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Effects of Hf addition on the thermal stability of 16Cr-ODS steels at elevated aging temperatures

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ABSTRACT

In this paper, the effects of hafnium (Hf) addition on the thermal stability of the microstructure and tensile properties of Al-containing 16Cr-ODS steels were investigated. High temperature aging tests of the ODS steels with and without Hf were conducted at 750 °C, 950 °C and 1150 °C for 100 h respectively. And the microstructure evolution after thermal aging was investigated using transmission electron microscopy (TEM) and electron backscatter diffraction (EBSD). The results indicated that Hf addition could improve the coarsening resistance of the oxide particles and the grains during aging treatment due to the formation of stable $Y_2Hf_2O_7$ particles. Tensile tests on the aged-steels showed that the ultimate tensile strength and yield strength of 16Cr-Hf-ODS steel were higher than those of 16Cr-ODS steel. It was considered that the excellent thermal stability and tensile properties of 16Cr-Hf-ODS steel were related with the refined microstructure.

1. Introduction

Oxide dispersion strengthened (ODS) steels have been considered as hopeful candidates for cladding materials in the next generation nuclear reactors due to their superior high-temperature mechanical properties and good resistance to coolants corrosion and neutron irradiation swelling [1]. The excellent properties of ODS steels mainly depend on the finely dispersed nanosized oxide particles, which serve as pinning points to dislocations motion and grain boundaries migration as well as stable sinks for irradiation induced defects [2]. In general, the operating temperature for the ODS steels is designed to be not lower than 650 °C or even higher (about 1000 °C). The performance of the ODS steels at such high service temperatures is of great importance for security. In view of this, the high temperature performance of the ODS steels, especially thermal stability of the microstructure have been paid considerable attention [3–7].

In high-Cr ODS steels, the increase of mean oxide particle size as well as the decrease of the particle number density after aging at elevated temperatures has been widely reported [4,5]. This studies owed this phenomenon to Ostwald ripening, which is associated with the dissolution of the small particles and the growth of large ones. According to Ostwald ripening mechanism, the phase boundary energy depends on the curvature of the particle [8]. As a result, the small particles usually have a worse stability during high temperature aging treatment because of their larger curvature radii when compared with the large particles. On the contrary, some other research demonstrates that fully coherent particles with relatively smaller diameters have better thermal stability, since the interfacial energy of the well coherent particles is lower than that of the randomly-oriented ones [7,9]. The particle coherency is size dependent and will lose as particle size increases, thus the smaller particles are more stable [10–12].

In our previous study, the effect of Hf addition on the microstructure and tensile properties of a 16Cr-ODS steel was investigated [13]. Considering the aforementioned security of the ODS steels at high service temperatures, it needs further study on the thermal stability of the two steels with and without Hf addition.

In this work, the effects of Hf addition on the thermal stability of the microstructure and tensile properties of the aged 16Cr-ODS steels were investigated. The aging experiment was carried out at 750 °C, 950 °C and 1150 °C for 100 h, respectively. The thermal stability of the microstructure was evaluated from the size evolution of the oxide particles and the grains. The crystal structure of oxides and the particle-matrix orientation relationship in the aged

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samples were characterized as well. Additionally, tensile tests were performed to study the mechanical properties of the steels after aging treatment.

2. Experimental procedures

16Cr-Hf-ODS (Fe-16Cr-3Al-1.5W-0.5Hf-0.35Y_2O_3, wt.%) steel and 16Cr-ODS (Fe-16Cr-3Al-1.5W-0.35Y_2O_3, wt.%) steel were prepared by mechanical alloying (MA) and hot isotropic pressing (HIP) processes. The pre-alloyed powders (Fe16Cr3Al1.5W, with a mean size of 50 μm) with and without Hf (with a mean size of 10 μm) were mixed with Y_2O_3 powders (with a mean size of 40 nm). Then the mixed powders and mill balls (ball-to-powder ratio was 10:1) were milled for 30 h under an argon atmosphere using a high-energy planetary ball mill (QM-2SP12, Nanjing NanDa Instrument Plant, China) at a rotating speed of 250 rpm. After being degassed at 450 °C to 0.002 Pa, the as-milled powders were sealed and consolidated by HIP at 1150 °C under 150 MPa for 3 h. The as-consolidated steels in shapes of round bar (φ8 mm × 60 mm) and cuboid (10 mm × 10 mm × 3 mm) were sealed in vacuum evaporated quartz tubes, and then isothermally aged at 750 °C, 950 °C and 1150 °C for 100 h respectively in a box type heat-treatment furnace (SX-GO7122, Tianjin ZhongHuan Furnace Plant, China).

The discs (φ3 mm × 55 μm) for TEM were etched using a polishing solution of 5% perchloric acid and 95% ethanol at −23 °C by a twin-jet electro-polishing device (MTP-1A, Shanghai JiaoDa Company, China). Carbon extraction replica was prepared from the polished surface. The surface was etched by a solution of 30% hydrochloric acid and 70% ferric chloride, then a carbon film was coated and carbon replica was removed by the same solution. EBSD specimens for grain size observation were prepared by a standard metallographic preparation method, followed by Ar^+-ion polishing (RES101, Leica, Germany) to remove surface stress layer. The samples for tensile tests were shaped to cylinders with 25 mm in gauge length and 5 mm in diameter. Tensile tests were carried out in air at room temperature with a strain rate of 7×10^{-4} s^{-1} using an electronic material testing machine (GNT300, NCS, China).

3. Results and discussion

3.1. Stability of oxide particles in the two steels

3.1.1. Size evolution and composition of the particles

Fig. 1 shows the bright field TEM (BFTEM) image of the oxide particles in 16Cr-ODS and 16Cr-Hf-ODS samples before and after aging treatment. As can be seen, the particles with spherical or faceted shapes distribute homogeneously in the matrix. Fig. 2 exhibits the statistical histograms of the particle size distribution by analyzing more than 500 particles from TEM micrographs of the samples. As the aging temperature increases, the Gauss fitting curves of particle size distribution broaden. It can be seen that the oxide particles in both the steels coarsened to some extent during high-temperature aging. At each aging temperature, the particles in 16Cr-Hf-ODS samples are distributed within a narrower range compared with the particles in 16Cr-ODS samples. As the aging temperature increases, large-sized particles (φ > 40 nm) in 16Cr-ODS samples appear and the number increases. Especially after being aged at 1150 °C (Fig. 1(h)), particle size distribution of the 16Cr-ODS sample appears a bimodal distribution with most particles larger than 40 nm in size and even over 80 nm. The above results indicate that the adding of Hf element inhibits the coarsening of oxide particles during the high-temperature aging process.

Table 1 summarizes the statistical results of the nanosized particles in 16Cr-ODS and 16Cr-Hf-ODS steels before and after aging treatment. At each aging temperature, both the mean and maximum diameter of the oxide particles in 16Cr-Hf-ODS steel are smaller than those in 16Cr-ODS steel. Besides, the particles in 16Cr-Hf-ODS possess shorter inter-particle spacing and higher number density. In order to examine the size evolution of the nanosized particles with increasing aging temperatures in these two steels, the statistical data of the particles is plotted in Fig. 3. As can be seen, the evolution of mean diameter and inter-particle spacing shows similar increasing trend for each steel. It is obvious that the coarsening process of oxide particles in the Hf-added steel is notably slow. These results demonstrate that the Hf addition is beneficial to improve the size stability of the dispersed particles during aging treatment.

Since the properties of the oxides are related with their crystal structure, it is necessary to characterize the structures of particles in the 16Cr-Hf-ODS steel. The sample aged at 750 °C is considered since the operating temperature for ODS steels is designed as around 700 °C. The compositions and structures of the oxides in the 16Cr-Hf-ODS sample aged at 750 °C are investigated and calibrated by HRTEM and fast Fourier transformation (FFT). Fig. 4(a) shows the HRTEM image of an oxide particle with a diameter of 5.9 nm. The inter-planar spacing measured from the reciprocal space (Fig. 4(b)) and the corresponding theoretical crystal plane distances of this oxide are listed in Table 2. Within the error allowance, the particle is identified to be $Y_2Hf_2O_7$ (the electron beam is paralleled to $[\bar{1}10]$ zone axis of the particle). The $Y_2Hf_2O_7$ particle has a space group symmetry of $[Fd\bar{3}m]$ (225) with a lattice constant of 0.5201 nm, and its crystal structure is also known as an oxide pyrochlore, a derivative of the fluorite structure (AX_2), e.g., cubic HfO_2. Thus the formation of $Y_2Hf_2O_7$ oxides can be revealed by the following reaction:

$$Y_2O_3 + 2HfO_2 \rightarrow Y_2Hf_2O_7 \tag{1}$$

Another typical oxide with a diameter of 8.5 nm is also identified and the result is coincident with the database table for $Y_2Hf_2O_7$ as well.

Fig. 5 shows the high resolution image and the corresponding FFT result of a larger particle with a diameter of 11.4 nm. The crystal structure of this particle is identified as perovskite $YAlO_3$ (YAP) structure with a crystal zone axis of [001]. The relevant data of the inter-planar distances is listed in Table 3. In addition, several particles with different diameters randomly selected from the 16Cr-Hf-ODS sample were also analyzed. It can be found that the $Y_2Hf_2O_7$ and Y-Al-O particles are coexistent in the 16Cr-Hf-ODS steel, and particles with relatively smaller sizes tend to be $Y_2Hf_2O_7$. The better thermal stability of the particles in 16Cr-Hf-ODS steel may relate to the formation of $Y_2Hf_2O_7$ oxides, but the mechanism still requires further study.

3.1.2. Coherency relationship at the interface

This part mainly focuses on the coherency relationship at the interface between the oxide particle and the surrounding matrix, which is beneficial to understand the thermal stability of the oxides.

The orientation relationship between the oxide particle and the matrix is revealed by HRTEM, FFT and inverse FFT (IFFT). The lattice misfit δ at the interface is calculated by the following equation:

$$\delta = \frac{|d_M - d_P|}{2(d_M + d_P)} \tag{2}$$

where d_M and d_P represent the atomic planes distances of the surrounding matrix and the oxide, respectively. As the value of δ increases, the interface is defined as coherent interface (<5%), semi-coherent interface (5%–25%) and incoherent interface (>25%)