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The effect of Ti on the coarsening behavior of oxygen-rich nanoparticles in oxide-dispersion-strengthened steels after annealing at 1200 °C

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Oxide-dispersion-strengthened (ODS) steels are candidate structural materials for future fusion reactors. For this application, the coarsening behavior of the yttria-based strengthening oxygen-rich nanoparticles is of particular importance. This paper reports on the coarsening behavior of oxygen-rich nanoparticles in two Fe–14Cr–2W–(0.1–0.3)Ti base alloys after annealing at 1200 °C up to 100 h. Nanoparticles with and without Ti enrichment are investigated, and it is shown that nanoparticles that do not contain Ti coarsen at the same rates as those with Ti.

Keywords: Three-dimensional atom probe; Ferritic steels; Coarsening; Nanostructure; Mechanical alloying

Reduced-activation oxide-dispersion-strengthened ferritic steels are currently regarded as the most promising group of materials for structural applications in fusion power plant and the next generation of fission reactors. The materials are often fabricated by mechanically alloying the base alloy with ~0.3% Y_2O_3 to produce a uniform dispersion of oxygen-rich nanoparticles. If the base alloy contains Ti, the nanoparticles contain Y, Ti and O, and are ~2 nm radius [1]. Without Ti, the nanoparticles are primarily Y–O-based, and are slightly larger, at 4–6 nm radius [2,3]. The oxygen-rich nanoparticles improve high-temperature strength and are believed to act as trapping sites for helium and point defects introduced by irradiation [4].

Materials strengthened with Y–O-based nanoparticles often have better impact properties than those strengthened with Y–Ti–O nanoparticles [5]. Yet the majority of current research is centered on steels strengthened with Y–Ti–O nanoparticles. This is because Y–Ti–O nanoparticles are often smaller and present in higher number densities than Y–O-based ones [5]. Ti-alloyed materials therefore show better strength and creep resistance, and the Y–Ti–O nanoparticles are believed to be more stable at high temperature than the Y–O-based ones [6,7].

For Y–Ti–O nanoparticles in the MA 957 commercial oxide-dispersion-strengthened (ODS) material, Alinger et al. [8] reported three separate coarsening regimes. Below 1000 °C, the authors found that the nanoparticles were stable. At 1200 °C, the nanoparticles coarsened according to classical coarsening theory. At higher temperatures (above 1300 °C), the nanoparticles coarsened rapidly and became unstable [8]. Ribis et al. [7] investigated a Fe–14Cr–1W–0.3 Ti–0.3 Y_2O_3 ODS alloy, and observed both Y_2O_3 nanoparticles and $Y_2Ti_2O_7$ nanoparticles in the same material after annealing at 1300 °C for 1 h. These authors reported that the coarsening behavior of the Ti-containing nanoparticles was very different to that of the Y_2O_3 nanoparticles at this temperature, and the Ti-containing clusters were much more stable.

While a full understanding of the effect of Ti on the nanoparticle coarsening would require a wider temperature range to be studied, the crucial temperature range for the processing of ODS alloys is 1150–1200 °C. Full consolidation is difficult at lower temperatures, and the nanoparticles coarsen rapidly at higher temperatures. The purpose of the present study is to investigate the stability of both Y–O and Y–Ti–O nanoparticles at this crucial temperature (after annealing at 1200 °C) and

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to investigate the influence of Ti on the coarsening of the nanoparticles at that temperature.

Two separate ODS alloys developed by Baluc et al. (EPFL) were used in this study, and the consolidation and annealing conditions were identical for both materials. The first (EPFL-Y_2O_3) was a Fe–14Cr–2W–0.3 Ti base alloy mechanically alloyed with 0.3% Y_2O_3. The powder was then canned and degassed at 800 °C for 2 h, and consolidated by hot isostatic pressing (HIP) at 1150 °C, 200 MPa for 4 h. The second alloy (EPFL-Fe_2Y) was very similar – this time a Fe–14Cr–2W–0.1 Ti base alloy, but mechanically alloyed with 0.5% Fe_2Y. The powder was canned and degassed at 600 °C for 2 h, then consolidated by HIP at 1150 °C, 200 MPa for 4 h. Both materials were annealed at 1200 °C after encapsulation in an evacuated silica tube.

The materials were characterized primarily using atom probe tomography (APT), using a Cameca LEAP 3000HR instrument operated in laser pulsing mode. Specimens were prepared using standard electropolishing techniques, as described in Ref. [2]. The specimen base temperature was maintained at 30 K, the laser energy was 0.2–0.4 nJ and an 8 μm laser spot size was used at a repetition rate of 200 kHz. The nanoparticles were identified using the maximum separation algorithm developed by Hyde et al. [9], using the "posgen" software. Y^{3+}, $Y\text{–}O^{2+}$, O^{2+} and TiO^{2+} were used as "cluster ions", with a maximum separation distance (d_{max}) and surrounds distance of 1.3 nm. No erosion step was carried out, as instead a matrix correction similar to that applied in Ref. [2] was used. A d_{max} value of 1.3 nm is larger than the values commonly used in the analysis of oxygen-rich nanoparticles in ODS steels (usually 0.6–1 nm [2,10]), but this value was found to compare most favorably with measurements of nanoparticle size made by transmission electron microscopy (TEM) in the EPFL-Fe_2Y material. Due to the matrix correction step described in Ref. [2], using larger d_{max} values does not significantly affect the composition measurements. The larger d_{max} value does, however, include any solute enrichment above the matrix level in the matrix immediately surrounding the nanoparticles. This accounts for the higher Cr content given in Table 1 for the nanoparticles using the maximum separation method compared to APT studies on other similar alloys.

TEM specimens were prepared by electropolishing 3 mm discs in a solution of 2% perchloric acid in methanol at −30 °C. Images were taken using a Philips CM20 microscope operating at 200 kV.

The two materials were chosen for this study due to the differences in the nanoparticle distribution. Figure 1 shows that there is a much higher density of smaller nanoparticles in the EPFL-Y_2O_3 material than in the EPFL-Fe_2Y material. Table 1 summarizes the results of the APT analysis of both materials. As well as differences in size distribution and number density, the Ti content of the nanoparticles is very different. Figure 2 shows the variation in concentration of elements for the Y–O and Y–Ti–O nanoparticles, measured from the matrix to the core (proxigram based on an iso-concentration surface of 1% Ti or 1% Y).

The composition of the Y–Ti–O nanoparticles inferred from the proxigram in Figure 2(b) is similar to the compositions of nanoparticles measured by the proxigram method in the 14-YWT and MA 957 alloys [11,12], particularly in terms of Y, Ti and Cr content. The larger nanoparticles in the EPFL-Fe_2Y material are Y–O based, whereas Table 1 shows the nanoparticles in the EPFL-Y_2O_3 material contain ~13% Ti. Both nanoparticle types contain high levels of Cr even after the matrix contribution has been removed. This is thought to be primarily the result of interfacial segregation. Figure 2(b) shows that the Cr level falls away near the core of the larger Y–O nanoparticles. It is not possible to determine whether the smaller Y–Ti–O nanoparticles have a core–shell-type structure, due to the limited lateral resolution of APT. Hirata et al. [13] suggest that the nanoparticles have an NaCl-type structure and can support significant levels of Cr; however, it is unlikely that Cr forms part of the oxide phase at the high levels indicated by the maximum separation method of APT data analysis.

The materials were annealed for 1, 4, 24 and 100 h at 1200 °C in a vacuum, and the distribution of nanoparticles was analyzed by APT. A minimum of 50 nanoparticles were analyzed in each condition from at least three separate specimens for the EPFL-Fe_2Y material, in regions with no visible grain boundaries. For the EPFL-Y_2O_3 material, in excess of 200 nanoparticles were analyzed from three or more specimens in each condition, again from regions with no visible grain boundaries. At this temperature, particle coarsening is expected to follow an $r \propto kt^{1/3}$ relationship according to the classical Lifshitz–Slyozov–Wagner (LSW) theory of coarsening for a dilute binary system [14]. Figure 3 shows that the time evolution of the particle radius is a good fit to this relationship, for both of the alloys studied. The gradients of the lines yield the coarsening rate constants (k) for the two alloys. These are equal, within error limits, for the time span and temperature studied.

The compositions of the Y–Ti–O nanoparticles in the EPFL-Y_2O_3 material were not observed to change significantly after annealing. After annealing for up to 24 h, the compositions of the Y–O nanoparticles in the EPFL-Fe_2Y material were also unchanged. However, in one instance, in the EPFL-Fe_2Y material after annealing for 100 h at 1200 °C, 4 out of 56 nanoparticles with a Y:O ratio of 2:3 were observed. A proxigram taken from one of these particles is shown in Figure 4. All

Table 1. Characteristics of the nanoparticle distribution as measured by APT.

APT nanoparticle characteristics	EPFL-Y_2O_3	EPFL-Fe_2Y
Radius of gyration (nm)	2.5 ± 0.1	3.8 ± 0.2
Number density (10^{23} m^{-3})	7.1 ± 0.7	0.43 ± 0.06
"Matrix corrected" cluster composition from maximum separation method (%) $\sigma < 2\%$	7% Y, 13% Ti, 25% O, 48% Cr	32% Y, 27% O, 34% Cr