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Size and structure evolution of yttria in ODS ferritic alloy powder during mechanical milling and subsequent annealing

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ABSTRACT

Oxide dispersion strengthening ferritic steels are fascinating materials for future high temperature energy production technologies. Mechanical milling with the aim of a fine dispersion of oxides in the metal matrix becomes the main process for the production of ODS steels. The mixed powder which is composed of iron, chromium and yttria (Fe-9Cr-15%Y_2O_3) was mechanically milled for a maximum period of 100 h. Size and structure evolution of Y_2O_3 and the microstructure changes of the mixed powder during mechanical milling and subsequent annealing were studied. The powder is fractured and welded with rotation and vibration of container during mechanical milling. The results show that the particle size and the grain size decrease with increasing milling time. Nanocrystalline of Y_2O_3 is gradually formed by severe plastic deformation. It can be explained that the long-range order structure of Y_2O_3 is damaged by mechanical milling. The formation processes of nanocrystalline in ordered oxides may follow the sequence: ordered phase → disordered phase (loss of long-range order) → fine-grained (nanocrystalline) phase. Growth of nanocrystalline Y_2O_3 occurs at about 891 K during subsequent annealing and the nanostructure of Y_2O_3 after mechanical milling and annealing was observed by TEM and HRTEM.

1. Introduction

High Cr ferritic creep resistant steels, which are used as header and main/reheat steam pipe in thermal power plant, possess enhanced creep strength at the elevated temperatures. Those materials are mainly strengthened by solid solution strengthening and carbide or nitride precipitation strengthening [1]. However, these strengthening mechanisms become ineffective due to the precipitation coarsening or dissolution above 650 °C. Large drop in creep strength of high Cr ferritic creep resistant steels was observed after long-term high temperature service condition [2], whereas higher temperature is required to improve the reactor's efficiency. Oxide dispersion strengthening (ODS) ferritic steels, which have more superior high-temperature creep resistance in comparison with the conventional ferritic steels, were developed in order to increase the working temperature [3,4]. The creep rupture strength of 9Cr Oxide-dispersion- strengthened steel was about three times greater than that of conventional 9Cr heat resistant steels [5]. The operating temperature of the first wall in future fusion may reach above 700 °C, resulting in an improved efficiency of ≥40% [6].

It is difficult to process ODS steels through conventional methods such as melting, working and casting due to the low solubility limit of the oxides in metals. Sakasegawa et al. stated that oxide particles aggregate together and coarsen during conventional casting processes [7]. Benjamin et al. firstly adopted mechanical alloy (MA) for elaboration of the Ni-based ODS alloys [8]. This technique, which is beneficial to the formation of uniform dispersion of nanosized oxides in the metal matrix, becomes an effective process for production of ODS steels [9,10]. After MA, nanoscaled oxide particles form with a very high density during the consolidation and heat treatment processes [11]. The excellent high-temperature creep resistance provided by ODS steels is attributed to the fact that the nanosized dispersoids act as obstacles against the movement of dislocations and growth of grains through dispersion interaction [12]. The movement of grain boundary is hindered by the pinning force exerted by the dispersoids [13]. Oxide particles with relatively small radius induce higher threshold stress exceeding 300 MPa, which can quantitatively show the effect of oxide dispersion strengthening [14,15]. Since the properties of ODS steels depend on the dispersion of nano-oxides, size and structure evolution of the oxides in mixed powder during the process of mechanical milling and the subsequent annealing becomes extremely important for the elaboration of ODS steels.

The oxide reinforcement that has been the most widely used is Y_2O_3 for its high thermal stability property. The structure form of Y_2O_3 remained stable over a wide range from 110 to 2225 K [16]. Y_2O_3 is a less unstable oxide under irradiation by neutrons, electron and ions in comparison with other oxides (MgO, Al_2O_3) [17]. The evolution of Y_2O_3 and corresponding microstructure of ODS steels were studied by some researchers. Okuda et al. (1995) revealed that Y_2O_3 is dissolved in the ferritic base matrix during the MA process [18]. Kimura et al. (1999) showed the milled powder of Fe–24%Cr–15%Y_2O_3 which was

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annealed at 973 K for 3.6ks that Y_2O_3 particles are almost decomposed and the yttrium and oxygen are enriched in amorphous grain boundary layers after mechanical milling [19]. Elucidation of size and structure evolution of the oxides particles in mixed powder is extremely important from the viewpoint of microstructure control.

Fe–9Cr–15%Y_2O_3 was selected in this study. The objective of this work was to study size and structure evolution of Y_2O_3 and the change in the microstructure of the mixed powder during mechanical milling and subsequent annealing. This paper presents recent achievements in the processes of elaboration of ODS alloy, to give important information for microstructure control.

2. Experimental procedures

Iron powder (99.99% Fe, with an average size of 45 μm), chromium powder (99.99% Cr, with an average size of 45 μm) and Y_2O_3 powder (99.99% Y_2O_3, with an average size of 30 nm, as shown in Fig. 1) were used. The powder mixtures were mixed in weight proportion of 76% Fe, 9% Cr and15% Y_2O_3. The iron, chromium and Y_2O_3 powder mixtures were manually mingled before mechanical milling, then mechanically milled in a high-energy planetary ball mill (QM-3SP2) at a rotation speed of 290 rpm in argon gas atmosphere. The weight ratio of ball to powder was 15:1.

X-ray diffraction analysis was performed on a RIGAKUD/MAX 2500 V/PC using Cu Kα radiation. The grain size changed by mechanical milling was estimated from the full width at half maximum (FWHM), using Scherrer's formula [20]:

$$L = 0.91\lambda/(\beta\cos\theta)$$

where λ is the X-ray wavelength and β is the FWHM. The peak position and the FWHM of the corresponding peaks were analyzed by software installed in the RIGAKUD/MAX 2500 V/PC diffractometer. Here the values of the FWHM from three planes, i.e. (110), (200) and (211), of the bcc phase were used. Prior to the above analyses, the peaks of XRD were corrected for the broadening of diffracted beams caused by the effects of instrument and $K_{\alpha 2}$ peak. The instrumental pattern was measured on unmilled Fe powder. And the background removal and $K_{\alpha 2}$ stripping were carried out by the attached software in the diffractometer. The true peak broadening was obtained using following equation:

$$c = \left(b^2 - a^2\right)^{1/2}$$

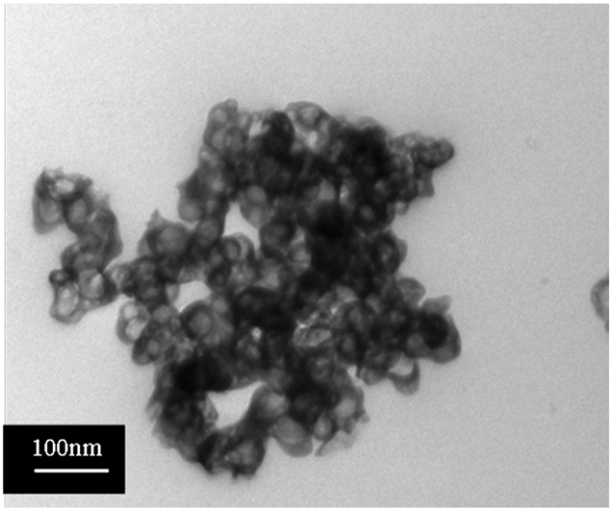

Fig. 1. The TEM image of initial powder of Y_2O_3.

where c is the true peak broadening, b is the FWHM of the experimental profile, and a is the FWHM of a profile for the same reflection from unmilled Fe powder. In this case, the obtained grain size is volume averaged in the direction perpendicular to the plane of diffraction. The microstructure of the mechanically milled powder was observed by XL30E scanning electron microscope (SEM) and JEM-2100 F transmission electron microscope (TEM). For TEM observation of the milled powder, the specimen was prepared by the following two steps: (i) The milled powder was dispersed in trichloromethane by ultrasonic agitation; (ii) Then the suspension was dropped onto the carbon film. The milled powder was fixed after drying of trichloromethane in order to prevent the movement of the particles inside the magnetic pole shoes of the microscope. For TEM observations of the nanostructure of Y_2O_3 after mechanical milling and annealing, chemical extraction was conducted using 5%HCl solution. In this condition, iron particles were dissolved, while Y_2O_3 particles remained. Afterwards Y_2O_3 particles were isolated by centrifugation. At last Y_2O_3 particles were dispersed in ethanol by ultrasonic agitation and then the suspension was dropped onto the carbon film. Differential thermal analysis (DTA) was performed on a NETZSCH DSC 404 PEGANUS at a heating rate of 10 K/min in an argon stream. X-ray photoelectron spectra (XPS) was obtained from RIGAV/DMAX 2500 by using nonmonochromatized Mg K_α X-ray as the excitation source.

3. Results and discussion

3.1. Microstructure of the mixed powders changed by mechanical milling

Fig. 2 shows the SEM observations of the initial iron powder and the Fe–9Cr–15%Y_2O_3 powder mixture after being mechanically milled for various periods. The initial iron powder has a globular shape (see Fig. 2a). With increasing milling time, the morphology of the mixed powder shows the typical plate shape with irregular edge. That is ascribed to severe plastic deformation during mechanical milling. The ductile metal of iron gets flattened (see Fig. 2b), while the brittle oxide of Y_2O_3 gets fragmented by the ball-powder-ball collisions. The particle size of the mixed powder is remarkably affected by mechanical milling, which is 40 μm, 10 μm and 3 μm for the mixed powder mechanically milled for 10 h, 30 h and 56 h, respectively. Fig. 3 shows the change in the grain size of the mixed powder after being mechanically milled for various times. Severe plastic deformation, coupled with the characterization of brittleness of yttrium oxide, brings about grain refinement with increasing milling time. The grain size is reduced from 76 nm to 21 nm. It is a notable decrease from 76 nm to 23 nm at the preliminary stage before 30 h, while a slow variation from 23 nm to 21 nm occurred for longer milling time. The change of the grain size can be explained that the notable decrease of the grain size is caused by intense collision during the initial stage of milling, and the slow variation occurred with the formation of the dynamic equilibrium between cold-welding and repeated fracture after longer milling time.

3.2. Size and structure of yttria after mechanical milling

Fig. 4 shows the X-ray diffraction patterns of the Fe-9Cr-15%Y_2O_3 powder mixture after being mechanically milled for a maximum period of 100 h. The intensity of the Y_2O_3 diffraction peak decreases with increasing mechanical milling time. The diffraction peak almost disappears as a result of broadening of the peak after being mechanical milled for 56 h and 100 h. The broadening of the diffraction peak can be attributed to decreasing size and strain arising from crystal imperfection and distortion after being mechanical milled for longer milling time. The cell parameter calculated from XRD result of the mixed powder after being mechanically milled for 100 h is 0.28608 nm, which is slightly greater than that of pure iron. It is confirmed that few yttrium and