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Regular Article

Relaxation path of nanoparticles in an oxygen-enriched ferritic oxide-dispersion-strengthened alloy

M.A. Thual [a,*], J. Ribis [b], T. Baudin [c], V. Klosek [a], Y. de Carlan [b], M.H. Mathon [a]

[a] LLB, CEA, CNRS, Université Paris-Saclay, CEA Saclay, F-91191 Gif-sur-Yvette, France
[b] DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
[c] ICMMO, SP2M, Univ. Paris-Sud, Université Paris-Saclay, UMR CNRS 8182, 91405 Orsay Cedex, France

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ABSTRACT

Excellent mechanical properties of oxide-dispersion-strengthened (ODS) alloys arise from a high density of Y-Ti nano-oxides finely dispersed in the matrix. Characteristics of this precipitation can strongly be influenced by oxygen contamination during milling. We studied an as-received and annealed (1 h 1150 °C) oxygen-enriched ferritic ODS alloy by High Resolution Transmission Electron Microscopy. The as-received sample has unknown b.c.c nano-oxides, while the annealed one has orthorhombic nanoparticles. We propose a phase relaxation during the annealing, confirmed by the observation of a particle where both cubic and orthorhombic structures coexist. The influence of oxygen on the particle structure is also discussed.

Since several decades oxide dispersion strengthened (ODS) alloys are extensively studied worldwide due to their strong potential for nuclear applications in future fission and fusion reactors. The most studied ones are iron-chromium-based materials either martensitic or ferritic both strengthened by Y_2O_3 addition and alloyed-Ti known to refine the precipitation. Once reinforced by stable $Y_2Ti_2O_7$ nanoparticles, ODS alloys display improved high-temperature mechanical properties and superior irradiation resistance compared to conventional ferritic/martensitic materials [1–4] due to the pinning of dislocation and grain boundary motions by the nanoparticles.

Conventional melt processing techniques cannot be applied to fabricate nanostructured iron-based alloys due to the low solubility limit of Y and O in iron [5]. The common approach is the powder metallurgy route, consisting of mechanical alloying (MA) followed by hot consolidation. First of all, micrometric base-alloy powder is milled together with nanometric Y_2O_3 and TiH_2 powders. Successive impacts between milling balls and powder result in the formation of a large amount of point defects together with the fragmentation, amorphization and dissolution of the alloyed components (Y_2O_3 and TiH_2) [6–10]. MA is therefore an out of equilibrium process and is known to form solid solutions of immiscible materials [11–14]. Numerous milling parameters are involved in mechanical alloying as the milling atmosphere, time and intensity, the mill type or different type of contaminations (powder or gas purity, milling balls, powder transfers). During hot consolidation of such powders Y, Ti or Y-Ti rich-oxides precipitate [15–17] and the different milling parameters mentioned before will influence the characteristics of this precipitation (size, stoichiometry, structure, density). In the literature, a large variety of structure and particle stoichiometry can be found. The nanoparticles encountered in Fe-14Cr ODS alloys are frequently f.c.c. pyrochlore type $Y_2Ti_2O_7$, orthorhombic Y_2TiO_5 and more rarely orthorhombic $YTiO_3$.

Thus Auger et al. [18] showed that for the same alloy composition a milling under hydrogen atmosphere leads after consolidation to a precipitation more refined than milling with helium. Xie et al. [19] focused on the milling time: by milling 20 h instead of 8 h in a Pulverisette under argon atmosphere at 260 r/min they refine their particle size by 22%. More surprisingly, Unifantowicz et al. [20] are the only one up to date observing the $YTiO_3$ phase in ODS alloys even if calculations predict the pyrochlore $Y_2Ti_2O_7$ or orthorhombic Y_2TiO_5 structures as the most stable ones [21]. On the contrary, Ribis et al. [22] with exactly the same chemical composition, milling atmosphere and intensity than Unifantowicz et al., have never encountered this structure in their alloy. However, the material in reference [20] has a very high oxygen level (0.48 wt%). Contamination during milling might be the origin of this difference. Indeed, the milling time and mill type are source of light element (C or O) contaminations. Olier et al. [23] observed titanium carbides of ~200 nm after consolidation in an ODS milled in an attritor while such precipitates have not been observed with the same milling conditions in a ball mill. They concluded that attrition is a high carbon contamination process. In the same study, they also measured an increase of the oxygen contamination with milling time leading to

* Corresponding author at: LLB, Bât. 563, CEA Saclay, 91191 Gif sur Yvette, France.
E-mail address: marc-antoine.thual@cea.fr (M.A. Thual).

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Table 1
Chemical composition of the as-received material.

Element	Fe	Cr	W	Ti	Y	O
wt%	Bal	13.45	0.90	0.18	0.2	0.48
at%	Bal	14.09	0.27	0.21	0.12	1.64

the formation of titanium and silicon oxides. Zhong et al. [24] studied the effect of a controlled oxygen addition in a Fe-14Cr-0.3Ti-0.3Y_2O_3 ODS alloy having nanoparticles with a slow coarsening kinetics during thermal treatment. They highlighted a clear acceleration of the coarsening kinetics while enriching the material in oxygen without identifying its origins.

Oxygen contamination during the milling process is one of the most difficult parameter to control. It is therefore essential to understand its potential effects on the nanoprecipitation. In this paper, we report a complementary study in the same oxygen rich ODS alloy studied by Zhong et al. [24]. The material is studied in the as-received condition and after annealing 1 h at 1150 °C. The crystallographic structure of the particles has been closely studied by High Resolution Transmission Electron Microscopy.

Atomized powder (Fe-14Cr-1W, wt%) from Aubert&Duval was mixed and milled with 0.3 wt% TiH_2, 0.3 wt% Y_2O_3 and 1 wt% Fe_2O_3. TiH_2 is chosen rather than usual elementary Ti powder in order to minimize the oxygen contamination from the powders. The oxygen enrichment is controlled by the Fe_2O_3 powder addition where Fe and O atoms will dissociate and dissolve in the matrix during the milling. Mechanical alloying was performed at LTMEx, CEA Saclay in an attritor at 400 rpm during 10 h under Ar-atmosphere with a mass to ball ratio of 1:10. The milled powder was then canned and degassed at 400 °C for 2 h followed by a heat treatment of 1 h at 1100 °C and immediately hot extruded. Post-extrusion the material was air cooled and labelled as "as-received". The as-received alloy composition has been measured and is summarized in Table 1.

A high resolution JEOL 2010F microscope operating at 200 kV was used to study the nanoparticles in both as-received and annealed state. Discs of 3 mm diameter were punched out from a 100 μm thick sample withdrawn perpendicularly to the extrusion direction. Thinning of the foil until electron transparency was made using a 10% perchloric acid – 90% ethanol solution at − 10 °C in a Struers Tenupol device.

A general view of the precipitation in the as-received condition and after annealing is presented by Fig. 1(a) and (b). The size distribution of the particles is presented Fig. 1(c). The annealing at 1150 °C for 1 h leads to an increase of the mean particle size from 1.6 nm to 4.6 nm together with a decrease of the particle density from 8.1×10^{23} m^{-3} before annealing to 5.0×10^{22} m^{-3} after annealing.

Characteristic particles found in the as-received material are shown in Fig. 2(a) and (d) with their respective FFT, Fig. 2(c) and 2(f). The atomic planes (132) of the two particles are continuous with the (110) planes of the matrix which suggests a total coherence in the direction of observation. Both particles seem to have a b.c.c. structure observed along the same [4–21] zone axis. The interplanar distances do not match the Y_2O_3 phase or any other type of known Y-Ti oxide structures, Fig. 2(b) and (e). The unknown b.c.c. structure of the particles must result from their coherent nucleation with the matrix. From one

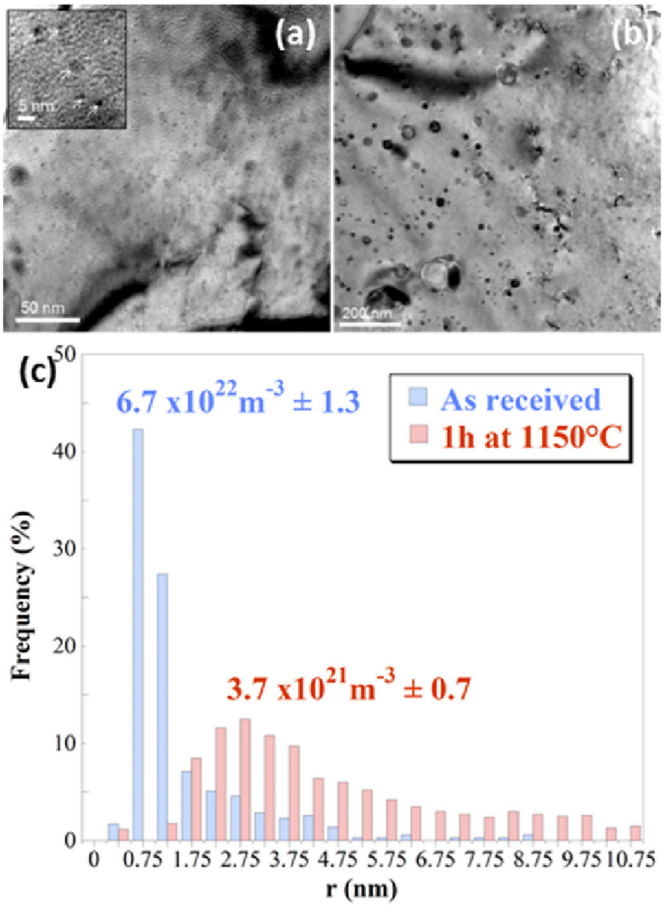

Fig. 1. Representative TEM images of the nanoprecipitation in (a) the as-received condition and (b) after annealing at 1150 °C for 1 h and (c) its associated size distribution histogram counted respectively on 350 and 1000 particles. The foil thickness is about 100 nm and was determined by EELS.

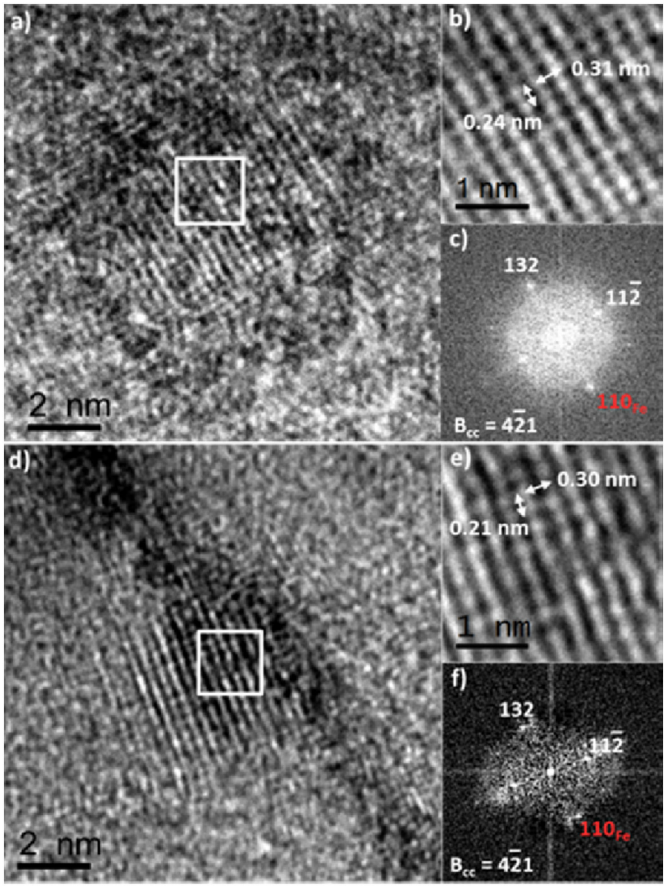

Fig. 2. High Resolution TEM images (a) and (d) of two unknown b.c.c. nanoparticles in the as-received state with (b) and (e) their respective enlarged filtered image and (c) and (f) their respective FFT.