Thermal stability of oxide particles in 12Cr ODS steel

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1. Introduction

Ferritic oxide dispersion strengthened (ODS) steels are regarded to be attractive candidate materials of cladding tubes of sodium-cooled fast reactors due to their superior creep strength at high temperatures as well as good irradiation resistance [1–5]. The high temperature creep strength and irradiation resistance of ODS steels mainly rely on the finely dispersed oxide particles. Oxide particles in ODS steels normally act as pinning points to dislocation movement and stable sinks for irradiation induced defects such as vacancies and interstitial atoms [6–10]. The pinning effect of oxide particles on the dislocation movement is mainly determined by the particle size and the inter spacing between particles, and uniformly dispersed finer oxide particles with higher number density are demanded. Processing at high temperature would play an important role in controlling the dispersion of the oxide particles, since coarsening of oxide particles could occur during these processes [11,12]. For example, coarsening of Y–Al–O particles and transformation of YAM (Y2Al2O5), YAH (hexagonal, YAlO3) and YAP (perovskite, YAO3) particles to YAG (garnet, Y3Al5O12) were observed in the as hipped sample. A significant coarsening of the YTaO4 particles was observed after hot rolling at 1200 °C. Additional coarsening, as well as phase transformation from monoclinic YTaO4 to cubic Y3TaO7 was detected after isothermal annealing at 1250 °C. These results imply that heat treatment temperatures of the ODS steel during fabrication processes should be controlled at low as possible to avoid the undesirable coarsening of oxide precipitates.

2. Experimental procedures

12Cr ferritic ODS steel was fabricated by mechanical alloying (MA), hot isostatic pressing (HIP) and hot rolling processes. Thermal stability of the oxide particles in the ODS steel sample was evaluated by isothermal annealing at 1250 °C for 500 h. High density YTaO4 particles with a mean size of about 9 nm were observed in the as hipped sample. A significant coarsening of the YTaO4 particles was observed after hot rolling at 1200 °C. Additional coarsening, as well as phase transformation from monoclinic YTaO4 to cubic Y3TaO7 was detected after isothermal annealing at 1250 °C. These results imply that heat treatment temperatures of the ODS steel during fabrication processes should be controlled at lower as possible to avoid the undesirable coarsening of oxide precipitates.

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comparison on the oxide particle number density can be made. Carbon extraction replicas were prepared from the mechanically polished surface. The surface was etched by a solution of 2%HF–2%HNO₃–96%H₂O and a carbon film was coated and carbon replicas were removed by electroetching with a solution of 5% perchloric acid and 95% ethanol. Thin foil TEM samples were prepared by standard procedures including slicing, grinding and polishing. The final thinning was performed by jet-polishing with 20 V at –20 °C with the same etchant for the above electroetching procedure.

3. Results and discussion

3.1. Characterization of oxide particles in as hipped 12Cr ODS steel

Fig. 1 shows the microstructure of the as hipped ODS steel sample. Equiaxed ferritic grains with a mean size of ~1 μm were observed (Fig. 1a). The image taken from carbon replica sample indicated that particles with a size less than 30 nm were relatively uniformly distributed (Fig. 1b). The mean particle size was measured to be ~9 nm and the surface number density was ~2.1 × 10⁹ cm⁻². The chemical compositions of these oxide particles were analyzed to be Y-, Ta-, Cr- and O-enriched particles, and a few Y-, Cr-, V- and O-enriched particles were also present. The Y–Cr–V–O particles appeared to be faceted and larger than Y–Ta–Cr–O particles and their size reached up to ~100 nm. EDS analyses on these faceted larger particles indicated that they contain ~55% O, ~20% Cr and ~22% Y (at.%) and a small amount of V. As one of them, the oxide particle arrowed in Fig. 1b was studied by SAD. The SAD pattern can be indexed as [011] zone axis diffraction of YCrO₃ (PDF: 34-0365, orthorhombic, a = 5.5237 Å, b = 7.5343 Å, c = 5.2427 Å) (insert SAD in Fig. 1b), allowing maximum errors of d-spacing with 3% and angle with 3°.

Fig. 2a shows the HRTEM image of a fine oxide particle with a size of ~15 nm in the as hipped ODS steel sample. The crystallographic structure of the 12Cr ODS matrix corresponded to BCC α-Fe with a lattice constant of a = 0.287 nm. The matrix grain was rotated to [011] zone axis by a double tilt holder, so that [011] planes were clearly shown. The d-spacing of {110} plane was 0.203 nm. EDS analyses had been applied on numerous fine

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Fig. 1. TEM images of the as hipped 12Cr ODS steel sample: (a) typical bright field (BF) image, (b) carbon extraction replica sample image.

Fig. 2. HRTEM image of an YTaO₄ particle with a size of ~15 nm (a) and orientation relationship between the particle and the matrix can be derived from the FFT image (b).
particles and they showed a similar composition of ~70% O, ~15% Y, ~12% Ta in at.% and a small amount of Cr. The measured plane distances of the two major directions were 2.90 Å and 2.02 Å with an angle of 75.2°, which corresponds to $d_{\text{YTaO}_4(121)}$ (2.94 Å) and $d_{\text{TaO}_4(001)}$ (2.02 Å). According to EDS analyses and FFT shown in Fig. 2b, the oxide particle was indexed to be YTaO$_4$ (PDF: 24-
1415, monoclinic, $a = 5.326 \text{ Å}$, $b = 10.931 \text{ Å}$, $c = 5.05 \text{ Å}$ and $\beta = 95.5^\circ$, allowing maximum errors of $d$-spacing with 3% and angle with 3°. Strong correlation between the oxide particle and the matrix can be derived from the FFT image. The orientation correlation was identified to be $(051)_O/(011)_M$ and $(715)_O/(011)_M$. The lattice misfit of the correlation was calculated as follows:

$$\delta_1 = \frac{d_{M(110)} - d_{O(051)}}{(d_{M(110)} + d_{O(051)})/2} = \frac{2.03 - 2.01}{(2.03 + 2.01)/2} = 1.0\%.$$ 

Another oxide particle with a size of ~8 nm is shown in Fig. 3. Here the particle was also identified as an YTaO$_4$ oxide. Orientation relation between the particle and the matrix, which was different from that in Fig. 2, can be derived from the FFT image: $(132)_O/(011)_M$ and $(313)_O/(011)_M$. Here a larger lattice misfit of the correlation was obtained:

$$\delta_2 = \frac{d_{M(110)} - d_{O(132)}}{(d_{M(110)} + d_{O(132)})/2} = \frac{2.03 - 1.99}{(2.03 + 1.99)/2} = 2.0\%.$$ 

The coherency of the oxide particles with the matrix was revealed by HRTEM in many other ODS steels. Y$_2$O$_3$ particles were found to be coherent with the FeCr matrix by $[110]_{Y_2O_3}/[111]_M$ and $(111)_{Y_2O_3}/(110)_M$ in EUROFER97 ODS steel [13]. The coherency of the YAH (YAlO$_3$, hexagonal) and YAP (YAlO$_3$, perovskite) particles with the matrix in Al-alloyed high Cr ODS steel was size dependent and stayed semi-coherent when the diameter was up to 30 nm and 15 nm, respectively [14]. Y$_4$Al$_2$O$_9$ particles were found to be coherent or semi-coherent with the matrix with the habit planes of $(011)_M$ [6]. The presence of coherency may cause an increased Zener pinning force per unit area exerted by the
particles on the grain boundaries, which can contribute to the refinement of the grain size in ODS steels [15].

A few coarse Cr-, V- and O-enriched oxide particles ranging from ~100 to ~500 nm were also observed mainly on the grain boundaries. A typical large Cr–V–O oxide particle with a size of around 200 nm is shown in Fig. 4a. Chemical composition of the particle was 50.4Cr, 4.4V and 45.2O in at.%. The SAD pattern (Fig. 4b) was indexed as a face centered cubic (fcc) crystal structure, which coincided well with the diffraction pattern from [011] zone axis of Cr–O (PDF: 06-0532, fcc, a = 8.36 Å). Hence, the coarse oxide particle was determined to be a V-partitioned Cr–O phase with an fcc structure.

3.2. Evolution of the oxide particles after hot rolling and heat treatment

Fig. 5 shows the TEM images of the hot rolled and heat treated sample. A high density of dislocations were found near the oxide particles (Fig. 5a), indicating that there were strong interactions between oxide particles and dislocations. A few coarse oxide particles of over 100 nm in size were observed within the grains as well as on the grain boundaries. Quantitative analysis of oxide particles in hot rolled and heat treated sample indicated that the mean particle size increased from ~9 to ~12 nm after hot rolling and final heat treatments (Fig. 5b). The corresponding surface area number
density of the oxide particles decreased from $\sim 2.1 \times 10^9$ to $\sim 1.4 \times 10^9 \text{ cm}^{-2}$. Large YCrO$_3$, Cr–V–O particles and fine YTaO$_4$ particles were present after hot rolling and heat treatment.

There was no change observed in the structure or chemical composition of YCrO$_3$ and YTaO$_4$ phases. Cr–V–O particles were frequently observed on the grain boundaries with size ranging from $\sim 100$ nm to $\sim 500$ nm. The V concentration was much lower compared to Cr and O in these particles. A typical coarse Cr–V–O particle was observed on the grain boundaries with size ranging from $\sim 100$ nm to $\sim 500$ nm. The V concentration was much lower compared to Cr and O in these particles. A typical coarse Cr–V–O particle was observed on the grain boundaries of the hot rolled sample (Fig. 6). EDS analysis showed a composition of 61% O, 38% Cr and 1% V in at.%. The SAD of the particle was index as [121] zone axis diffraction from a rhombohedra Cr$_2$O$_3$ phase (PDF: 38-1479, $a = 4.9588 \AA$, $c = 13.5942 \AA$). Other types of Cr–V–O (mainly Cr–O and Cr$_8$O$_{21}$) particles were also present, but it was not revealed yet whether there were phase transformations among these particles.

Some (Cr,W)$_{23}$C$_6$ carbides of 1–2 µm in size were identified by STEM and SAD (Fig. 7). The carbides were distributed along grain boundaries. Normally, M$_{23}$C$_6$ carbides are formed during tempering at 750 °C [16,17].

The growth of the YTaO$_4$ oxide particles during the preheating at 1200 °C for 2 h prior to the hot rolling indicates that lower temperatures should be applied to avoid particle coarsening, because particle coarsening could lead to the decrease of oxide particle number density, and thus lowering of the high temperature creep strength.

### 3.3. Thermal stability of the oxide particles during isothermal annealing

Fig. 8 shows the results on the observation on the isothermally annealed 12Cr ODS steel sample. The area number density of the oxide particles from the carbon replica samples showed a significant decrease compared to that before annealing, coupled with a remarkable increase of the particle size (Fig. 8a). The mean particle size and surface area number density of the oxide particles from carbon replica sample were measured to be $22 \pm 2$ nm and $(1.8 \pm 0.5) \times 10^8 \text{ cm}^{-2}$, respectively. The compositions of the oxide particles were Y-Ta-Cr-O, Y-Cr-V-O and Cr-V-O. EDS analyses were applied on numerous Y-Ta-Cr-O and Y-Cr-V-O particles, and they showed a similar composition of $\sim 60$% O, $\sim 37$% Y, $\sim 10$% Ta and $\sim 5$% Cr in at.%. EDS analyses on different types of oxide particles showed that Y-Ta-Cr-O particles were very fine (normally smaller than 30 nm) and spherical, while most Y-Cr-V-O and Cr-V-O were much larger (>100 nm) and faceted. SAD analyses were applied on more than ten Y-Ta-Cr-O particles from different zone axes and all these particles were identified as fcc structured Y$_3$TaO$_7$ (PDF: 48-0265, $a = 10.518 \AA$). Two SAD patterns of a typical Y$_3$TaO$_7$ are shown in Fig. 8b. EDS analyses indicated that Y$_3$TaO$_7$ particles also contained a small amount of Cr and V. In the as hipped condition, fine particles were identified to be YTaO$_4$ and no Y$_3$TaO$_7$ was found. However, all Y-Ta–Cr–O particles analyzed after annealing were Y$_3$TaO$_7$, which indicated that a phase transformation from monoclinic YTaO$_4$ to fcc Y$_3$TaO$_7$ may have occurred during isothermal annealing. The Y–Cr–O particles were identified as YCrO$_3$ particles (Fig. 8c). No structure or morphology change of the YCrO$_3$ particles was observed before and after the annealing at 1250 °C for 500 h.

A Cr–V–O particle with a size of $\sim 200$ nm was observed and had a composition of $\sim 60$% O, $\sim 37$% Cr and $\sim 3$% V in at.%. The SAD fit well with [301] zone axis diffraction of triclinic Cr$_8$O$_{21}$ (PDF: 47-1312). The size and morphology of Cr–V–O particles remained unchanged, indicating that these Cr–V–O particles were also stable at high temperatures.

### 3.4. Statistical analysis of the oxide particle size and number density

Fig. 10 shows the evolution of the mean particle size and number density of the oxide particles in as hipped, hot rolled and isothermally annealed conditions. The estimation of the mean particle size and number density was based on the particles ranging from 3 to 50 nm in size. Particles smaller than 3 nm, which...
were not clearly seen or possibly not extracted on the carbon replica samples, were not included in calculation. The particle size and surface area number density were calculated from several TEM frames of carbon replica samples and the error bars in the figure shows the scattering of the values from different TEM frames. Those larger than 50 nm had a very low number density and thus would contribute scarcely to the analyses. In as hipped condition, oxide particles had the finest mean size and the highest number density. Hot rolling induced significant coarsening and reduction of the number density of the oxide particles by over 30%. After isothermal annealing at 1250 °C for 500 h, the mean particle size increased from 12 to 22 nm (by 83%) and the number density decreased by over 85%.

The size distributions of the oxide particles determined by statistical analysis of carbon replica samples in as hipped condition, hot rolled condition and after annealing are shown in Fig. 11. In as hipped condition, particles with size around 3 nm have the highest number density. After hot rolling and heat treatment, the size distribution shows that the fraction of the fine particles smaller than 8 nm decreased dramatically, indicating the dissolution of the fine particles. Based on the increase of the mean particle size and the dissolution of fine particles, it could be assumed that the dissolution of the fine particles induced the particle coarsening. This is a case of the general phenomenon known as Ostwald ripening. Smaller particles dissolve and the larger ones grow. The oxide particle coarsening in ODS alloys was once reported to be diffusion-controlled [12].

After annealing at 1250 °C for 500 h, however, the oxide particles showed bimodal size distribution. The coarsening of the oxide particles here cannot be compared with the Ostwald ripening mechanism, because the oxide particles became richer in yttrium content during annealing and phase transformation took place, shifting the main composition towards Y2TaO7. The increase of the yttrium content in the oxide particles indicates that the dissolution of the finest YTaO4 particles is not the only source for oxide coarsening. Otherwise the yttrium content should keep the same. Compared to YTaO4, Y2TaO7 particles contain higher yttrium and oxygen content. So part of the coarsening should be caused by the uptake of yttrium and oxygen. Different from conventional steels produced by melting and solidification processes, ODS steels contain an exceptionally high oxygen content. Y3O3 is not the only source of oxygen in the ODS steels. A large portion of oxygen, which is stated as excess oxygen in many studies, is incorporated during the milling process from the absorbed oxygen on the surface of the metal powders and oxygen from the atmosphere. Though oxygen has a very low solubility in defect-free iron (<10 ppm), the solubility in ODS steels is significantly enhanced by high density of dislocations and vacancies induced during MA process. Calculation by Fu et al. using first principles showed that oxygen in Fe has a strong affinity for vacancies [18]. As a consequence the formation energy of oxygen-vacancy pairs would be extremely small if these vacancies pre-exist, allowing the oxygen concentration to approach that of the vacancies. The oxygen-vacancy pairs could enable the nucleation of oxygen-enriched nano-clusters that attract solutes with high oxygen affinities (Ti and Y), which were revealed in MA957 and 14YWT ODS steels [19,20]. The presence of high density of vacancies could reserve high excess oxygen content in the MA powders and induce the formation of nano-clusters with oxygen and high oxygen affinities during high temperature process. However, the vacancy concentration will move towards the equilibrium concentration during annealing, and the super-saturated vacancies will diminish. Correspondingly, the excess oxygen content that can be retained by vacancies will decrease. The amount of oxygen that exceeds the vacancy concentration would either precipitate as new phase or diffuse to the surface of nano particles and lead to the coarsening of the nano particles. Therefore, the particle coarsening during annealing at 1250 °C for 500 h can be interpreted as an uptake of yttrium and oxygen with the tendency for transformation to Y2TaO7 due to the decrease of oxygen solubility in the matrix during annealing, as well as the dissolution of the fine particles.

4. Conclusion

A 12Cr ferritic ODS steel containing high number density of fine YTaO4 particles (mean size ∼9 nm) was fabricated by MA (mechanical alloying) and HIPping (hot isostatic pressing) processes. Most
fine YTaO₄ particles were found to be coherent with the matrix in the as hipped condition. A significant coarsening of the oxide particles occurred coupled with a decrease of the particle number density, after hot rolling and heat treatment, reaching a mean particle size of ~12 nm. Isothermal annealing of the samples at 1250 °C for 500 h led to an increase of mean particle size to ~22 nm and a decrease of number density by over 85%.

Transformation of monoclinic YTaO₄ particles to cubic Y₃TaO₇ particles may have occurred during isothermal annealing at 1250 °C for 500 h. The particle coarsening during hot rolling was mainly attributed to the dissolution of the fine oxide particles, while the coarsening during isothermal annealing at 1250 °C is interpreted by an uptake of yttrium and oxygen with the tendency for transformation from YTaO₄ to Y₃TaO₇ due to the decrease of oxygen solubility in the matrix phase.

Considering the coarsening of oxide particles during high temperature processes, it is thus suggested that the fabrication processes of 12Cr ODS steel should be kept at lower temperatures than 1200 °C.

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References