Materials Characterization 135 (2018) 134–138

Contents lists available at ScienceDirect

Materials Characterization

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

Determination of the volume fraction of precipitates in a nitrided Fe-0.354 wt% C-2.93 wt% Cr model alloy by anomalous small angle X-ray scattering

S. Jégou[a], M. Dumont[b,*], L. Barrallier[a]

[a] Arts et Métiers ParisTech, MSMP laboratory, 2 cours des Arts et Métiers, F-13617 Aix-en-Provence, France
[b] Aix Marseille Univ, Univ Toulon, CNRS, IM2NP, Marseille, France

ARTICLE INFO

Keywords:
Steel
Nitriding
Nitrides
Synchrotron radiation
Anomalous small angle scattering

ABSTRACT

Anomalous small angle scattering (ASAXS) is a powerful non-destructive technique that can provide characteristic features of nanoscale precipitates such as the volume fraction, and chemical composition. In this paper, the technique is used for the first time to explore nanoscale MN nitrides (M = Cr,Fe) after nitriding of a model iron alloy (Fe-0.354 wt% C-2.93 wt% Cr).

1. Introduction

Anomalous small-angle X-ray scattering (ASAXS) is a powerful technique that combines the capability of SAXS to characterize the size distribution of nano-objects embedded in a matrix and the variation in contrast allowed by tunable wavelength of the Synchrotron incident X-ray beam, giving access to information about the composition of scattering nano-objects [1–2].

In this study, ASAXS technique is applied to characterize precipitates in a ternary Fe-Cr-C nitrided steel. Nitriding is a surface engineering process applied to enhance surface properties such as corrosion, wear and fatigue resistance [3–4]. Gaseous nitriding consists in the diffusion of nitrogen atoms through the surface of steels from the dissociation of a nitrogen rich atmosphere (gas or plasma) at the atmosphere/solid interface [5]. It results in the formation of an iron nitride layer (Fe_4N and/or $Fe_{2-3}N$) and a diffusion zone where nitrogen is found as solid solution in the ferritic matrix and combined as MeN (Me = Cr, V, Al…) nitrides with alloying elements having high affinity with nitrogen such as chromium, aluminium or vanadium [6]. The volume fraction of nitrides formed in the diffusion layer is of prime importance for requested surface properties. In fact this affects the resulting hardness; moreover the volume change induced by precipitation takes part to the generation of compressive residual stresses [7].

In the case of binary Fe-Me (Me = Cr, Al or V) alloy, formed nitrides are close to pure MeN phase having a fcc NaCl-type structure [5]. In the case of C-containing ternary Fe-Cr-C, pre-existing carbides (generally $M_{23}C_6$ or M_7C_3, M = Fe or Cr) are expected to dissolve due to a lower stability as compared to nitrides [8]. Therefore nitrides are formed either by direct formation by reaction with Cr remaining in solid solution or by transformation of carbides [9]. Carbon is then rejected toward grain boundaries where it forms coarse cementite aggregates [10] or toward the diffusion front where it participates to the coarsening of carbides.

This paper aims at using small-angle scattering to characterize nitrides in the diffusion layer after gas nitriding of a model ternary Fe-Cr-C alloy (Fe-0.354 wt% C-2.93 wt% Cr). The major goal is the determination of the volume fraction of nitrides that is the key parameter for resulting surface properties. However the volume fraction cannot be determined by SAXS independently of the composition of the nano-precipitates. Using anomalous dispersion effect, ASAXS is an element-selective technique based on the anomalous variation of the scattering factor near the absorption edge of one chosen element, therefore it allows to overcome this difficulty by giving access to the chemical information, allowing the determination of the volume fraction of scattering precipitates [11]. Results are discussed with respect to the literature and thermodynamics calculations performed using the Thermo-Calc software [12].

2. Materials and Experimental Methods

2.1. Materials and Microstructural Characterization

A Fe-0.354 wt% C-2.93 wt% Cr ternary alloy was used in this study. It was oil quenched and annealed at 590 °C. Gas nitriding was

* Corresponding author at: IM2NP – UMR CNRS 7334 – Aix-Marseille Université, Faculté des Sciences et Techniques de St-Jérôme – Service 251, 13 397 Marseille Cedex 20, France.
E-mail address: myriam.dumont@univ-amu.fr (M. Dumont).

https://doi.org/10.1016/j.matchar.2017.11.036
Received 21 August 2017; Received in revised form 9 November 2017; Accepted 14 November 2017
Available online 15 November 2017
1044-5803/ © 2017 Elsevier Inc. All rights reserved.

performed by Aubert & Duval at 550 °C during 100 h for a given nitrogen potential (K_N = 2.65 $atm^{-1/2}$). Composition profiles along the nitride layer were carried out by electron probe microanalysis (EPMA) as well as glow discharge optical emission spectrometry (GDOES) [7]. Observations of the case and core microstructure were carried out by optical microscopy as well as scanning and transmission electron microscopy.

2.2. Anomalous Small Angle Scattering (ASAXS)

Small-Angle X-ray Scattering (SAXS) experiments were carried out on the BM02-D2AM, a French CRG beamline at the European Synchrotron Radiation Facilities (ESRF) in Grenoble. Regarding the composition of the system, the most reliable conditions for anomalous measurements are based on the Cr K-absorption edge. Four energies slightly below the Cr K-edge (5.96 keV) as well as one far from the Cr-edge was used for anomalous SAXS measurements. As SAXS experiments are performed in transmission mode, the relatively low energy of the Cr K-edge represented a challenge in the sample preparation since it required the preparation of relatively thin samples, around 30 μm in thickness, to ensure a satisfactory transmission through the thickness of the sample. Moreover in order to investigate the precipitation variations with depth (down to 1 mm), samples were cut along a bevel so that all depths can be studied by a profile measurement adapted to the lateral resolution of the beam (~300 μm). A preparation procedure was optimised and consisted in gently polishing 20 × 10 mm^2 surfaces using a bevel of ~3 degrees, so that 500 μm steps for profile measurement along samples correspond to 25 μm steps within the depth of the nitrided layer.

A small-angle set-up was chosen to well characterize nano-precipitates in the 2–50 nm radius range, *i.e.* in a *q*-range ranging from 0.03 nm^{-1} to 0.6 nm^{-1}, where *q* is the amplitude of the scattering vector q ($q = \frac{4\pi sin\theta}{\lambda}$) where θ is the half scattering angle and λ the wavelength. The SAXS patterns were acquired using a two-dimensional CCD camera. Data files were corrected from electronic noise, spatial distortion, pixel efficiency, the flat field of the detector, and background noise. A circular average was taken around the transmitted beam to obtain the intensity as a function of the scattering vector. The scattered intensity was finally converted into absolute values, *I*, using measurement of the intensity of the direct beam through calibrated filters.

The analysis method of ASAXS data to extract chemical information of nanoparticles is described in details in [11] and is summarised hereafter. The measured quantity used for the ASAXS analysis is the integrated intensity Q_o defined as:

$$Q_0(\lambda) = \int_0^\infty I(q)q^2dq = 2\pi^2\ |\Delta\rho(\lambda)|^2 f_v(1-f_v) \tag{1}$$

where λ is the wavelength, *q* is the module of the scattering vector, f_v is the volume fraction of scattering objects, Δρ(λ) is the electronic contrast, defined as the difference in electronic density between the scattering particle (ρ_{ppt}) and the matrix (ρ_m) in which it is embedded: $|\Delta\rho| = |\rho_{ppt} - \rho_m|$.

The electronic contrast can be varied by changing the energy in a range close to the absorption edge of one element of the system. In fact, the electronic density of a phase constituted by *N* elements can be written:

$$\rho(\lambda) = \frac{\sum_{i=1}^{N} X_i f_i(\lambda)}{V_{at}} \tag{2}$$

where X_i is the atomic fraction of element i $\left(\sum_{i=1}^{N} X_i = 1\right)$, V_{at} is the mean atomic volume of the particle or the matrix, $f_i(\lambda)$ is the atomic scattering factor of element *i*, which is tabulated as a function of the wavelength of the beam.

In the vicinity of the absorption edge of the element *k*, the electronic contrast can be written:

$$|\rho_{ppt} - \rho_m| = \frac{1}{V_{at,m}} \left| \sum_{\substack{i=1 \\ i\neq k}}^{N} [f_i(\alpha X_{i,ppt} - X_{i,m})] + f_k(\lambda)(\alpha X_{k,ppt} - X_{k,m}) \right| \tag{3}$$

with $\alpha = \frac{V_{at,m}}{V_{at,ppt}}$.

Using this formalism, $\sqrt{Q_0}$ is expected to vary linearly with the scattering factor $f_k(\lambda)$:

$$\sqrt{Q_o} = \theta + pf_k(\lambda) \tag{4}$$

where:

$$\theta = \frac{\pi}{V_{at,m}}\sqrt{2f_v(1-f_v)}\ \ \delta\ \left(\sum_{\substack{i=1 \\ i\neq k}}^{N} f_i(\alpha X_{i,ppt} - X_{i,m})\right)$$

$$p = \frac{\pi}{V_{at,m}}\sqrt{2f_v(1-f_v)}\ \ \delta\ \ (\alpha X_{k,ppt} - X_{k,m})$$

with $\delta = 1$ if $(\rho_{ppt} - \rho_m) \geq 0$
$\delta = -1$ if $(\rho_{ppt} - \rho_m) < 0$.

Using the ratio θ/p is a straightforward way for extracting chemical information from ASAXS measurements (independently of the volume fraction):

$$\frac{\theta}{p} = \frac{\sum_{\substack{i=1 \\ i\neq k}}^{N} f_i(\alpha X_{i,ppt} - X_{i,m})}{(\alpha X_{k,ppt} - X_{k,m})} \tag{5}$$

In the following, this approach is used to extract the Cr, Fe or N contribution to nitrides or matrix. In a second part the volume fraction of nitrides can be calculated using Eq. (1).

3. Results and Discussion

3.1. Microstructure of the Nitrided Layer

Fig. 1 gives in-depth composition profiles of carbon and nitrogen from the Fe-0.354 wt% C-2.93 wt% Cr alloy nitrided 100 h at 550 °C [7].

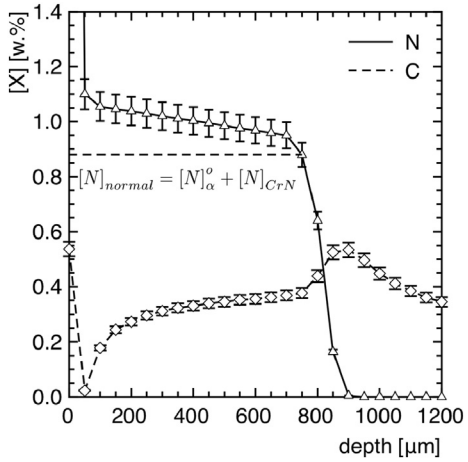

Fig. 1. Nitrogen and carbon in-depth profiles of the Fe-0.354 wt% C-2.93 wt% Cr ternary alloy nitrided at 550 °C for 100 h (EPMA/GDOES analyses) [7]. "Normal" N content refers to the precipitation of all Cr atoms as binary CrN and the equilibrium solubility of nitrogen in the ferritic matrix ($[N]^\circ_\alpha$ = 0,05 wt%).

Download English Version:

https://daneshyari.com/en/article/7969492

Download Persian Version:

https://daneshyari.com/article/7969492

Daneshyari.com