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High resolution Transmission Electron Microscopy characterization of a milled oxide dispersion strengthened steel powder

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HIGHLIGHTS

- We observed an ODS ball-milled powder by high resolution transmission microscopy.
- The ODS ball-milled powder exhibits a lamellar microstructure.
- Small crystalline nanoclusters were detected in the milled ODS powder.
- The nanoclusters in the ODS milled powder are enriched in titanium.
- Larger NCs of 15–20 nm in size are, at least, partly coherent with the matrix.

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ABSTRACT

Oxide Dispersion Strengthened (ODS) steels are promising materials for generation IV fuel claddings as their dense nano-oxide dispersion provides good creep and irradiation resistance. Even if they have been studied for years, the formation mechanism of these nano-oxides is still unclear. Here we report for the first time a High Resolution Transmission Electron Microscopy and Energy Filtered Transmission Electron Microscopy characterization of an ODS milled powder. It provides clear evidence of the presence of small crystalline nanoclusters (NCs) enriched in titanium directly after milling. Small NCs (<5 nm) have a crystalline structure and seem partly coherent with the matrix. They have an interplanar spacing close to the $(011)_{bcc}$ iron structure. They coexist with larger crystalline spherical precipitates of 15–20 nm in size. Their crystalline structure may be metastable as they are not consistent with any Y-Ti-O or Ti-O structure. Such detailed observations in the as-milled grain powder confirm a mechanism of Y, Ti, O dissolution in the ferritic matrix followed by a NC precipitation during the mechanical alloying process of ODS materials.

1. Introduction

Oxide Dispersion Materials are promising structural materials for next generation nuclear power plants – gen IV - as they exhibit a good resistance to irradiation and creep. Their excellent mechanical properties come from a fine dispersion of oxygen-rich nano-clusters (NCs) that pin dislocations [1–4]. Since the pinning mechanism is inversely proportional to the inter-particles distance, the optimal microstructure would be reached with the highest density as possible of NCs [1]. The chemical nature and structure of the NCs are still in debate [5], especially for the smallest ones, as their size reaches the limits of almost all known characterization techniques. They are size dependent. The largest NCs, over 35 nm in size, are usually TiO_2 [6] whereas the NCs between 15 nm and 35 nm in size are mostly consistent with $Y_2Ti_2O_7$ [6–10], although new phases were observed [11]. For particles with sizes below 5 nm, Sakasegawa et al. [6] suggest that they are non-stoichiometric $Y_xTi_yO_z$ oxides while Hirata et al. [12] show that they exhibit unknown f.c.c rocksalt like structure. Atom Probe Tomography (APT) results confirm that NCs are non-stoichiometric compounds [13] and show that they have a Cr rich shell [14].

ODS steels are manufactured through powder metallurgical

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routes. Powders are milled, canned and consolidated by hot isostatic pressure or/and extrusion. Reactants vary from one publication to another. A pre-alloyed powder of FeCrWTi or FeCrW is mixed with additional Ti, Y and O under various forms (Y_2O_3 [15–17], YFe_2 [5,18], TiH_2+YH [19], TiH_2+Y_2O_3 or Fe_2Ti+YFe_3+Fe_2O_3 [20,21], Fe+Cr+W+Ti+Y_2O_3 [15,22]). All processes lead to ODS materials containing NCs [5,15–21]. Their analysis by APT tend to indicate a similar composition of NCs enriched in titanium, yttrium and oxygen [5,20,21,23]. Although they have been studied for years, neither reference material nor procedure exists because the process includes numerous parameters and because the mechanism of NC precipitation is not yet understood. Apart from the issue of the exact NC composition, this is due to the clear lack of milled powder characterization. There are extensive studies on consolidated materials but very few on the corresponding powders mainly because of an issue on sample preparation.

APT and Transmission Electron Microscopy (TEM) analysis of powder with a granulometry over 1 μm require specific preparation of samples much more complex than the one for consolidated materials. APT samples from powders are made with a focused ion beam (FIB) [5,20,21]. Those for TEM can be obtained with a FIB [5,24–26], but also with a microtome preparation [17,27] or even an ion thinning [28,29]. In most cases, the thin sections are too thick to be analyzed finely and these samples provide only few results [5,17,24–26]. However, using samples prepared by ion thinning, De Castro et al. [29] were able to observe monoclinic Y_2O_3 precipitates of 10 nm in size from a powder milled 24 h on a horizontal attritor. Without explaining their sample preparation, Liu et al. [30] claim to observe amorphous yttria in a model powder of Fe-25% Y_2O_3 (%wt).

By Small Angle Neutron Scattering (SANS), the difference between the signals from powders milled with or without reinforcements is usually interpreted as the presence of nanoporosities [16,31]. However, with a combination of SANS and APT analysis, Brocq et al. [20,21,32] have shown that under certain milling conditions, this signal difference may be attributed to the existence of NC germs enriched in titanium and yttrium. Williams et al. [5], with APT observations, have confirmed the NC germs right after milling in a powder elaborated from different reactants than Brocq's powder.

In fact, the ODS steel powder is poorly known. Yet, different theories concerning the formation of oxides have been put forward based on SANS data hardly exploitable [16,31] or from direct observation of consolidated ODS steels only [33]. From High Resolution Transmission Electron Microscopy (HRTEM) observations of consolidated steels, Husing et al. [33] have proposed a three step mechanism where Y_2O_3 fragments amorphize during ball milling and recrystallize with a chromium shell during annealing. Alinger et al. [16], based on only SANS data, have proposed that Y, Ti, O dissolve in the matrix during milling and then precipitate during subsequent annealing. Recently, using APT and SANS observations of either a solid solution or fragments of NCs in powders obtained after different milling times, Brocq et al. [20,21] have proposed a more complex path starting with a dissolution of reactants followed by a nucleation of NCs during milling followed by a precipitation during annealing.

However, none of the above mechanisms has ever been confirmed with direct observation by HRTEM of a milled powder showing either some nucleation or some amorphization. Only Dai et al. [22] have shown the presence of amorphous Y_2O_3 precipitates in a shortly milled powder after chemical extraction.

In the aim to bring some clues about the NC precipitation mechanism in ODS steel, the present article gives a detailed analysis of an as-milled powder. A preparation technique to obtain foils thin enough for HRTEM imaging, inspired from the sandwich method, is developed and applied to an ODS milled powder. Conventional TEM, HRTEM and Energy Filtered TEM (EFTEM) analysis are then used to characterize the powder.

2. Experimental

The experimental procedure of the ODS powder elaboration is described in details elsewhere [20]. A FeCrWTi alloy with the nominal composition Fe–14Cr–2.0W–1.0Ti wt.% (Fe–15.03Cr–0.61W–1.17Ti at.%) was milled together with YFe_3 and Fe_2O_3 powders in proportions which lead to a final alloy containing 0.8 wt % of Y and 0.2 wt% of O (respectively 0.50 and 0.70 at.% respectively). A Fritsch P0 mill with a tungsten carbide (WC) ball (1 kg) and vial was used for a 144 h milling under secondary vacuum (10^{-6} mbar). Five grams of compounds were introduced into the vial. The milling intensity as defined by Chen et al. [34] was 2000 m s^{-2}. Compositions of the starting materials as well as the final powder were measured with a microprobe Cameca SX50, operated at 15 kV and 40 nA.

Previous experiments on the final powder composed of Fe-14Cr-2W-1Ti-1Y_2O_3 (% wt) using APT have shown a NC density $1.3 \pm 0.3 \times 10^{24}$ m^{-3} with a mean radius $R = 0.84 \pm 0.3$ nm [20]. Besides, by Small Angle Neutron Scattering (SANS), their density and size were estimated at $1.4 \pm 0.3 \times 10^{24}$ m^{-3} and $R = 0.8 \pm 0.2$ nm [32].

No standard technique for the preparation of TEM samples from powders exists. Several techniques are available, but the choice of the best-suited one, as well as the determination of the optimal operating conditions, strongly depends on the considered material and on the imaging mode. In this study, ion thinning was used to get thin foils thinner than 50 nm that allows high-resolution imaging and EFTEM analysis. The specific preparation of ion thinning avoids any compression or excessive heating that might trigger a precipitation of NCs that would not be related to the milling process. To prevent any excessive heating, the sample was cooled with liquid nitrogen during ion thinning. As the Gatan G1 resin undergoes a glass transition at 150 °C that would break the thin section (rupture at the interface between the copper ring and the resin or between the powder particles and the resin), we know the material has not been heated above 150 °C. Therefore, the sample is always well below 400 °C, temperature at which a start of NC precipitation has been reported after 2 h by Brocq et al. [28] and Couvrat et al. [32]. To our knowledge, no study has ever shown a NC precipitation below that temperature.

The ODS powder thin sections were obtained by ion polishing using the following procedure. The milled ODS powder was mixed with an epoxy resin (Gatan G1) and the corresponding hardener with a mass ratio powder/resin/harderner of 20/10/1. The mixture was transferred into a copper tub (Fig. 1), placed into an oven at 100 °C for an hour and sliced into 300 μm thickness discs with a diamond saw. As an alternative, the mixture can also be directly placed into the oven, thinned to 70 μm and punched as 3-mm diameter disks. Specimens were mechanically thinned to 50 μm (±10 μm) using 1200, 2400 and 4000 paper-grit with deionised water and then diamond suspensions (3 and 1 μm). The specimens were then ion-polished with a Gatan Precision Ion Polishing System (PIPS). The polishing occurred at 4 keV, −170 °C, in dual beam mode with angles at ± 8° until a hole localized near powder particles was observed. Then, angles and energy were gradually decreased to 4° and 3 keV (6° at 4 keV for 15 min; 6° at 3.5 keV for 2 h, 4° at 3 keV for 30 min). The quality of samples obtained by the two alternative technics is about the same. One advantage of suppressing the copper tub is to avoid the frequent rupture at the copper tub/resin interface during the mechanical thinning but also during the ion polishing. The drawback is the difficulty to thin the mixture and to punch 3-mm diameter disk in the brittle material.