Journal of Nuclear Materials 492 (2017) 279–291

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Experimental artefacts occurring during atom probe tomography analysis of oxide nanoparticles in metallic matrix: Quantification and correction

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ARTICLE INFO

Article history:
Received 10 January 2017
Received in revised form
28 April 2017
Accepted 11 May 2017
Available online 11 May 2017

ABSTRACT

Oxide Dispersion Strengthened (ODS) steels are promising candidates for future nuclear reactors, partly due to the fine dispersion of the nanoparticles they contain. Until now, there was no consensus as to the nature of the nanoparticles because their analysis pushed the techniques to their limits and in consequence, introduced some artefacts. In this study, the artefacts that occur during atom probe tomography analysis are quantified. The artefacts quantification reveals that the particles morphology, chemical composition and atomic density are biased. A model is suggested to correct these artefacts in order to obtain a fine and accurate characterization of the nanoparticles. This model is based on volume fraction calculation and an analytical expression of the atomic density. Then, the studied ODS steel reveals nanoparticles, pure in Y, Ti and O, with a core/shell structure. The shell is rich in Cr. The Cr content of the shell is dependent on that of the matrix by a factor of 1.5. This study also shows that 15% of the atoms that were initially in the particles are not detected during the analysis. This only affects O atoms. The particle stoichiometry evolves from $YTiO_2$ for the smallest observed (<2 nm) to Y_2TiO_5 for the biggest (>8 nm).

1. Introduction

Future generations of nuclear reactors, either based on nuclear fission or fusion, represent a technological breakthrough compared to the current facilities for the production of nuclear electricity. In particular, structural materials of these reactors will be subjected to high temperatures (~500 up to 1000 °C) and severe irradiation conditions (fast neutrons, damage up to ~200 displacements per atom) [1]. Oxide Dispersion Strengthened steels (ODS) could be good candidates for specific components, such as fuel cladding for sodium fast reactor type, since they show good mechanical and creep properties at high temperature and good radiation resistance [2–4]. These properties are partly due to a fine and dense distribution of oxide nanoparticles containing O, Y and in some cases Ti [5], embedded in a (Fe,Cr) ferritic/martensitic matrix. It has been shown [6,7] that there is a strong correlation between the elaboration process of ODS steels and the characteristics of this particles dispersion (in terms of size and number density). Therefore, it is necessary to establish an accurate description of these particles in order to improve or optimize the elaboration process and to obtain the targeted mechanical properties. To add complexity in this characterization task, Sakasegawa et al. [8] have demonstrated, that the particles composition evolves according to their size. Finally, it must be added that most of the nanoparticles of these distributions have a diameter well below 5 nm [9]. The characterization of such small particles is a challenge. Atom Probe Tomography (APT) [10,11] and High Resolution Transmission Electron Microscopy (HRTEM) [12–14] are among the suitable techniques for these characterizations at fine scale. These two techniques generally show a reasonable agreement in terms of particles size and number density measurements but often differ as far as the chemical composition is concerned [9,10], experimental bias of each techniques being the reason of this difference.

A large number of articles in literature focus on artefacts that can occur during APT analysis of nanostructured materials such as multilayers [15,16] or embedded particles [17,18]. In the case of particles, it is observed that these experimental artefacts can modify the particles' morphology [17–19], their size and also their

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http://dx.doi.org/10.1016/j.jnucmat.2017.05.008
0022-3115/

chemical composition [20,21]. The physical origin of these artefacts, without going into too much details (see Ref. [22] for details), is due to the difference in the field evaporation behavior of different chemical species (atoms of the material) under the high applied field. This is what is called: local magnification effect.

The goal of this work is to carefully study if and how APT artefacts can affect measurements concerning oxide nanoparticles of ODS steels and to quantify the measurement bias resulting from these artefacts and to suggest correction modes. A protocol for particle analysis and their data mining using APT technique is presented for these ODS steels and nano-objects. It permits identifying if analyses are prone to bias and if it is the case, how to correct them.

The purpose of this work is to provide a chemical composition of the ODS nanoparticles measured by APT free of artefacts. It provides a way to obtain the correct amount of Fe and Cr and how Y, Ti and O concentration is modified in the nanoparticles. Based on the artefacts that occur in the nanoparticles, it is possible to obtain the chemical composition of the shell surrounding the particles.

2. Materials

2.1. Materials

The ODS steel used in this study, named MKCR and elaborated by Mecachrome Company, was prepared by mechanical alloying, under Ar atmosphere, of a pre-alloyed powder, containing a relatively high level of Cr: Fe-18Cr-1W-0.3Ti wt.% (Fe-19.26Cr-0.30W-0.46Ti at. %) and 0.3 wt% of Y_2O_3 powders provided by Osprey company. The milled powder was then canned 2 h at 400 °C and hot extruded at 1100 °C. Those two last steps have been done in the SRMA department (Service de Recherches Métallurgiques Appliquées) from the CEA Saclay (Commissariat à l'Énergie Atomique et aux Énergies Alternatives). The bulk composition of the extruded material is: Fe-18Cr-1W-0.3Ti-0.2Ni-0.3Si-0.3Mn-0.3Y_2O_3 wt. % (*i.e.* Fe-19.2Cr-0.3W-0.31Ti-0.19Ni-0.6Si-0.3Mn-0.15Y-0.22O at. %).

2.2. APT and analyses conditions

The analyses have been performed with two instruments, a Cameca Laser Assisted Wide Angle Tomographic Atom Probe (LAWATAP), using femtosecond laser pulses and a pulse repetition rate equal to 100 kHz and a Cameca FLEXible Tomographic Atom Probe (FLEXTAP), using also femtosecond laser pulses and a pulse repetition rate equal to 50 kHz and a 15° diaphragm. More details on APT principle can be found in Refs. [23,24].

The first step of an APT experiment is to determine the optimal analysis conditions to first obtain a high mass resolution, high enough to separate two close peaks (for example, in this case to be able to separate Y^{3+} and $^{60}Ni^{2+}$ peaks separated by 0.3 a.m.u.) and second, to lower as much as possible the noise level, in order to reach the best accuracy on chemical composition measurements. Three parameters play a major role: the laser wavelength (UV, green or IR), the sample temperature during analysis (usually between 20 and 80 K) and the equivalent pulse fraction. The equivalent pulse fraction is defined by the ratio $(V_T - V_0)/V_0$ where V_T and V_0 are respectively the total voltages needed to field evaporate ions without laser pulses and the standing voltage applied to the needle to get a given flux in presence of laser pulses. This pulse fraction has been tested in the range 5–85%. During APT analysis, the radius of curvature of the apex of the sample evolves because of the destructive nature of the experiment. This also influences the mass resolution, as it has been shown by Arnoldi et al. [25]. To avoid this phenomenon, only a few atoms (~3 × 10^5 ions *i.e.* a small volume) are collected for each analysis under testing conditions.

The large set of experiments performed shows that the optimal experimental conditions to study ODS steels are a laser wavelength of 343 nm (UV), a sample temperature of 40 K and a laser pulse energy adjusted to obtain an equivalent pulse fraction of 25% of the DC potential [26]. These conditions first make it possible to get the best mass resolution while reducing the noise level and in second place, to limit bias in chemical composition measurements.

3. Data treatment

An example of the spatial distribution of solute atoms is depicted in Fig. 1. Particles enriched in Y, Ti and O are observed. To characterize particles, a cluster identification algorithm, developed at GPM laboratory, is used. This algorithm is based on chemical concentration and atomic distance criteria. Details can be found in other works [27]. In this part, detailed descriptions of various measurements that have been carried out on each individual particle of the analyzed volumes are given. The results obtained on all particles will be presented in the next part.

3.1. Shape factor of a particle

From the spatial distribution of ions (YO^{2+}, and TiO^{2+}/O_2^+ in Fig. 2) belonging to a given particle, the X, Y and Z dimensions of the particle can be given. The Z dimension is oriented along the evaporation direction (here [110] of the ferritic matrix, Fig. 2a) [18,28]. X and Y dimensions are in the plane, perpendicular to that previous direction, as reported in Fig. 2.

In the same ODS steel, Couvrat et al. [29] observed cubic particles using TEM. From initially being cubic, the particles are reconstructed as parallelepiped volume after APT analyses. To follow this morphological variation, a shape factor (S) is introduced and defined as:

$$S = \frac{X \times Y}{Z^2} \quad (1)$$

with X, Y and Z the particle dimensions. A perfect cubic volume will be S = 1.

Fig. 3 shows the composition profiles through the particle in Fig. 2 to determine the Z (Fig. 3a), Y (Fig. 3b) and X (Fig. 3c) values.

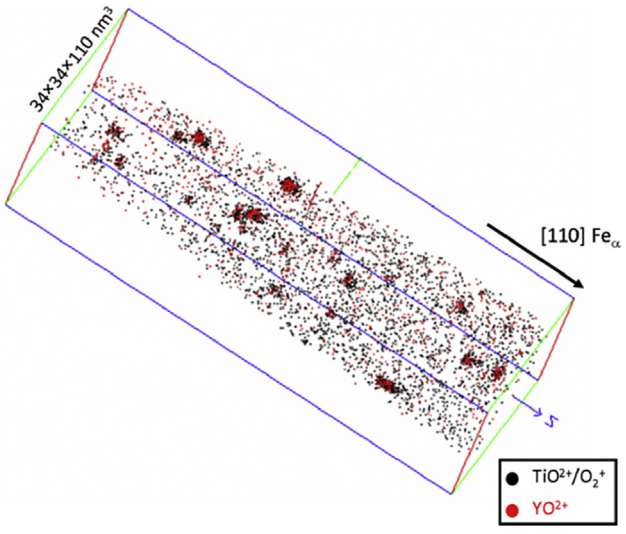

Fig. 1. APT 3D reconstruction of a volume of MKCR ODS steel studied. YO^{2+} and TiO^{2+}/O_2^{2+} ions are shown. TiO^{2+} and O_2^{2+} are represented together due to isotopic overlap.