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Oxide dispersion strengthened ferritic steels: a basic research joint program in France

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ABSTRACT

AREVA, CEA, CNRS, EDF and Mécachrome are funding a joint program of basic research on Oxide Dispersion Strengthened Steels (ODISSEE), in support to the development of oxide dispersion strengthened 9–14% Cr ferritic–martensitic steels for the fuel element cladding of future Sodium-cooled fast neutron reactors. The selected objectives and the results obtained so far will be presented concerning (i) physical–chemical characterisation of the nano-clusters as a function of ball-milling process, metallurgical conditions and irradiation, (ii) meso-scale understanding of failure mechanisms under dynamic loading and creep, and, (iii) kinetic modelling of nano-clusters nucleation and α/α' unmixing.

1. Introduction

Due to their heat and radiation resistance [1–3] ODS 9–14% Cr ferritic–martensitic steels have been selected as cladding material for the fuel element of future commercial Sodium-cooled fast neutron reactors. ODS steel cladding will be qualified in the demonstration reactor ASTRID to be built in France at the 2020 horizon [4]. A development program is being carried out by AREVA, CEA and EDF in order to produce fuel element clads, which should meet the operating requirements of a future commercial Sodium-cooled fast neutron reactor: an end of life maximum dose up to 180–200 dpa, a high dimensional stability, i.e. negligible swelling and creep deformation, and, a thermal creep lifetime as long as 8.10^4 h at 750 °C for a hoop stress ~100 MPa. The clad should also be resilient enough under dynamical loadings of handling and transport situations [5].

Because of the nanoscale of oxide particles and microstructure the presently available physical–chemical characterisation techniques such as atom probe tomography and transmission electron microscopy are often at the limit of their resolution with possible important artefacts, making it difficult to identify the nano-particles, determine their chemical composition and crystalline structure. For better controlling the clad fabrication process, AREVA, CEA, CNRS, EDF, and the manufacturer Mécachrome decided to fund a four years (2012–2015) basic research program called ODISSEE (Oxide Dispersion Strengthened Steels).

Based on a critical analysis of the open literature and experience gained in CEA, the first section briefly describes the objectives of the eleven PhD thesis involved within ODISSEE. The selected ODS materials that are jointly studied in ODISSEE are given in a second section. A third section will give the main results obtained so far. A last section will formulate interim conclusions.

2. ODISSEE: objectives and selected ODS materials

2.1. Chemical characterisation at the nanoscale

High densities of Ti, Y and O enriched nanometric particles are evidenced in ODS steels via atom probe tomography (APT) [6–9] and energy-filtered transmission electron microscopy (EFTEM) [10,11]. Assuming a Gaussian distribution of nonmagnetic spherical particles, analysing the small angle neutron scattering (SANS) intensity gives number densities $\sim 10^{23}$–10^{24} m^{-3} and average sizes

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~1–2 nm, in excellent agreement with corresponding APT data [12].

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 [13], and, Y/Ti ~ 0.15–0.45 and (Y + Ti)/O ~ 1 [7–9], which are inconsistent with stoichiometric compounds such as $Y_2Ti_2O_7$, Y_2TiO_5 or Y_2O_3 pyrochlores. Conversely atomic plane spacing and lattice structure of these Ti–Y–O enriched particles observed in high resolution transmission electron microscopy (HRTEM) are found to be compatible with the face-centred cubic $Y_2Ti_2O_7$-type pyrochlore oxide [10,14]. Chemical compositions measured by energy dispersive X-ray spectroscopy (EDS) on chemically extracted nanoscale particles show a large range of Y/Ti ratios that may be correlated with the particles size [15]. A possibly large range of nano-particle chemical composition, differences in the statistical algorithms used to reconstruct nano-particles or artefacts in APT process itself [16–18] could explain these apparent inconsistencies.

The objectives of ODISSEE are to (i) highlight APT artefacts and select reasonable algorithms to define the nanoparticles and determine their chemical composition, and, (ii) obtain the fine structure of EELS spectra of Titanium, Oxygen and possibly Yttrium in order to obtain information on their valence and coordinance. Two PhD students, C. Hatzoglou and V. Badjeck, are working on these subjects, respectively in Groupe de Physique des Matériaux (GPM) of the University of Rouen and Laboratoire de Physique des Solides (LPS) of the University of Orsay-Paris-Sud.

2.2. Mechanical properties

Strengthening by nano-particles and grain-boundaries (Hall and Petch effect) may be the major hardening mechanisms at room temperature [19,20]. Post-tensile test TEM examinations and in-situ TEM straining reveal highly bowed-out dislocation lines confirming hardening due to nano-particles [21,22]. Thermal creep of ODS ferritic–martensitic steels is characterized by low secondary creep rates and a quasi-absence of tertiary creep [2]. Under in-situ TEM straining experiments at high temperature, dislocations move more easily than at room temperature, thermal activation of dislocation sources at grain boundaries becomes effective and dislocations pile-ups could promote grain-boundary failure [22].

The research effort in ODISSEE was devoted to the failure behaviour at the mesoscale under dynamic loading and thermal creep conditions. One PhD student, A.L. Rouffié, is studying, in Service de Recherches Métallurgiques Appliquées (SRMA) at CEA/Saclay, in collaboration with Centre des Matériaux Mines-Paris Tech, the plastic and failure behaviour under dynamic loading. Another PhD student, H. Salmon-Legagneur, is studying, in SRMA at CEA/Saclay, in collaboration with Mines Paris-Tech and CIRIMAT Toulouse, creep damage accumulation on the basis of mechanical testing complemented by microscopic observations.

2.3. Microstructure stability under high temperature and irradiation

Despite their great stability, nano-scale particles clearly exhibit growth under heat-treatment at high temperature above ~1000–1100 °C [23]. Abnormal grain growth could also occur under recrystallization heat-treatment [24]. Because of fine grain size, the unpinning of triple or quadruple points might dominate stability of grain size and the net pinning force per unit grain-boundary area may depend on grain size, conversely to the conventional Zener model [25]. No systematic quantitative data exists concerning nano-scale particles growth, dislocations density, grain size and morphology or crystallographic texture evolution under heat-treatments during clad fabrication process. A PhD student, N. Sallez, will address these issues in the laboratory Science et Ingénierie des MAtériaux et Procédés (SIMAP) at INP-Grenoble.

Most studies have shown the great radiation resistance of Y–Ti–O enriched nano-particles (see for instance [6]), conversely to the first generations of ODS ferritic–martensitic steels reinforced with Y_2O_3 and Ti_2O_3 particles [26]. A PhD student, A. Bhattacharya, in Service de Recherches de Métallurgie Physique (SRMP) at CEA/Saclay is studying, in collaboration with CSNSM-IN2P3 at University of Paris-Sud, the effect of Cr on radiation induced microstructure, unmixing of Fe–Cr matrix and nano-particle evolution under point defect and helium production. Although helium production is not an issue in fission fast neutron spectra, helium is used to probe the possible defective structure of nano-clusters and their interfaces with matrix [27].

2.4. Mastering and comparing mechanical-alloying processes

ODISSEE selected two laboratory scale ball milling devices, which are susceptible of upscaling towards industrial production: a horizontal ball-mill capable of ~15 kg batches at the Research Center of Mécachrome and a vertical attritor capable of ~1.5 kg batches in the Service de Recherches Métallurgiques Appliquées (SRMA) at CEA/Saclay. Two PhD works were decided.

The work of PhD student M. Loyer-Prost, in the Service de Recherches de Métallurgie Physique (SRMP) at CEA/Saclay, in collaboration with SRMA and the Laboratoire d'étude des microstructures (LEM) in ONERA is devoted to characterize microstructure and mechanical properties of ODS steels obtained from mechanically alloyed powder in SRMA's attritor, to be compared with the ODS steels obtained with powder milled at Mécachrome or with materials of previous studies by M. Brocq with a laboratory device capable of ~10 g batches (called Frish 0 in Table 1)[13].

The milling intensity [28], which controls, with temperature, the stationary state of alloys under mechanical alloying, cannot be easily defined in usual milling devices as it is the case for simple laboratory device such as Frish 0 with one ball. This is a difficulty to compare productions of different mills. Nevertheless, the sound emitted while processing powder is evolving with time. In an exploratory work, a PhD student, L. Barguet characterizes in the Laboratoire d'accoustique de l'Université du Maine (LAUM), in collaboration with SRMA and Mécachrome, the spectrum of sound emitted and the ultrasonic response of powder versus milling time, in order to correlate these data to the size distribution of powder grains and to the microstructure, which evolve with milling time.

2.5. Atomic scale modelling: nucleation of nano-clusters

Based on ab initio calculations, two publications draw opposite conclusions concerning the role of alloying elements and vacancies in the nucleation of nano-clusters. In presence of pre-existing vacancies introduced by high energy ball-milling, the formation energy of the oxygen–vacancy (O–V) dimer vanishes because of the significant O–V binding energy. Having a relatively low mobility, these O–V dimers may enable the nucleation of O-enriched nano-clusters by attracting Ti and Y atoms, which have high affinity with O [29]. Conversely, because of significant binding energies, forming O–O, Y–O and Ti–O dimers lowers the energy of the mechanically alloyed powder [30]: ab initio calculations showed for instance that energy gained in forming Y_2TiO_3 pattern is higher than the energy excess of the system in solid solution. Therefore assistance of vacancy may not be necessary and O–O, Ti–O and Y–O might be the main building blocks of the nano-clusters. In order to try to understand the early stage of nucleation, a PhD student, C. Barouh, in CEA/SRMP at CEA/Saclay, is calculating ab initio the binding energies and migration barriers of the various possible n-mers in a Fe–Ti–Y–O–vacancies dilute alloy in order to study the