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Characterization and modeling of oxides precipitation in ferritic steels during fast non-isothermal consolidation

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ABSTRACT

The precipitation behavior of nanosized binary Y_2O_3 and complex $Y_2Ti_2O_7$ precipitates in oxide-dispersion strengthened ferritic steels was modeled by a nucleation, growth and coarsening thermodynamic approach. Focus was made on non-isothermal treatments that simulate typical consolidation processes of nanostructured steels. In order to assess the model for fast non-isothermal treatments, a field-assisted consolidation process was used. The precipitation state was characterized at nanoscale by transmission electron microscopy, small-angle neutron scattering and atom-probe tomography. Both simulation and experimental results demonstrated the following precipitation mechanisms: (i) rapid nucleation of both Y_2O_3 and $Y_2Ti_2O_7$ during the heating stage (ii) limited growth and coarsening of nanoclusters during soaking time and further annealing at high temperature (1100 °C). A new coefficient diffusion of yttrium in ferrite was proposed to assess the thermal stability of nano-oxides.

1. Introduction

Oxide-Dispersion Strengthened (ODS) ferritic steels have been widely developed these recent years for high temperature applications. Processed by powder metallurgy, these materials are usually produced by hot isostatic pressing (HIP), hot extrusion, or more recently by Spark Plasma Sintering technique (SPS) [1–5]. They owe their good high-temperature mechanical properties to a fine dispersion of nanosized oxides that act as efficient obstacles for dislocations and grain boundaries. Depending upon the chemical composition and the consolidation technique and parameters, various kinds of oxides have been reported in the literature. The most common are yttrium oxides Y_2O_3 and ternary oxides $Y_2Ti_2O_7$. The latter were observed to enhance tensile strength and creep resistance due to an increased number density and a lower mean radius of the precipitated particles. They have been the subject of numerous characterization studies at the nanoscale, including transmission electron microscopy [6–8], small-angle neutron scattering [9–11] and more recently atom-probe tomography [12]. What is widely recognized is that these nanoparticles exhibit an extraordinary thermal stability [13], even at temperatures close to the solidus of the ferritic matrix. Thanks to an observation at the atomic scale, this coarsening resistance was linked to the large amount of oxygen vacancies (≈10%) that could stabilize the clusters [14]. However, another study by Ribis and de Carlan demonstrated that the morphology of the particles $Y_2Ti_2O_7$ evolved upon heating in order to minimize their energy within the system [15]. The shape transition from spherical to cubical geometry was described as a way to reduce the elastic distortion created at the interfaces. Thus, the elastic energy governed by the misfit between the precipitates and the matrix can influence the precipitation of these fine particles. Whether the coarsening resistance is only of thermokinetic nature (slow diffusion of yttrium) or related to more complex phenomena is still questioned.

Most studies were made on extruded or HIPed materials with stabilized precipitation. Hence, a few data is available on the early stage of precipitation, specially on the nucleation behavior of these particles. Since the particles are nanosized, the characterization can be tedious, expensive and sometimes subject to controversy. Experimental tools are limited when dealing with the nucleation kinetics during non-isothermal treatments, which are representative of the consolidation processes of ODS steels. In this context, modeling tools are excellent means to understand the precipitation

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mechanisms. For instance, the role of yttrium diffusion or the influence of the elastic misfit during nucleation and further growth and coarsening are still debatable. Various models can be used to simulate the solid-state precipitation in metallic materials. Readers are referred to [16] for an elaborate review of solid-state precipitation theories and associated calculation algorithms. Three main categories are distinct and complementary. First of all, the predictive models like DFT (density functional theory) or Monte Carlo tend to determine analytically the behavior of the material at the atomic scale [17,18]. Then, semi-predictive models combining thermodynamic and diffusion databases can model solid-state precipitation in multi-components systems [19]. Finally, JMAK-type (Johnson-Mehl-Avrami-Kolmogorov) mathematical formalisms allow to describe phase transformation kinetics using both physical and arbitrary coefficients. These different kinds of model involve complementary time and space scales. JMAK models encounter difficulties to reproduce non-isothermal treatments and physical mechanisms [20]. At the opposite, atomistic models are powerful tools to understand physical mechanisms but the time scale is reduced to approximately 10^{-6} s and involve very long time calculation for a limited number of atoms [21,22]. For precipitation, a good compromise consists of thermokinetic model using the nucleation, growth and coarsening theories [23,24].

Classic thermodynamic modeling consists in calculating the driving force of the formation of a possible compound (phase) from a supersaturated solid solution. In ODS steels, some controversial studies lead to contradictory conclusions on whether yttrium, oxygen atoms transform into a solid solution in the iron matrix. Indeed, mechanical alloying involves far-from-equilibrium mass transport, local heating, cold welding and other mechanisms that are difficult to model [25]. From recent atom-probe tomography, clustering of yttrium and titanium-rich particles was observed after a certain milling time [12,26,27]. This is not surprising since perfect solid solution is always difficult to achieve, especially for highly non soluble elements. However, the community mainly agrees with the fact that these subnanometric clusters are quite homogeneously distributed in the powders. Also, after annealing or consolidation at high temperature, the clusters tend to crystallize and form stoichiometric phases [7,15,14,28]. Thus, the starting point before high-temperature consolidation still deals with the need of diffusion-governed atoms transport to form well-defined, crystalline precipitates. In this sense, this study applies a diffusion-based precipitation model using the nucleation, growth and coarsening theory.

The assessment of this model is based on:

(i) the validation of the numerical model thanks to the case study of unique phase Y_2O_3.
(ii) Then, the precipitation of complex $Y_2Ti_2O_7$ is studied in ODS steels containing yttrium, titanium and oxygen. The numerical results are compared to SANS data after Alinger et al. [29,30].
(iii) Finally, this model is applied to rapid non-isothermal treatments using field-assisted consolidation process. These results are compared to experimental data collected in the present study by Small Angle Neutron Scattering (SANS), Transmission Electron Microscopy (TEM) and Atom-Probe Tomography (APT).

2. Material and methods

2.1. Materials

A powder of high-chromium ferritic steel was produced by ingot gas atomization by Aubert&Duval. The powder particles were then mechanically alloyed with submicronic yttria powder (Y_2O_3) using a high-energy attritor by Plansee SE. Milling conditions and microscopic evaluation of the as-milled powder are recalled in Ref. [9]. Using Focused Ion Beam (FIB) cross-sectioning of powder particles, the nanostructure was investigated by scanning electron microscopy (SEM) and Electron Back Scatter Diffraction (EBSD). Most of the grains are highly deformed and the smallest nanosized grains are not indexed due to a huge amount of dislocations, roughly estimated by Kernel Average Misorientation as over 1×10^{16} m^{-2}.

The chemical composition of the milled powder is reported in Table 1. This powder is representative of common industrial nanocrystalline powder widely used to process nanostructured materials. In this particular alloy, yttrium, titanium and oxygen are expected to form nanoparticles during hot processing.

2.2. Characterization methods

Transmission Electron Microscopy (TEM) characterization was performed on an apparatus TEM JEOL 2010F equipped with an Energy Dispersive X-Ray Spectroscopy (EDX) XMAX 80 for chemical analysis. The thin foils were prepared using the following method: (i) Mechanical polishing to get a final thickness between 60 and 90 μm (ii) 3-mm disk stamping and further polishing with diamond paste up to 3 μm (iii) Electrolytic etching with a solution composed of 70% of ethanol, 20% ethylene glycol monobutyl ether and 10% of perchloric acid and cooled to 0 °C (iv) Ionic polishing to eliminate eventual oxidation before observation. The apparatus was a PIPS (Precision Ion Polishing System) from Gatan equipped with a double ion gas gun polishing the surface with an incident angle from −10 to 10°. Gun energy was set at 4.2 keV with a magnitude of 20 A.

SANS experiments were performed at the Laboratoire Léon Brillouin CEA Saclay, using the PAXY small angle scattering spectrometer for high resolution in q-space, under strong magnetic field (1.7 T). As mentioned in Refs. [31], a magnetic field of magnitude 1.2 T is sufficient to separate the magnetic and nuclear contributions. SANS experiments were set to determine the distribution of particles smaller than 15 nm in radius. This corresponds to a scattering vector q between 0.1 and 1.6 nm^{-1}. This was obtained by selecting neutron wavelengths of 0.6 and 1 nm (±10% due to monochromator dispersion) and a distance between sample and detector of 2 and 5 m, respectively. A 2D detector with area 64×64 cm^2 was used to collect scattered neutrons. As detailed in Refs. [11], a direct modeling was used in the current study. The scattering function was calculated for a given distribution of nanoscatterers and compared to the experimental function. A least squares method was used to obtain the best fitting parameters. The particles were assumed spherical - even some can have cuboidal or ellipsoidal shapes [15] - and of constant chemical composition. Particle mean radius r_m of the scattering population was calculated assuming a normalized number density function of radii $h(r)$. Given these assumptions, one can write the scattering intensity as:

$$I(q,r) = \Delta\rho^2 N_p V_p^2 F_{sph}(q,r) S(q,r) \quad (1)$$

where N_p is the scatterers density, V_p the volume of a scattering

Table 1
Mean Composition (in wt%) of the milled powder.

Fe	Cr	W	Y	O	Ti	C
bal.	13.9	1.0	0.16	0.15	0.32	0.04