oxides are trigonal δ -phase $\text{Y}_4\text{Zr}_3\text{O}_{12}$ compounds. The $\text{Y}_4\text{Zr}_3\text{O}_{12}$ oxide has a space group: R-3(148) with $a = b = 0.9723$ nm and $c = 0.909$ nm, $a = b = 90^\circ$, $c = 120^\circ$ [27]. The investigation of individual

Figure 1: Inversed pole figures (IPF) maps of 14Cr-ODS steels (a) non Zr-ODS steel (b) Zr-ODS steel.

Figure 3: Typical morphology of oxides retrieved in a carbon replica from the ODS steels (a) non Zr-ODS steel (b) Zr-ODS steel.

Figure 4: Size distributions of the oxides retrieved in a carbon replica from the ODS steels.

oxides with SAD patterns usually tend to make use of relatively big particles, the results are not a good statistics especially for nano-sized oxides. Therefore the polycrystalline rings from SAD over a large number of nano-sized oxides for non Zr-ODS steel and Zr-ODS steel in a region of the carbon replica specimens were used, as shown in Figure 4(c) and 4(d). The radius of the relatively intensive rings (obtained under an acceleration voltage of 200 kV and a camera length of 80 cm) and matches are given in Tables 1 and 2. It can be seen that the intensive rings of the SAD pattern can be readily ascribed to some like (2 2 0), (4 0 0)

and (4 4 4) for non-Zr ODS steel. Another rings of the SAD pattern for Zr-ODS steel are (0 2 1), (2 1-2) and (3 1-1).

More details about the chemical composition of the oxides can still be obtained using the carbon replica method, which supplies an enhanced image contrast and reduced background absorption. According to the EDS analyses in Figure 5(a) and 5(b), the chemical compositions of these oxides were analyzed to be Y- and O-enriched particles, and Y-, Zr- and O-enriched particles in the non-Zr and the Zr-ODS steels, respectively. These results are in good agreement with the SAD results in Figure 4(c) and 4(d).

Table 1: Radius of rings from SAD pattern and possible matches for non Zr-ODS steel.

Ring No.	Radius (nm)	Match Crystal: index of reflections
0	0.375	Y_2O_3 cubic (2 2 0)
1	0.265	Y_2O_3 cubic (4 0 0)
2	0.153	Y_2O_3 cubic (4 4 4)

Table 2: Radius of rings from SAD pattern and possible matches for Zr-ODS steel [27].

Ring No.	Radius (nm)	Match Crystal: index of reflections
0	0.382	$\text{Y}_4\text{Zr}_3\text{O}_{12}$ Rhomb centered (0 2 1)
1	0.261	$\text{Y}_4\text{Zr}_3\text{O}_{12}$ Rhomb centered (2 1-2)
2	0.226	$\text{Y}_4\text{Zr}_3\text{O}_{12}$ Rhomb centered (3 1-1)

During HIP, Y–O rich oxides and Y–Zr–O particles start nucleation and then grow through Ostwald ripening mechanism. Y–O rich oxides grow more quickly than Y–Zr–O particles. This result is in good agreement with the first principle calculation results that the Y–Zr–O phase is easier to form and more stable due to the strong interaction of Zr with vacancy and attractive interaction between Y and Zr [16].

SAXS were employed in this study to obtain the statistical density and size distribution of oxides in the ODS steels from large specimen volume. Figure 6(a) shows the SAXS profiles from the ODS steels in the non Zr-ODS steel and Zr-ODS steel, respectively. According to the TEM results, most of oxides size is less than 10 nm. So the scattering vector range from 0.5 to 1.5 nm^{-1} is analyzed in this study. The size distributions and number density of the oxides in the specimens from SAXS fitting are shown in Figure 6(b). The average size decreases from 4.1 to 2.8 nm and the number density increases from $2.1 \times 10^{23}/\text{m}^3$ to $4.3 \times 10^{23}/\text{m}^3$ of oxides at an almost constant volume fraction by Zr addition. The average size obtained from SAXS is smaller than that from TEM. The statistics difference between SAS and TEM data probably is due to the resolution restriction of TEM and/or the larger analyzed volume of SAXS [28, 29].

Mechanical properties

The addition of Zr element in the ODS steels modifies the size, density and composition of the oxides. In this

Figure 5: EDS spectrum of the oxides retrieved in a carbon replica from the ODS steels (a) non Zr-ODS steel (b) Zr-ODS steel. **Figure 6:** (a) SAXS profiles of the ODS steels; (b) Number density and size distribution of oxides calculated from scattering curves.

regards, it also affects the mechanical properties of ODS steels. The micro-hardness increases from 431 ± 6 to 552 ± 8 HV by Zr addition. Increase of the hardness in ODS steel is attributed to the grain refinement, the average size decreases and the number density increases of oxides. Tensile tests were performed at room temperature (RT, 25°C) and 650°C, respectively. Figures 7 and 8 show tensile stress-strain curves of the ODS steels and average values of tensile properties of two ODS steels at each temperature. The ultimate tensile strength (UTS) and TE of non Zr-ODS steel are 1201 MPa, 3.7% and 334 MPa, 13.2% at RT and 650°C, respectively. The UTS and TE of Zr-ODS steel are 1372 MPa, 5.2% and 421 MPa, 16.1% at RT and 650°C, respectively. It is found that the UTS and the TE of ODS steel increases by Zr addition. With the increase of test temperature, it can be seen that the UTS of the ODS steels decreases and TE increases. The Zr-ODS steel exhibits the higher UTS and TE at RT and 650°C. This is because the higher density of oxides and the finer grains in Zr-ODS steel. Dou et al. [27] have proved that nano-size $Y_4Zr_3O_{12}$ oxides are coherent with matrix. The coherent interface between the $Y_4Zr_3O_{12}$ oxides and matrix hinders the formation and propagation of micro-crack which can effectively pin dislocations.

Conclusion

14Cr-ODS steels were prepared by MA and HIP. The effect of Zr addition on microstructure and mechanical properties were investigated. The main conclusions are as follows:

- (1) The presence of zirconium addition has improved the mechanical properties (microhardness, strength and ductility) of the ODS ferritic steel as a result of two linked factors: (a) a refinement of the ferritic matrix grains, and (b) formation of fine Y–Zr–O nano-oxides randomly dispersed in the matrix, which in part suppresses the formation of larger Y–O nano-oxides in the matrix.
- (2) The results reported here provide the foundation for understanding the unusual microstructure characteristics and outstanding irradiation tolerance of the oxide particles as well as the superior strength and will help to guide future design and optimization of ODS alloys.

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Figure 7: Tensile stress-strain curves of 15Cr-ODS steels at RT and 650°C (a) non Zr-ODS steel (b) Zr-ODS steel.

Figure 8: Tensile properties of 14Cr-ODS steels at RT and 650°C (a) UTS, (b) TE.

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