



Relaxation path of metastable nanoclusters in oxide dispersion strengthened materials



J. Ribis^{a,*}, M.A. Thual^b, T. Guilbert^a, Y. de Carlan^a, A. Legris^c

^a DEN-Service de Recherches Métallurgiques Appliquées, CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

^b LLB, CEA, CNRS, Université Paris-Saclay, CEA Saclay, 91191, Gif-sur-Yvette, France

^c UMET, CNRS/UMR 8207, Bât. C6, Univ. Lille 1, 59655 Villeneuve d'Ascq, France

HIGHLIGHTS

- The nanoclusters display a f.c.c. cubic symmetry and a non-equilibrium YTiCrO chemical composition.
- During thermal annealing the coherent nanocluster transform into semi-coherent pyrochlore particles.
- A Cr ring is observed around the relaxed pyrochlore type particles.

ARTICLE INFO

Article history:

Received 10 October 2016

Received in revised form

7 December 2016

Accepted 8 December 2016

Available online 9 December 2016

Keywords:

Nanoclusters
Nano-oxides
Non-equilibrium
Relaxation path
TEM

ABSTRACT

ODS steels are a promising class of structural materials for sodium cooled fast reactor application. The ultra-high density of the strengthening nanoclusters dispersed within the ferritic matrix is responsible of the excellent creep properties of the alloy. Fine characterization of the nanoclusters has been conducted on a Fe-14Cr-0.3Ti-0.3Y₂O₃ ODS material using High Resolution and Energy Filtered Transmission Electron Microscopy. The nanoclusters exhibit a cubic symmetry possibly identified as f.c.c and display a non-equilibrium YTiCrO chemical composition thought to be stabilized by a vacancy supersaturation. These nanoclusters undergo relaxation towards the Y₂Ti₂O₇-like state as they grow. A Cr shell is observed around the relaxed nano-oxides, this size-dependent shell may form after the release of Cr by the particles. The relaxation energy barrier appears to be higher for the smaller particles probably owing to a volume/surface ratio effect in reason to the full coherency of the nanoclusters.

© 2016 Elsevier B.V. All rights reserved.

Contents

1. Introduction	184
1.1. The non- and near-stoichiometric oxides	184
1.2. The nanoclusters	184
2. Experimental details	185
3. Results	185
3.1. Characterization of the nano-oxides	185
3.2. Characterization of the nanoclusters	185
3.2.1. The lattice structure	185
3.2.2. The chemical composition	185
3.3. Evolution of the nanoclusters when the system is driven towards equilibrium by thermal annealing	186
3.3.1. During 1 h at 1300 °C	186
3.3.2. Annealing during 5000 h at 600 °C	186
4. Discussion	186
4.1. The non-equilibrium composition of the YTiCrO nanoclusters	187

* Corresponding author.

E-mail address: joel.ribis@cea.fr (J. Ribis).

4.2.	Relaxation path of the non-equilibrium YTiCrO nanoclusters	190
4.2.1.	The change of structure during relaxation	190
4.2.2.	Hypothesis on the formation of the Cr shell	190
4.3.	Hypothesis of the origin of the high thermal stability of the nanoclusters	191
5.	Conclusion	192
	References	192

1. Introduction

Gen IV and fusion power plants require new materials able to withstand extreme conditions met in service as high temperature and high irradiation damage. Under such demanding conditions, ODS materials constitute a new promising class of structural materials for these advanced fission and fusion energy applications [1]. These materials are elaborated using a non-equilibrium process route, involving mechanical alloying of pre-alloyed powders and consolidation through thermo-mechanical processes. The ultra-high density of dispersion-strengthening nanoclusters emerges within the matrix during the elaboration process. This dispersion is responsible for the excellent mechanical properties exhibited by the alloy. Usually, nanophase materials are normally usable only at relatively low temperature due to rapid coarsening at elevated temperature. But these nano-particles are distinguished by their high stability and resistance to coarsening even at high temperature and, thus, have aroused considerable attention in the materials research community. To date, previous studies suggested that these nano-particles range from coherent solute-enriched nanoclusters (1–3 nm in diameter) to non- and near-stoichiometric complex oxide (more than 3 nm in diameter) [2].

1.1. The non- and near-stoichiometric oxides

It is now well established that the structure of the particles with diameter exceeding 3 nm matches with the $Y_2Ti_2O_7$ structure [2,3] or with the Y_2TiO_5 structure [2]. However, a discrepancy between structural and chemical analysis persists since all chemical analysis report that these particles do not meet the $Y_2Ti_2O_7$ stoichiometry. Many APT (Atom Probe Tomography) results suggest that Y/Ti and (Y + Ti)/O ratios are inconsistent with the $Y_2Ti_2O_7$ structure [4–8]. Williams et al. [9] provided detailed results by APT and found that the stoichiometry change is a shift of the Y/O ratio from: ~1:2 in the 2 nm oxides to 1:1 for 5–10 nm oxides. As a consequence, the values of Y/Ti and (Y + Ti)/O ratios deduced from APT experiments can be gathered into two groups: Y/Ti ~1 and (Y + Ti)/O ~1 [10] and Y/Ti ~0.15–0.45 and (Y + Ti)/O ~2 [11–13]. Using Transmission Electron Microscopy (TEM) along with Energy Dispersive X-ray Spectroscopy (EDS), Sakasegawa et al. [14] confirmed that particles from 2 to 15 nm are non-stoichiometric.

As proposed by Yamashita [15], the explanation of the structure and chemical composition discrepancy could reside in that the $Y_2Ti_2O_7$ structure must tolerate stoichiometric gap by accommodating a high concentration of point defects. Then, these non- and near-stoichiometric nano-oxide are expected to achieve relaxation towards equilibrium since Sakasegawa et al. [16] reported that some $Y_xTi_yO_z$ compounds transformed into $Y_2Ti_2O_7$ compounds after thermal annealing at 1200 °C during 1 h. This result is confirmed by Dawson and Tatlock [17] who analyzed the structure of 5 nm diameter oxides after thermal annealing at 1300 °C during 1 h using High-Angular Annular Dark-Field (HAADF) microscopy. These authors reported that the intensity profiles measured along adjacent {004} atomic planes were consistent with the cationic sublattice of the pyrochlore crystal structure and concluded that

the concerned particle possesses the ordered pyrochlore structure. However, Badjeck et al. [18] brought new insight into the chemical structure of $Y_2Ti_2O_7$ nanoparticles. They observed that nanoparticles of size greater than 5 nm adopt a non-stoichiometric pyrochlore $Y_2Ti_2O_7$ structure. They demonstrated that the Ti oxidation state varies from Ti^{4+} in a distorted octahedral environment to reduced $Ti^{<3+}$ and possibly almost metallic in some cases, going from the center of the nanoparticle to its periphery. Concerning the growth kinetics, Barnard et al. [19] showed that pipe diffusion is the dominant mode of the coarsening of these pyrochlore-type particles, and predict that they are stable for 80 or more years below 900 °C.

In addition, Marquis reported [20] that these non-stoichiometric $Y_2Ti_2O_7$ -type particles are surrounded by a Cr shell. Badjeck et al. [18] estimated the thickness of the Cr shell to range between 0.6 and 1.6 nm and also reported that the Cr shell thickness appears to decrease when the particle size decreases, which has recently been confirmed by London et al. [21]. They estimated the possible Cr oxidation state to range between Cr^{2+} and Cr metal. The origin of this Cr shell remains unclear, Hirata et al. [22] argued that the enrichment of Cr can mediate the lattice mismatch between the b.c.c. lattice of the matrix and the oxide and lower the interface free energy, then favouring nucleation [23].

1.2. The nanoclusters

The crystallographic structure of these solute-enriched nanoclusters, ranging from 1 to 3 nm in diameter, has been debated for many years. Hirata et al. [22] recently reported that these solute-enriched clusters coherently overlap the b.c.c. lattice of the matrix and display a NaCl type structure. Ribis and de Carlan [24] using arguments based on the elastic theory proved that these nanoclusters are well coherently embedded in the lattice matrix as proposed [22]. Hirata et al. [22] also reported that these metastable nanoclusters contain a large amount of vacancies. Vacancies were suggested to be an important factor in stabilizing the oxide nanoclusters [25] and are very likely to form in high concentration within the matrix during the mechanical alloying process. Hirata et al. [23] indicated that the NaCl-type structure has great chemical flexibility and pointed out the high vacancy capability to form nanoclusters with multiple components. Based on APT measurement, several authors [4,8,9,21] reported that the nanoclusters are YTiO rich but also Cr rich although the measured compositions can be affected by evaporation artifacts. Recently, London et al. [21] confirmed the Cr enrichment of the smaller clusters (<2 nm) by APT examinations. Since Matteucci et al. [26] readily proved that Cr is almost insoluble in the Y-Ti-O system, it can be inferred that these nanoclusters are likely to be non-equilibrium compounds.

In conclusion of the literature review, the nanoclusters, which has been less studied than the non- and near-stoichiometric pyrochlore, appear to be metastable compounds and thus must obey to a relaxation path.

Hence, the present paper proposes a fine characterization of the nanoclusters to clarify this relaxation pathway. To bring new insight on these small particles, the nanocluster system was

Download English Version:

<https://daneshyari.com/en/article/5454416>

Download Persian Version:

<https://daneshyari.com/article/5454416>

[Daneshyari.com](https://daneshyari.com)