Development in Preparing Methods of the Nano-Structured ODS RAFM Steels

Jian-sheng QIAO¹, Yin-feng LI² and Shi-zhong YIN²

¹School of Teacher Education, Xingtai University, Xingtai 054001, China
²School of Physics and Electronic Engineering, Xingtai University, Xingtai 054001, China

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Abstract. The Mechanical alloying method, the sol-gel-spark plasma sintering method and the vacuum casting method are researched which are used to prepare nano-structured oxide dispersion strengthened (ODS) RAFM steels. Nano-structured ODS RAFM steels can be obtained by the Mechanical alloying methods and the sol-gel-spark plasma sintering methods. Micron-structured ODS RAFM steels can be obtained by vacuum casting method. The microstructure of the material manufactured by different methods are compared.

Introduction

As a candidate structural material for future fusion power reactors, reduced activation ferritic/martensitic (RAFM) steels have good properties[1]. But its strength will drop at higher operating temperature. So the conventional RAFM steels limit the reactor operating temperature to around 550°C. Nano-structured oxide dispersion strengthened (ODS) RAFM steels allow increased operating temperatures (650 °C or higher) due to the high densities of the Y2O3-rich clusters/precipitates, sub-micron grain sizes and high densities of dislocations. Further, the dispersed nano-scale oxide particles may provide a large number of trap sites for transmutant helium and radiation-induced defects.

The classic method of manufacturing ODS alloys is powder metallurgy(PM), Which consists of powder mixing, pressuring mould and sintering. However, this classic method has some inherent defects involved with ODS production, including: inducing anisotropy to its micro-structural and mechanical properties, introducing impurities, rendering batch production complicated and expensive[2,3]. The impact toughness and the fracture toughness of ODS alloys are also lower. So the powder metallurgy has been improved by the researcher. And the more methods have been used to manufacture the ODS RAFM alloys.

In this paper, three methods of manufacturing ODS-RAFM alloy are introduced. The microstructure manufactured by different methods are compared.

The Methods of Preparing ODS RAFM Steels

The Mechanical Alloying Method (MA)

There are three methods used in manufacturing ODS-RAFM alloys in recent years. The first one is improved classic power metallurgy method which consists of mixing powders, mechanical alloying, canning and degassing of the milled powders, compaction of the powders by hot isostatic pressing(HIP)[4]. This method can be summarized in figure 1. The improved measure compared to the classic power metallurgy includes using Mechanical alloying instead of powder mixing, using HIP or hot extrusion instead of ordinary pressure and sintering. So this method is named Mechanical alloying method. Dissolution of Y2O3 during mechanical alloying (MA) and precipitation of Y2O3-rich nano-scale clusters/precipitates during hot isostatic pressing/hot extrusion play key roles in producing nano-structured ODS steels. So preparing ODS alloys by adding Y2O3 to RAFM to
improve its high-temperature creep resistance and radiation-induced swelling resistance has become an important research area[5 - 7].

The ingots with a microstructure composed of a homogeneous distribution of small grains containing a high density of small Y2O3 clusters are obtained by optimizing Mechanical alloying and HIPping parameters.

The Sol-Gel-Spark Plasma Sintering Method (SPS)

To further improve the property of ODS steels, a new route using sol-gel-spark plasma sintering method in combination with hydrogen reduction, mechanical alloying and the spark plasma sintering was used by Q.X. Sun[8]. This method is shown in Figure 2.

The raw powders used in this study were Cr, W, Ti, V, Si, Mn, Ta, and C commercial powders and the Fe-0.3 wt.%Y2O3 powders produced by sol-gel and reduction method. The aim of adding Ti element to matrix was to form nano-sized Y2Ti2O7 phase. To synthesize the Fe-0.3wt.%Y2O3 powders, the Fe(NO3)-9H2O and Y(NO3)-6H2O compounds in mass ratio according to the formula of Fe-0.3%Y2O3 were dissolved in deionized water and then the citric acid (CA) was added at a molar ratio of CA: cationic ions (including Fe3+ and Y3+) = 2:1 to chelate the cationic ions. The solution was stirred vigorously at 60°C until a brown gel was formed. The brown gel was heated at 110°C for 12 h firstly and then calcined between 500°C and 600°C for 5h to obtain the multi-component oxides. Finally, the multi-component oxide powders were reduced in high purity hydrogen at 650°C for 3h to produce pure Fe-0.3%Y2O3 powders. The all powders were weighted according to the nominal composition and mixed by ball milling in a chrome steel bowl at a rotation speed of 300 rpm for 30h under an argon atmosphere.

The spark plasma sintering (SPS) was used to sinter the as-prepared 9Cr-ODS powders under a flowing argon atmosphere. In the sintering process, the powders were firstly pressed in a 30 mm diameter die under a uniaxial pressure of 50 MPa, then heated to 1150°C with a heating rate of 100 °C/min, sintered at 1150°C for 5 min, and finally cooled down to room temperature with a cooling rate of 100°C/min. After sintering, the obtained steel disk was normalized-and-tempered.

This method has an advantage of ultrafine oxide powders (8nm), high purity, and composition homogeneity. Compared to hot isostatic pressing technique, the spark plasma sintering (SPS) process allows the consolidation of powder materials into fine-grained products and spends less time in total sintering progress. This method is considered to be the effective approach to obtaining ODS alloys with uniform dispersion of nano-particles.
The Vacuum Casting Method (VC)

The vacuum casting method is invented by Zimu Shi and Fusheng Han[9]. This method is shown in Figure 3. The micro-scale Y2O3 strengthened 9Cr steel has been fabricated by vacuum casting and the micro-structure has been researched. The raw materials were simple metals of technical purity, and the Y2O3 particles were 2µm in diameter. The materials were melted under the protection of an argon atmosphere, and continuously stirred using a magnetic stirrer. The casting process was as follows: when the air pressure in furnace decreased to below 60 Pa, argon was introduced so as to produce an air pressure of 0.04 MPa, and the temperature was increased to, and maintained at 1580 °C. After the pure iron had been melted, the following components were added in sequence: Cr, W, V, Ta, Mn, and C. After all of the alloys had melted, the Y2O3 was added. Then steel ingots were cast after heat preservation for 5 minutes. Finally, 9Cr-ODS steel containing Y2O3 were obtained. To distribute the added Y2O3 particles uniformly as well as to improve the metallographic organization, the ingots were forged and heat-treated.

The Microstructure of the ODS RAfM Steels Prepared by Different Methods

The Microstructure of the ODS RAfM Steel Prepared by the MA Method (MA)

Figure 4[4] shows the TEM microstructures of the alloys prepared by the mechanical alloying method. The 9Cr-ODS RAfM steel has smaller and homogeneous grains and higher density of carbide precipitates. 9Cr-ODS has a tempered martensitic phase with carbides and dislocations. Figure 4[4] is a collection of low and high magnification TEM images of the alloys. High density of nano-particles was observed in the alloys. The measured data for the nano-particles are the size of 3.1 nm and the density of $1.2 \times 10^{23}m^{-3}$ for 9Cr ODS alloys.

The Microstructure of the ODS RAfM Steel Prepared by the Sol-Gel-Spark-Plasma Sintering Method (SSPS)

Compared to the first method, the sol-gel process, hydrogen reduction and the SPS are the characteristic of the second method. The Fe-0.3Y2O3 powders prepared by the sol-gel process and hydrogen reduction method exhibit a relatively uniform size of 100-300 nm. After 30 hours mechanical alloying, the XRD patterns of 9Cr-ODS powders shows the pure ferritic phase. It indicates that the ball milling is effective to alloy the other elements into the Fe matrix.

Figure 4. TEM of the MA [4]. Figure 5. TEM of the SPS[8]. Figure 6. SEM of the VC [9].

Typical optical microscopy images of 9Cr-ODS ferritic/martensitic steel ingots with thermal treatment shown that the microstructure is mixture of the acicular martensite and ferrite with a grain size of 1-5µm. To investigate the microstructure and dispersion homogeneity of the oxide particle, TEM analysis was carried out for the 9Cr-ODS ferritic/martensitic steel consolidated by the sol-gel-spark plasma sintering method. Figure 5[8] displays the TEM images of the 9Cr-ODS
ferritic/martensitic steel. More oxide particles dispersed in the matrix can be seen. The spherical oxide particles disperse homogeneously and are tightly embedded in the matrix. The average size of oxide particles are 14 nm to 20 nm.

**The Microstructure of the ODS RAFM Steel Prepared by the Vacuum Casting Method (VC)**

The conventional casting method failed to produce ODS alloys. Zimu Shi suggested that vacuum casting could be an alternative method for ODS alloy fabrication. [9]

To detect the Y2O3 particles distributed uniformly in the matrix, Zimu Shi and Fusheng Han [9] studied the fracture morphology of 9Cr-ODS steel by SEM and EDS. The inclusions in 9Cr steel with Y2O3 addition is the convex grains which contained elemental Fe, Cr, Mn, V, Y, and O. The inclusions were considered to be complex oxides which were formed by Y and O reacting with the matrix element. That meant micro-scale Y2O3 had been effectively added to the matrix during casting. To detect the Y2O3 directly, extracted liquor in hydrochloric acid solution was used for dissolving metal elements but retaining the Y2O3 present in the steel matrix. Figure 6 [9] shows SEM micrographs of particles extracted from 9Cr-ODS steel at micro-scale size, which was proved to be Y2O3 by EDS analysis, and coincide with the size of that material added during melting. This directly evinces the introduction of Y2O3 to the matrix and its reaction with the metal element.

**Summary**

The mechanical alloying method is characterized by mechanical alloying and hot extrusion which plays key roles in producing nano-structured ODS steel. The sol-gel-spark plasma sintering method uses the sol-gel, hydrogen reduction, mechanical alloying and the spark plasma sintering technology. The ultrafine oxide powders and high number density and ultrafine grains and nano-structured ODS steel can be obtained.

The ODS-RAFM steel can be manufactured by the vacuum casting method. Since 2µm diameter Y2O3 particles were used by Zimu Shi and Fusheng Han[9] to prepared the ODS-RAFM steel, they can only prepare the micro-structured ODS RAFM steel. It can be believed the nano-structured ODS steel can be obtained using nano-scale Y2O3 particles by the vacuum casting method. It will be the next work.

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**References**


