Materials Science & Engineering A 647 (2015) 294–302

Contents lists available at ScienceDirect

Materials Science & Engineering A

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

Precipitation strengthening of Nb-stabilized TP347 austenitic steel by a dispersion of secondary Nb(C,N) formed upon a short-term hardening heat treatment

Christian Solenthaler [a], Mageshwaran Ramesh [b], Peter J. Uggowitzer [c], Ralph Spolenak [a,*]

[a] Laboratory for Nanometallurgy, Department of Materials, ETH Zurich, Vladimir-Prelog-Weg 5, CH 8093 Zurich, Switzerland
[b] Paul Scherrer Institute, Laboratory for Nuclear Materials, CH-5232 Villigen-PSI, Switzerland
[c] Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, Vladimir-Plelog-Weg 4, CH 8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Received 7 May 2015
Received in revised form
4 September 2015
Accepted 6 September 2015
Available online 9 September 2015

Keywords:
Austenitic steels
Carbides
Precipitation strengthening
Orowan mechanism
Transmission electron microscopy

ABSTRACT

A dense intra-granular dispersion of small secondary Nb(C, N) precipitates in commercial TP347 Nb-stabilized austenitic steel was formed during a short-term hardening heat treatment in the temperature window $\Delta T = 1050–950$ °C, starting with isothermal annealing at 1050 °C and followed by continuous cooling from 1050 °C to 950 °C. The precipitates are semi-coherent in cube-on-cube orientation relationship with the austenitic matrix, of characteristic faceted octahedral shape with {111} facets and typically $d = 15 \pm 4.6$ nm in size. The experimentally determined volume fraction $f = 1.4 \pm 0.2 \cdot 10^{-3}$ correlates well with thermodynamic calculations. The precipitation gives a significant strengthening of the steel from $\sigma_{y\ \mathrm{initial}}$ ~529 ± 42 MPa to $\sigma_{y\ \mathrm{hardened}}$ ~703 ± 39 MPa, corresponding to a strength increment $\Delta\sigma_y$ ~174 MPa (~33%) in good agreement with the prediction for Orowan strengthening. The present work is relevant to the exploration of the application potential of short term hardening heat treatments for precipitation strengthening austenitic steels.

1. Introduction

The Nb-stabilized austenitic steel AISI TP347 is widely used in the power generating industry for piping and tubing systems in power-plants. There are two main application fields to be distinguished: (i) at intermediate service temperatures of typically 340 °C in nuclear power-plants (e.g. cooling circuits of light water reactors) where an optimal combination of good mechanical properties and high resistance against inter-granular corrosion is the primary aim, and (ii) at high service temperatures of typically 700 °C and above in fossil-fired steam power-plants (e.g. superheater tubes) where high creep strength is an additional concern [1,2].

Nb in TP347 steel forms Nb-carbonitrides Nb(C,N) (in the following referred to as NbX) due to the strong affinity between Nb and C and between Nb and N. NbX has a fcc crystal structure, type Fm3m (like the austenitic matrix), with a lattice parameter $a_{0\ \mathrm{NbX}}$ between 0.447 nm (NbC) and 0.437 nm (NbN) [3]. NbX forms as primary NbX_P during solidification of the steel and as secondary NbX_S due to the decreasing Nb-solubility in the austenitic matrix with decreasing temperature. NbX formation provides two beneficial effects: (i) it stabilizes the steel against inter-granular corrosion because it prevents the precipitation of $Cr_{23}C_6$ at grain boundaries and concomitant local Cr-depletion. (ii) Intra-granular dispersions of fine secondary NbX_S may result in substantial precipitation hardening and improvement of creep strength. Volume fraction and particle size of hardening NbX_S depend on the heat treatment history of the material, including processing and long-term service exposure at high temperature. Nb:C ratios of the steel composition of 8:1–10:1 (wt%) are normally assumed as optimal to precipitate as much NbX_S as possible while still maintaining a low coarsening rate and sufficient stabilization against inter-granular corrosion [4–7].

Owing to the technical importance of Nb-stabilized austenitic steels, research on precipitation phenomena has been of high interest over many years, and comprehensive reviews are available [4,5,8]. Efforts were primarily aimed at characterizing precipitation reactions involving the formation of carbides, carbonitrides, nitrides and intermetallic phases [9–13]. and the evolution of secondary NbX populations with regards to volume fraction, particle size and stability against coarsening during long-term ageing and creep [13–16].

The present paper demonstrates that a short-term hardening

---

* Corresponding author.
E-mail address: ralph.spolenak@mat.ethz.ch (R. Spolenak).

http://dx.doi.org/10.1016/j.msea.2015.09.028
0921-5093/© 2015 Elsevier B.V. All rights reserved.

heat treatment of commercial TP347 steel at unusually high hardening temperatures in the range of 1050–950 °C can result in a dense intra-granular dispersion of small secondary NbX particles and substantial precipitation strengthening. The morphological properties of the precipitate dispersion (nature, size, shape and volume fraction of the particles) are characterized by means of transmission electron microscopy (TEM). The thermodynamic background and the strengthening effect are discussed and available options for maximizing the strengthening effect are addressed.

2. Experimental

2.1. Material and hardening heat treatment

The investigated material was a commercial TP347 Nb-stabilized austenitic stainless steel supplied as seamless pipes with 219 mm outer diameter and 18 mm wall thickness. The pipes were fabricated by the Pilgering process, solution annealed at 1100 °C for 1 h and water quenched before delivery. The major chemical composition is given in Table 1. For the present study tubular test specimens (8 mm outer diameter, 5.5 mm inner diameter, 20 mm long) were annealed at 1050 °C for 1 h in vacuum, followed by continuous cooling to 950 °C at a rate of 10 K min^{-1}, and subsequent fast cooling in argon atmosphere to room temperature at 85 K min^{-1}. This heat treatment causes a significant hardening of the steel due to an intra-granular dispersion of small secondary NbX precipitates and is therefore referred to as “hardening heat treatment”, HHT.

2.2. Methods

Transmission electron microscopy (TEM), including selected area electron diffraction (SAD) and energy dispersive x-ray analysis (EDX), was applied to characterize the morphology of the precipitate dispersion and to identify the precipitates unambiguously as NbX. TEM was performed with a Philips CM 200 at 160 kV and with a FEI Technai F30ST at 300 kV. TEM samples were thin foil disc samples, electro-polished in a solution of 90% acetic acid and 10% perchloric acid at 40 V/10 °C, and mounted on a low background double tilt holder. Particle size *d* was measure manually from kinematical bright field images (i.e. from images without strain field contrast) and from dark field images formed with NbX {200} reflections, always from images with the beam direction $z=<100>$. Since the particles are of {111} faceted octahedral shape, *d* was defined as the $<110>$ edge length of the octahedron. The detailed procedure is given in Section 3.2.2. Sample thickness *t* for the determination of the NbX volume fraction was derived from the number of thickness fringes at grain boundaries observed in dynamical {200} and {220} bright field images, assuming extinction distances for fcc Fe of ξ_g {200}= 47 nm and ξ_g {220}=70 nm [17]. For EDX spectral imaging a beam diameter of 0.5 nm and a step width of 2 nm were chosen. The effect of the precipitate dispersion on the strength of the steel was evaluated by means of Vickers micro-hardness measurements on material with and without HHT (series of 20 indents at a load of 1 N, indents separated by 3 indent diameters). The obtained hardness values, H_V, were converted to approximate yield strength values, σ_y, using the relation $\sigma_y=3.03\ H_V$ recommended for austenitic stainless steels [18].

Table 1
Chemical composition of the investigated TP347 sample material (wt%).

C	Si	Mn	P	S	Cr	Ni	Nb	N
0.058	0.20	1.72	0.025	0.006	17.4	10.4	0.571	0.045

3. Results

3.1. Microstructure before and after the hardening heat treatment, and strength increase $\Delta\sigma_{y\ exp}$

The initial state of the material before the short term heat treatment is shown in Fig. 1. The grain structure is homogeneous and consists of equiaxed 20–50 μm large grains. Primary NbX is present as coarse 1–15 μm large plates, arranged in dense lines across the grain structure parallel to the pipe axis, independently of grain boundaries (Fig. 1a). TEM micrographs (Fig. 1b) reveal that the grain interior is free of any secondary phases. Dislocations are present in a moderate density ρ ~$1.75\pm0.25\cdot10^9\ \mathrm{cm}^{-2}$ and are heterogeneously distributed and typically arranged in planar arrays on the {111} slip planes.

After the HHT a dense intra-granular dispersion of small NbX precipitates is observed (Fig. 2; phase identification see Section 3.2.1). The particle distribution appears to be rather homogeneous in images with the beam direction $z=<100>$ (Fig. 2a, c and d). However, images with the beam direction $z=<110>$ (Fig. 2b) show clearly that the particles form preferentially on selected {111} planes. These densely populated planes are separated from each other by an approximate spacing of ~300–500 nm, over which the particle density is significantly lower. The particles give under near dynamical TEM bright-field imaging conditions a strong strain field contrast, which is much wider than the true particle size.

Hardness measurements reveal a significant strengthening of the steel (Fig. 3) from $\sigma_{y\ \mathrm{initial}}$ ~529 ± 42 MPa to $\sigma_{y\ \mathrm{hardened}}$ ~703 ± 39 MPa. The strength increment corresponds to $\Delta\sigma_{y\ \mathrm{exp}}=\sigma_{y\ \mathrm{hardened}}-\sigma_{y\ \mathrm{initial}}$ ~174 MPa ~0.33 $\sigma_{y\ \mathrm{initial}}$.

3.2. Nature and morphology of the secondary NbX precipitate dispersion

3.2.1. NbX identification by means of electron diffraction and EDX spectrometry

Results from electron diffraction confirm that the observed precipitate dispersion consists in fact of NbX as follows. Fig. 4a–c shows three different selected area electron diffraction patterns (SAD) obtained from 0.5 μm wide intra-granular areas containing only small precipitates. The beam directions *z*, with reference to the matrix grains, are $<110>$, $<100>$ and $<111>$. Indexing and unit cells for each pattern are given in schematic drawings. Apart from the strong matrix reflections (big spots, strong lines), each pattern contains a set of weak reflections from the precipitates (small spots, dashed lines). Though weak, the diffracted intensities from the precipitates are clearly visible and the patterns are well defined. Compared with the patterns from the matrix, always the same common properties are observed: (i) the same symmetry and orientation, correlating with the fcc crystal lattice, type Fm3m, and (ii) the smaller reflection spacing $R_{\mathrm{NbX}}=0.82\ R_{\mathrm{matrix}}$, indicating a larger lattice parameter $a_{0\ \mathrm{NbX}}=1.22\ a_{0\ \mathrm{matrix}}$. With R_{matrix} normalized to the lattice parameter $a_{0\ \mathrm{matrix}}=0.3597$ nm [19], the lattice parameter of the precipitates is obtained as $a_{0\ \mathrm{NbX}}=a_{0\ \mathrm{matrix}}\ R_{\mathrm{hkl\ matrix}}/R_{\mathrm{hkl\ NbX}}=0.439$ nm, independently of beam direction and choice of R_{hkl}. This experimental value fits well with the established value for NbC, $a_{0\ \mathrm{NbC}}=0.447$ nm [3]. The slight deviation (1.8%) may be partially due to the restricted precision which is inherent to the evaluation of such electron diffraction patterns, however it is consistent with the tendency $a_{0\ \mathrm{Nb(C,\ N)}}<a_{0\ \mathrm{NbC}}$. The secondary NbX particles grow