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Influence of titanium on nano-cluster (Y, Ti, O) stability in ODS ferritic materials

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A B S T R A C T

The addition of titanium is well known to refine the precipitation of nano-phases (Y, Ti, O) in oxide dispersion strengthened (ODS) ferritic materials. In order to understand the influence of titanium on the nano-cluster nucleation, two powders of ferritic materials Fe–18Cr–1W were mechanically alloyed with a nano-powder of yttrium oxide Y_2O_3 in a planetary mill, one without titanium and one with 0.8 wt% of titanium. Several analyses were conducted by small angle neutron scattering (SANS) on powders after different milling conditions and heat treatments. The SANS technique appeared to be extremely useful to follow the precipitation of the nano-phases in ODS ferritic materials. The analysis of these tests indicates that the role played by titanium is clearly observed during the reprecipitation of the nano-oxides though the effect of titanium on the oxide dissolution during the milling is not obvious. Titanium is usually considered to refine the precipitation in ODS materials. This study shows that the nano-phases formed in powders with some titanium are much more resistant to the coarsening than the phases formed without titanium.

1. Introduction

Many studies are directed toward the development of innovative metallic materials for applications in the nuclear industry [1,2], fulfilling the design requirements for fission or fusion nuclear reactors. Among these are oxide dispersion strengthened (ODS) alloy materials [3] obtained by powder metallurgy [4] which are of interest as structural materials due to their creep rupture strength at high temperature [5] and their resistance to severe neutron exposure.

This high temperature creep strength [6] comes from the presence within the matrix of nanometric size oxide populations, blocking the motion of dislocations and thus making it possible to consider nominal operating temperatures over 1000 °C for some ODS materials. The phenomenon of nano-precipitation occurring during the consolidation process of the material follows the dissolution of an yttrium oxide (Y_2O_3) during a mechanical milling with metallic powders.

The population of nano-clusters is a function of, among other parameters, the chemical composition of the material used. It was noticed that the presence of titanium in solid solution in the matrix guarantees a precipitation of ultrafine particles in a larger number density thus shortening inter-particle spacing [7–11]. This is a major benefit as the precipitate dispersion in the matrix controls the creep properties of the material.

The essential goal of this work was to characterize the influence of titanium at each step of the material processing procedure of an ODS steel. The investigation was based on the essential technique of small angle neutron scattering (SANS) [12] in order to observe the nanometric structure in the samples at each stage. This technique enabled us to clarify the mechanisms of dissolution and precipitation of nano-oxides occurring during mechanical milling and hot consolidation.

2. Aim of the study

To perform this study, two ferritic materials were used, one with a composition of Fe–18Cr–1W (wt%) and the other one with the same composition but with 0.8Ti. The average diameter of both pre-alloyed powders was 100 μm. Each powder was mechanically milled for 48 h with 0.3% of yttria powder (Y_2O_3) in a planetary mill and then subjected to various heat treatments. The purpose was first to follow the dissolution of Y_2O_3 during the mechanical milling and then to characterise the precipitation of nanometric phases during heat treatments at 850 °C, 1100 °C and 1300 °C.

3. Experimental facility

Dissolution and precipitation were investigated by SANS under a magnetic field, at the Laboratoire Léon Brillouin, Saclay on the PAXY small angle instrument. Two complementary configurations were used to cover a large scattering vector (from 0 to 0.160 nm^{-1}): the wavelength was 0.6 or 0.9 nm, the distance

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between sample and detector was 2 or 5 m. Measurements were made at room temperature under a magnetic field of 2 T perpendicular to the incident neutron beam direction. In a ferromagnetic material the neutron scattering cross-section is composed of a nuclear contribution and a magnetic one [13,14].

There were two types of sample. The ones to study the dissolution were sampled from the planetary mill and are powders. After heat treatment at 850 °C the ODS material was still a powder, but in those heat-treated at 1100 °C and 1300 °C the powder was sintered so platelets were cut into pieces each of 1 mm thicknesses.

4. Results

4.1. The effect of titanium on the dissolution of yttrium oxide (Y_2O_3) during the mechanical milling

Three times were chosen to sample powders during the milling: 1 h, 12 h and 48 h. The results of the SANS data for these different intermediate milling times are given in the Table 1. At the start of milling, $t = 0$ h, the two samples do not show any nanometric population. From 1 h to 48 h of milling, nanometric particles are observed. Their volume fraction increase continuously with the milling time. The volume fractions of particles smaller than 10 nm reach 1.8% and 1.2% for the samples with and without titanium, respectively. No saturation of the particle size distribution was noticed with our mill but this phenomenon could be dependent on the nature of the mill employed. Profiles of size distributions are plotted in Figs. 1 and 2. The ratio h(r) corresponds to the number of particles with a radius r divided by the total number of particles. It is continuously increasing during the milling. There is almost no change in size distribution of the particles formed during the mechanical milling, whereas the volume fraction increases enormously and rises above the yttria fraction added at the beginning of mechanical alloying.

4.2. The effect of titanium on the precipitation of yttrium oxide during the annealing

Heat treatments were carried out at three temperatures: 1 h at 850 °C, 1 h at 1100 °C and 1 h at 1300 °C. The results of SANS data are given in the Table 2. Profiles of size distributions are plotted in Figs. 3 and 4. An increase in the volume fraction of nano-clusters is observed in the powders heat-treated for 1 h at 850 °C when compared to the volume fraction sampled after 48 h of milling and not heat-treated. This is apparent for both samples with or without titanium. After heat treatment for 1 h at 1100 °C the volume fraction of nanometric particles decreases strongly in both materials. The average size of these particles increases to 12 nm in the material without titanium and stay nanometric, with an average size of 2 nm, in the material with titanium. After the heat treatment for 1 h at 1300 °C no nanometric phases are observed in the material without titanium, whereas a population of phases with an average size of about 10 nm is still observed in the material with titanium.

Table 1
Volume fraction of Y_2O_3 precipitates smaller than 10 nm after different milling times.

Milling time (h)	Grade without Ti + 0.3 Y_2O_3 (wt%)	Grade with Ti + 0.3 Y_2O_3 (wt%)
0	0	0
1	0.3	0.3
12	0.6	0.7
48	1.2	1.8

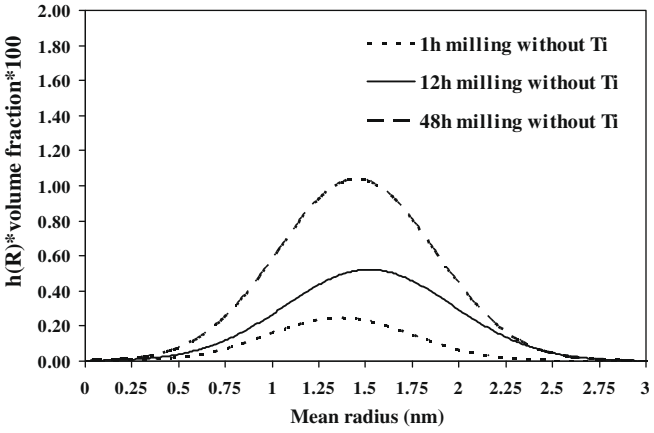

Fig. 1. Particle size distributions during milling: ODS material *without* titanium.

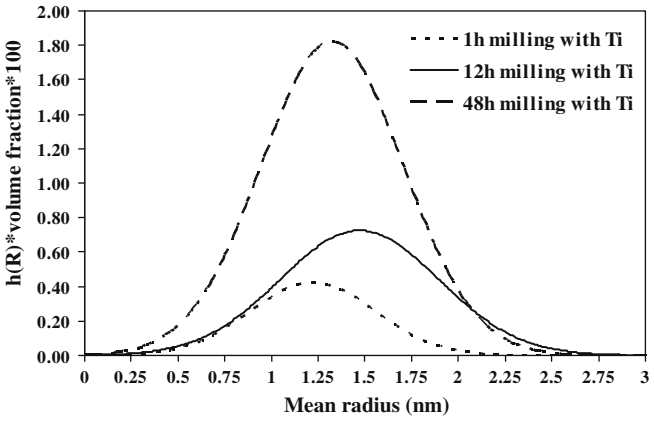

Fig. 2. Particle size distributions during milling: ODS material *with* titanium.

5. Discussion

Nanometric phases appeared during the milling. Under some conditions the SANS technique allows determination of the chemical composition of the particles. However, the ratio "*A*" of diffused intensities in directions parallel and perpendicular to the magnetic field is the same in the materials with and without titanium and it does not give any chemical information about the nature of the phases. Full results of this study will be published subsequently in another paper but further works should be done to identify these nanometric phases. Some hypothesis can be proposed about the nature of these clusters. They may be:

- Residual material from the fragmentation of yttrium oxides.
- "Fragments" of material coming from matrix particles.
- Metastable aggregates of atoms.
- Clusters of point defects caused by milling.

Other studies using SANS on the same type of powders in the framework of the European program called ExtreMat already showed the formation of unstable clusters during mechanical milling. The effect of the titanium on the kinetic dissolution of Y_2O_3 is not obvious. Further diffraction (XRD) experiments performed on powders with up to 10 wt% of titanium and Y_2O_3 indicate that titanium does not enormously influence the dissolution kinetic of yttria [15]. Nevertheless, in this experiment with 0.8% of titanium, the powder showed an increased hardness (about more than 10%) when compared to the material without titanium. Harder powders

Table 2
Volume fraction of Y_2O_3 precipitates smaller than 10 nm after 48 h milling and various heat treatments.

Heat treatment	Grade without Ti + 0.3 Y_2O_3 (wt%)	Grade with Ti + 0.3 Y_2O_3 (wt%)
850 °C/1 h	1.8	2.5
1100 °C/1 h	1.1	1.3
1300 °C/1 h	0	0.9

could be possibly less able to plastically deform and then fractionate into more undefined clusters.

The evolution of the nano-phases after heat treatments is described in the Part 4.2. This behaviour is consistent with the disappearance of the unidentified phases formed during the mechanical alloying and the precipitation of new stable phases during the heat treatments. The non-identified phases could disappear by coarsening or by dissolution. During the heat treatments, the influence of the titanium is clear. The determination of the chemical composition has not been achieved but particles which appear during the heat treatment (Figs. 3 and 4), are supposed to be the nano-oxides already observed in consolidated materials, see for example [7]. Specific studies by TEM are in progress to obtain more detailed information on the species. After the heat treatment at 850 °C, clusters remaining from the milling seem still stable, but the formation of a new phase is also observed. When subtracting the volume fractions of nano-clusters

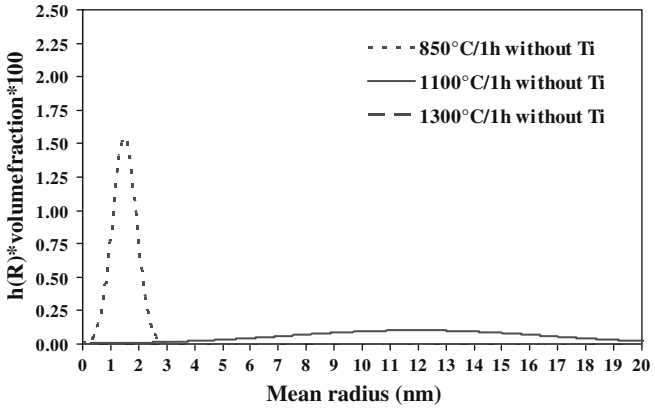

Fig. 3. Particle size distributions after 48 h milling and various heat treatments: ODS material *without* titanium.

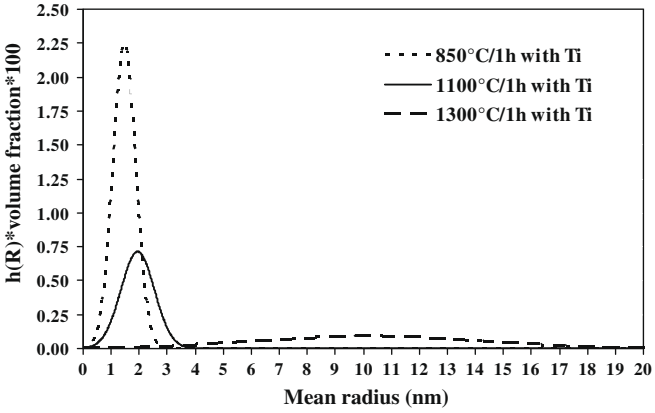

Fig. 4. Particle size distributions after 48 h milling and various heat treatments: ODS material *with* titanium.

before and after annealing, the following equations can be obtained: $\Delta fp = (1.8–1.2) = 0.6\%$ for the material without titanium and $\Delta fp = (2.5–1.8) = 0.7\%$ for the material with titanium. This rough estimation for volume fraction could show that the precipitation after this heat treatment could occur in the same order of magnitude in the two materials. After the annealing at 1100 °C, undefined phases from milling are supposed to be dissolved in the two types of powders. In the material without titanium, yttrium oxides are assumed to be coarsened already because their average size is 12 nm whereas in the other material, titanium allows the stabilization of the phases (Y, Ti, O) with an average size of about 2 nm. These results are in very good agreement with the study published by Ukai et al. [7] in which they observed the same differences between two ODS materials (one with and one without titanium) after consolidation. According to the literature, the nano-oxides formed in the materials with or without titanium are not the same and this study shows clearly that the coalescence kinetic of nano-clusters is delayed in the material with titanium. Indeed, at 1300 °C nano-oxides are no longer present in the powder without titanium whereas in the material with titanium their average size is still around 10 nm.

These results tend to confirm that nano-precipitation of (Y, Ti, O) clusters in ODS materials occurs before the consolidation process. This behaviour has already been observed by Nagai et al. [16] who observed in TEM scans the precipitation of nano-oxides in different powders after annealing for 2 h at 850 °C and 1150 °C. Indeed, during the fabrication of ODS materials, before the hot consolidation, the milled powders are heated in a furnace for at least one hour. During this heat treatment, the precipitation of nano-phases seems to happen. One might have thought that hot consolidation affects nucleation and growth of nano-phases, however the duration of the heat treatment before hot consolidation seems, according to this study, long enough to enable the precipitation of the nano-oxides. After the mechanical milling the powder is full of dislocations and interfaces which can act as preferential nucleation sites for the nano-phases. So, in order to study the nano-precipitation in ODS materials it seems unnecessary to perform the whole consolidation process: it seems sufficient to study the precipitation inside the powder after heat treatments.

6. Conclusion

The SANS technique under applied magnetic field has proved to be very powerful in the study of nanometric populations in both consolidated materials and powders, and there is no need to perform the whole consolidation process to study the nano-clusters in ODS materials.

At the end of milling for 48 h, nano-clusters of unstable phases seem to appear in the powders. Different assumptions can be made on the nature of those phases: segregation of point defects, fragments of yttrium oxides, metastable clusters of atoms or tiny milled particles of the starting elemental powders. More characterisation is necessary to clarify this point. Titanium dissolved in the matrix mainly increases the volume fraction of these phases and only slightly decreases their average size.

Heat treatments were performed for one hour to simulate the precipitation which occurs during hot consolidation of the milled powders. At the lower temperature, 850 °C, both precipitates and particles formed during the milling were observed. After the heat treatments at 1100 °C and 1300 °C, clusters from milling tend to disappear and only nano-oxides are present. Titanium is usually thought to refine the precipitation in ODS materials. This study indicates that the nano-phases formed in powders with some titanium are much more resistant to coarsening than the phases formed in the material without titanium.

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