Microstructure and mechanical properties of 16 Cr-ODS ferritic steel for advanced nuclear energy system

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Abstract: A 16Cr-0.5Ti-1W-0.35Y2O3 oxide dispersion strengthened (ODS) ferritic steel was fabricated by mechanically alloying and hot isostatic pressing (HIP). Subsequent thermo-mechanical treatments were performed to improve the microstructure homogeneous and service properties of the HIPed 16Cr-ODS steel. Nano-oxide particles were observed by TEM, which can be identified to be (Y, Ti) complex oxide by EDS and SAED. The mechanical property was measured by tensile test, and the oxidation behaviour of the ODS steel was performed at high temperature in a muffle.

Keywords: 16Cr-ODS ferritic steel; Mechanical alloying(MA); Hot isostatic pressing(HIP); Micro-structure; Mechanical properties

1. Introduction

The candidate cladding materials of Generation IV nuclear energy systems must have a high resistance to neutron irradiation embrittlement and void swelling as well as a good performance of mechanical properties at elevated temperatures. In addition, a good corrosion resistance of the claddings in the relevant environments has been certainly required for practical long term operation of the advanced fission reactors [1].

Oxide dispersion strengthened (ODS) ferritic steel which contains a high number density of small oxide particles has been considered as one of the most promising structural materials for advanced nuclear systems [2-5]. Due to the unique microstructure, the ODS ferritic steels show both excellent high-temperature tensile properties, creep resistance, and promising irradiation resistance [3].

For fission application, the Cr content in ODS steels is usually in the range of 9-14% [6-7]. However, the low-Cr-ODS ferritic/martensitic steels are not suitable for super critical water reactor (SCWR) owing to an insufficient corrosion resistance of the materials. Corrosion resistance of iron based alloys is influenced by chromium. The Cr content can be balanced between a merit of corrosion resistance and a demerit of aging embrittlement with maintaining strength at elevated temperatures [8].

In this work, a 16Cr-0.5Ti-1W-0.35Y2O3-ODS ferritic steel was fabricated by high-energy
Mechanical ball milling and HIP. The microstructure was observed by TEM. Mechanical properties and oxidation resistance were tested and evaluated.

2. Experiment

2.1 Sample preparation
The nominal composition of the ODS ferritic steel is listed in Table 1. The average size of nitrogen-gas-atomized metallic powders and nano-Y2O3 were 45 μm and 30 nm respectively. The pre-alloyed powders were mechanical alloyed in a high-energy planetary ball mill under a pure argon atmosphere. The weight ratio of grinding media to material was 5:1 and rotation speed of 380 revolutions per minute (RPM) were conducted with milling time up to 30 h. In the next step, the milled powders were degassed and sealed in a stainless-steel container in vacuum so that it was suitable to be consolidated by HIP. The process of HIP had two stages: the first step was 1100 °C for 2h and the second one was 1150 °C for 1h. Both of these two stages, the pressure was around 200 MPa. Then the as-HIPed specimen would be given hot working treatment, which includes forging and rolling. The effects were reducing the defects in sample and Ar bubbles which resulted from progress of mechanical alloying [9]. The process of forging was 1150 °C with a forging ratio of 3:1. Additional hot rolling was performed three times with a reduction ratio of about 20% each stage. Then microstructure observation can be obtained and service properties test would be performed.

| Table 1 | Nominal composition of ODS pre-alloy powders |
|---------|---------------------------------------------|
| element | Cr  | W  | Ti  | Y2O3 | Fe  |
| wt%     | 16.0-16.5 | 1.0-1.5 | 0.5 | 0.35 | Bal. |

2.1 Microstructure observation
The disk shaped specimens with a diameter of 3 mm and a thickness of 0.25 mm, were cut and their surfaces were polished by mechanical polishing and electropolishing. Final thinning of the foils was performed using a standard twin-jet electropolishing technique in an electrolyte (90vol.% acetic acid+10vol.% perchloric acid) at 30V at room temperature. Microstructure and chemical composition were identified by Transmission Electron Microscope (TEM,JEM-2010) with an Energy Dispersive Spectroscope (EDS). Combining with selected area electron diffraction (SAED), the software Gatan Digital Micrograph and database Ppddfwin were used to simulate electron diffraction patterns in order to identify the crystal structures of nano-oxide particles in the 16Cr-ODS steel.

2.2 Mechanical properties test
Tensile specimens with a gauge length of 15mm were made along the deforming direction and tensile tests were carried out at 23 °C and 700 °C with a strain rate of 5×10⁻²s⁻¹. The tensile fracture morphologies were investigated by Scanning Electron Microscope (SEM, LEO-1450). The specimens for ultrasonic non-destructive test were cut into size of 10mm×10mm×10mm. And the instrument model is MH-6.

2.3 Oxidation resistance test
Specimens were cut from as-HIPed product with size of 10mm×10mm×10mm for the oxidation resistance testing. There were two stages in this test: at first, put the sample into the muffle furnace at 700 °C for 100h in atmosphere, and calculated oxidation weight gain rate of the post-oxidation sample. Then put the same sample into the muffle furnace at 1000 °C for 2h in atmosphere, and calculated the oxidation weight gain rate again, then observed the oxidation layer by SEM.
3. Results and discussion

3.1 Mechanical alloying effect

Fig 1 shows the comparison between the SEM images of original gas atomized powders and MA powders. In the aspect of raw atomized powders, the shape was easily specified for regular sphere, and the particle sizes were ranging from 10 µm to 30 µm. During the process of MA, the powders were forced to collide with others and with much larger and more hardened balls contained in a mill. The collisions were very energetic, involved large contact pressures and led eventually to the formation of an intimate solid solution. Refractory yttrium oxides can also be finely dispersed into the mechanically alloyed powders in order to obtain dispersion strengthening. Due to the high energy ball milling role, the accumulated strain and work hardening led to increasing brittleness and deformation happened [10]. Thus the shape of particles became irregular and the size distribution was not very uniform, and the mean particle size was about 50 µm.

Excess oxygen (total oxygen concentration except for oxygen concentration in Y₂O₃), resulted from the process of high energy ball mill, was harmful to the microstructure and mechanical properties of ODS Ferritic steel, which can be estimated by the method named inert gas pulse infrared thermal conductivity (ASTM1019-2005). The excess oxygen in this MA powders is only 0.066%, which shows that the parameter control of MA is reasonable.

![Fig.1 Mechanical alloying effect on original atomized powder](image)

(a) Original atomized powder  (b) Mechanical alloying powder

3.2 Microstructure observation

Typical morphologies of dispersed particles in the specimens of as-HIP-16Cr-ODS ferritic steel are shown in Fig.2, there are many small grains with sizes ranging from a few nanometers up to less than 30 nm in the grains. The small particles distribute well and uniformly, as shown in Fig. 2(a). EDS analysis showed that the chemical composition of the dispersed particles contains Fe, Cr, Y, Ti, and O element. Because the dispersed oxide particle with a diameter is smaller than the thickness of the foil having several tens nm thick, the EDS data of oxides includes both the matrix and oxide [11]. However, this result of EDS inhibits what main composition the fine particle contains.

Recent studies demonstrated that Y-Ti complex-oxide cores can form in Ti-contained ODS steels such as MA957 steel, and Y₂O₃ cores can form in ODS steels with no additions of Al and Ti [12, 13]. Fig.2(b) shows the selected area electron diffraction pattern (SADP) of the fine particle indicated by the red arrow in Fig.2(a), which was observed from the direction zone axis <11T>. By means of calculating the crystal lattice plane spacing and crystal plane angle, the complex oxide particles were characterized to be cubic structure Y₂Ti₃O₇, which was supposed to enhance the properties of materials.
3.3 Mechanical properties test

Table 2 shows the tensile properties of 16Cr-ODS Ferritic steels at room temperature and high temperature. The results demonstrate that the as-HIPed 16Cr-ODS ferritic steel exhibited relatively qualified at room temperature, the ultimate tensile strength (UTS) reached about 767MPa, and the ductility represented excellent, the elongation and percentage reduction of area(R.A) reached 17.00% and 57.0% respectively. By means of hot plastic deformations process, both the UTS and elongation have been improved in different degree. Compared with the as-HIPed sample, the UTS enhanced 22.30% and the elongation also enhanced 31.76%. Plastic deformations can improve the microstructure of materials by applying force to specimens and reduce the porosity [10]. At high temperature, the UTS of material will decrease significantly, and the ductility will obtain a observably improvement.

Table 2 shows the fracture morphology of 16Cr-ODS ferritic steel, high density of deep dimples can be observed, which represent excellent ductility ,and it is difficult to find any cleavage cracks due to the very small grains in this specimen.

Though the ultrasonic waves non-destructive test, Young modulus and shear elasticity of specimen can be measured, they were 211.47Gpa and 82.4Gpa, compare with conventional commercial steel, the range of Young modulus is 190Gpa to 200Gpa, the 16Cr-ODS Ferritic fabricated in this experiment exhibited a better pressure resistance and hardness.

| samples            | temperature | UTS  | Rp0.2 | elongation | R.A |
|--------------------|-------------|------|-------|------------|-----|
| 16Cr (HIP)         | 23          | 767  | 594   | 17.00      | 57.0|
| 16Cr (HIP+foering+Rolling) | 23          | 938  | 476   | 22.40      | 53.0|
| 16Cr (HIP)         | 700         | 189  | 164   | 45.50      | 74.0|
3.4 Oxidation resistance test

This experiment was divided into 2 stages. The high temperature oxidation behavior of 16Cr-ODS ferritic steel was performed in a muffle furnace from 50h at 800 °C to 2h at 1000 °C in dry air atmosphere. The two stages oxidation weight gain rates were 0.002445% and 0.1934% respectively. The results showed a excellent oxidation resistance.

Fig. 3 shows the cross-sectional morphology of alloys after oxidation test. The thickness of oxidation layer was about 2μm. The connection along the oxidation layer/alloy substrate interface was compact. There was no cracks and voids in the contact areas. EDS analysis indicated that the oxide layer was mainly Cr-enriched oxide layer. The superior oxidation resistance of ODS ferritic steels was attributed to the early formation of a protective α-Cr2O3 layer on their surface, which is stabilized by the finely dispersed Y-content oxide precipitates. It may contribute to scale formation by promoting a fine grain size in the matrix that increases the diffusion of Cr to the scale-metal interface.

Fig. 4 SEM image of cross section morphology of oxidation layer
4. Conclusions

16Cr-0.5Ti-1W-0.35Y₂O₃ ODS ferritic steel was fabricated by MA and HIP. Subsequent thermo-mechanical treatments were carried out to make the microstructure and service properties better. Though microstructure observation and mechanical properties tests, the main results are summarized as follows:

(1) A high number density of nano-scale particles can be observed by TEM in specimen, by the means of EDS analysis and SADP, the fine particles can be identified to be cubic structure Y₂Ti₂O₇, which was supposed to enhance the properties of materials.

(2) The results of tensile strength tests of 16Cr-ODS ferritic steel show that the ultimate tensile strength reached nearly 767MPa at room temperature and the elongation reached 17%. At 700°C, the UTS of specimen still maintained around 189MPa. It represented that 16Cr-ODS Ferritic steel possess reasonable UTS and excellent ductility. Hot working treatments, such as forging and rolling, can improve the UTS and ductility significantly of material. The result of ultrasonic waves non-destructive test demonstrated 16Cr-ODS Ferritic fabricated in this experiment exhibited a better pressure resistance and hardness.

(3) 16Cr-ODS ferritic steel also possess excellent oxidation resistance. After exposed in air at 800°C for 50 h and then 1000°C for 2h. The thickness of oxidation layer was only about 2 μm. The oxidation layer was dense and showed a good adherence to the matrix. Fine Y-content oxide precipitates and the Cr content in ODS Ferritic steel controlled in a appropriate range was helpful to oxidation resistance of material.

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