Journal of Nuclear Materials 455 (2014) 426–430

Contents lists available at ScienceDirect

Journal of Nuclear Materials

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

# High resolution neutron diffraction crystallographic investigation of Oxide Dispersion Strengthened steels of interest for fusion technology

R. Coppola [a,*], J. Rodriguez-Carvajal [b], M. Wang [c], G. Zhang [c], Z. Zhou [c]

[a] ENEA-Casaccia, Via Anguillarese 301, 00123 Roma, Italy
[b] Institut Max von Laue – Paul Langevin, 71 Av. des Martyrs, 38042 Grenoble, France
[c] School of Materials Science and Engineering, University of Science & Technology Beijing, Beijing 100083, China

ARTICLE INFO

*Article history:*
Available online 1 August 2014

ABSTRACT

High resolution neutron diffraction measurements have been carried out to characterize the crystallographic phases present in different Oxide Dispersion Strengthened (ODS) steels of interest for fusion technology. The different lattice structures, Im3m for the ferritic ODS and Fm3m for the austenitic ODS, are resolved showing line anisotropy effects possibly correlated with differences in dislocation densities and texture. Many contributions from minority phases are detected well above the background noise; none of the expected crystallographic phases, such as $M_{23}C_6$ and including $Y_2O_3$, fits them, but the TiN phase is identified in accordance with results of other microstructural techniques.



## 1. Introduction

It is well known that Oxide Dispersion Strengthened (ODS) ferritic steels are attractive candidates as structural materials for fusion technology due to their excellent high temperature strength, creep rupture life and irradiation resistance [1–3]. However, their corrosion resistance is poor compared to austenitic steels, which in turn need to be modified as ODS steels in order to significantly improve their performance under irradiation [4]. The processing of ferritic and austenitic ODS steels optimized for fusion applications is very complex and implies a series of metallurgical modifications which need to be carefully characterized and understood.

This contribution presents the results of an investigation, carried out by means of high resolution neutron diffraction, to determine the crystallographic phases presented in different ODS steels of interest for fusion technology, already characterized by other microstructural techniques such as X-ray diffraction and electron microscopy [5,6]. As reported in the general Refs. [7,8] neutron diffraction is extremely useful for such investigations, first due to the selectivity of cold neutron beams for light elements (H, C) and for elements of close atomic number, such as Fe and Cr. Furthermore, due to the low absorption coefficients of neutrons, massive samples can be investigated, with high statistical relevance of the collected data, and *in-situ* experiments can be carried out to test in real time the evolution of the diffraction pattern under thermal or mechanical treatments, requiring for instance a furnace to be installed on the neutron diffractometer. As a matter of fact, the work presented in this paper, consisting in room temperature neutron diffraction measurements, has to be considered as the first step of a scientific program aiming to characterize the evolution with increasing temperature of the crystallographic phases in the investigated materials.

## 2. Material characterization

Two kinds of ODS steels were investigated in this paper. Basic microstructural and mechanical properties were reported in Refs. [5,6]. For both ODS samples, pre-alloyed matrix powders, Ti and $Y_2O_3$ were used as the starting materials.

The pre-alloyed matrix powders were 304 austenitic and 9Cr ferritic powders respectively. The compositions are shown in Table 1. The fabrication process for both ODS steels was the same. The starting powders were mechanically alloyed by a planetary ball mill for 30 h. The as-milled powders were degassed, sealed and consolidated by hipping at 1150 °C for 3 h. Then hot forging were applied to the samples at 1150 °C with a forging ratio 3:1. The conditions of samples were summarized in Table 2.

As shown in Ref. [5], electron microscopy, X-ray diffraction and Energy Dispersive Spectrometry (EDS) measurements of ODS 304 steel in the form of mechanically alloyed powder show a distribution of complex oxides less than 20 nm in average size and a significant amount of TiN particles, several hundred nm in size, shown in Fig. 1. $Y_2O_3$ phase and Y–Ti–O complexes are also detected. It is stressed that these microstructural observations refer to spatially

* Corresponding author.
*E-mail address:* roberto.coppola@enea.it (R. Coppola).

http://dx.doi.org/10.1016/j.jnucmat.2014.07.015
0022-3115/

**Table 1**
The chemical compositions of ODS steels (wt%).

| Sample | Fe | Cr | Ni | Mo | W | Si | Ti | $Y_2O_3$ |
|---|---|---|---|---|---|---|---|---|
| ODS-304 | Bal. | 18 | 8 | 1 | – | 0.15 | 0.5 | 0.35 |
| ODS-9Cr | Bal. | 9 | – | – | 1.5 | 0.15 | 0.5 | 0.35 |

**Table 2**
Nomenclature of samples.

| Samples | Conditions | |
|---|---|---|
| ODS-304 | A1 | As-hipped ingot |
| | A2 | As-forged ingot |
| | A3 | As-milled powders |
| ODS-9Cr | B1 | As-forged ingots |
| | B2 | As-milled powders |

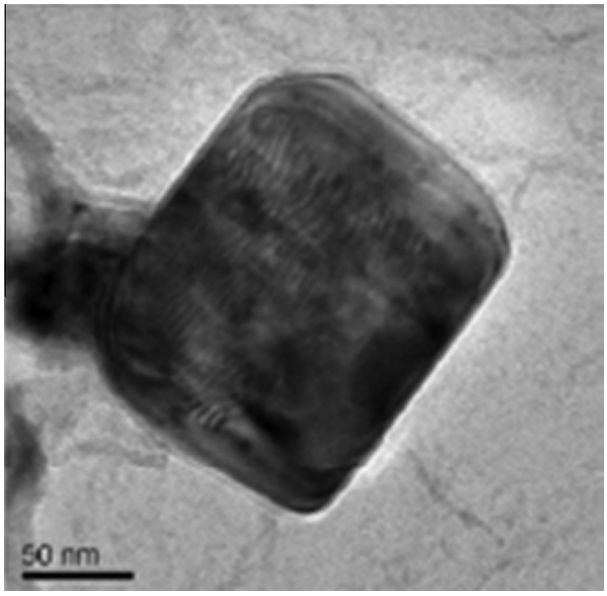


**Fig. 1.** TiN particle in ODS-304 steel (after Ref. [5]).

limited regions of the investigated sample, while the neutron diffraction measurement reported here below refer to an investigation volume orders of magnitude larger.

## 3. Experimental technique and data analysis

The neutron diffraction measurements were carried out at the D20 instrument, at the high flux reactor of the Institut Max von Laue – Paul Langevin, Grenoble [9]. The different samples, under the shape of cylindrical ingots or powders, were placed in Vanadium cans of 7 mm or 9 mm, under vacuum and at room temperature; a neutron wavelength $\lambda$ of 1.36 Å with a monochromator take-off angle of 118° was selected in order to optimize the experimental resolution and the capability to detect also minority phases. The size of the neutron beam was $1 \times 3\ cm^2$ and consequently the effective diffracting volume was more than $1\ cm^3$. The data were collected during the necessary time to get the appropriate statistics. Some detector cells were behaving abnormally in well-defined angular regions, therefore at these few isolated positions suitable corrections were made to incorporate them into the data sets, with minor effect on the data treatment.

The experimental data have been treated by the Rietveld method (FULLPROF suite) to characterize the main phases and further refined to identify the minority ones [10]. The diffractometer was calibrated measuring the diffraction pattern of a standard sample of $Na_2Ca_3Al_2F_{14}$, in order to prepare an instrumental resolution function file according to the conditions of the experiment, and to allow obtaining microstructural information directly from the data treatment. This Rietveld refinement of the standard reference data was carried out fixing the crystal structure and cell parameters, then refining the scale factor, the background parameters, the zero-shifts, wavelength and sample displacement parameters as well the *U*, *V*, *W*, *X* parameters, defined as follows [11]:

$$H_G^2 = U\tan^2\theta + V\tan\theta + W \tag{1}$$

where $H_G{}^2$ is the Gaussian component of the Bragg peak profile, $\theta$ is the half scattering angle and the parameter *X* governs the Lorentzian contribution to the profile, $H_L = X\tan\theta$. *U*, *V*, *W*, *X* contain mainly instrumental parameters (collimator divergences, take-off angle of the monochromator diffracted beam and mosaicity of the monochromator) and govern the full width at half-maximum (FWHM). For details of the profile parameters consult the manual of FULLPROF [10].

The instrumental resolution file constructed from the refined data is read by FULLPROF, when required by the input control file (PCR-file), and the broadening of the experimental peaks is interpreted in terms of microstructural parameters. This refined broadening, obtained from the automatically generated microstructure file, provides the total Gaussian and Lorentzian FWHM's, the instrumental Gaussian and Lorentzian FWHM of the instrument contribution and the intrinsic integral breadth of the peak, from which the strain and size parameters are obtained. As explained in [10], the strain values correspond to the so called "maximum strain" and have no units. The expressions for calculating the apparent size and strains respectively, for each Bragg reflection corresponding to lattice spacing *d*, are:

$$D_{app} = \frac{\lambda}{\beta_{size}\cos\theta} = \frac{1}{\beta^*_{size}} \qquad e = \frac{1}{2}\beta^*_{strain}d = \frac{\beta^*_{strain}}{2s} = \frac{\beta_{strain}\cos\theta}{2s\lambda} \tag{2}$$

in which the integral breadths $\beta$ (without "*") are expressed in radians and the integral breadth $\beta$ with a "*" symbol are expressed in reciprocal space ($Å^{-1}$), they are already corrected from instrumental resolution.

## 4. Results and discussions

The observed and calculated neutron diffraction patterns of B2 are shown in Fig. 2. Both this sample and B1 present the same average structure corresponding to that of ferrite (α-Fe), however additional minor (precipitate) phases are detected above the background, clearly shown in Fig. 3. A Bragg *R*-factor of 1.46 is found. The ingot B1 sample presents a strong preferred orientation (texture) preventing the treatment using the Rietveld method. A refinement of the full pattern can be performed using the Le Bail fit in which the integrated intensities of the peaks are not fixed by the crystal structure; however the results of this refinement are not as good as that of the powder sample because of large, textured grains giving rise to a peak shape that is not as smooth as for a random powder. From the point of view of the microstructure, the diffraction pattern of B1 does not show broadening with respect to the instrumental resolution. Only a small Lorentzian size effect can be refined $Y = 0.054(1)$ corresponding to an isotropic coherence domains of apparent (volume averaged) size of $D_{app} \approx 91.3$ nm. If we consider that the shape of the coherence domains is spherical the corresponding diameter is $D = 4/3D_{app} \approx 122$ nm. The powder sample B2 shows a microstructure characterized by the presence of anisotropic micro-strains, most probably due to the presence of a high density of dislocations.