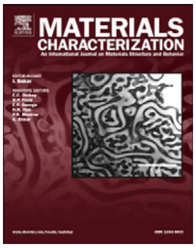
Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/matchar



Three phase crystallography and solute distribution analysis during residual austenite decomposition in tempered nanocrystalline bainitic steels

F.G. Caballero[a,*], Hung-Wei Yen[b,c], M.K. Miller[d], J. Cornide[a], Hsiao-Tzu Chang[b], C. Garcia-Mateo[a], Jer-Ren Yang[b]

[a]Centro Nacional de Investigaciones Metalúrgicas (CENIM-CSIC), Avda Gregorio del Amo, 8, Madrid E-28040, Spain
[b]Department of Materials Science and Engineering, National Taiwan University, 1, Roosevelt Rd. Sec. 4, Taipei 10617, Taiwan
[c]Australian Centre for Microscopy and Microanalysis, The University of Sydney, NSW 2006, Australia
[d]Oak Ridge National Laboratory (ORNL), Materials Science and Technology Division, Oak Ridge, TN 37831-6139, USA

ARTICLE DATA

Article history:
Received 5 August 2013
Received in revised form
5 November 2013
Accepted 28 November 2013

Keywords:
Steels
Bainite
Precipitation
Atom probe tomography (APT)

ABSTRACT

Interphase carbide precipitation due to austenite decomposition was investigated by high resolution transmission electron microscopy and atom probe tomography in tempered nanostructured bainitic steels. Results showed that cementite (θ) forms by a paraequilibrium transformation mechanism at the bainitic ferrite–austenite interface with a simultaneous three phase crystallographic orientation relationship.

1. Introduction

Many commercially successful steel concepts have been developed based on a mixed microstructure of bainitic ferrite (α) and carbon-enriched retained austenite (γ) [1–9]. The austenite is found to occur in two forms: as blocks (a few microns thick) of retained austenite located between the sheaves of bainite, and as fine 20–200-nm-thick films of austenite, which are retained between the subunits of a given sheaf of bainite. This retained austenite is not thermodynamically stable. There is ample evidence that austenite will decompose into a mixture of ferrite and carbides during tempering [1,4,10]. In order to accomplish cementite precipitation, the carbon content of the austenite should exceed that given by the extrapolated γ / (γ + θ) phase boundary.

The shape, size and carbon content of retained austenite play an important role in controlling its decomposition behavior. Coarse blocks of austenite tend to decompose into fine pearlite, whereas films of austenite decompose into discrete particles of cementite in a ferrite matrix, basically because they are too thin to permit the onset of the cooperative growth needed to establish a pearlite colony [11]. In addition, the nano-scale austenite films seem to be less stable than those with a sub-micron thickness, as recently revealed by in-situ high-energy synchrotron X-ray diffraction experiments [12,13]. This is because the nano-scale films of austenite are much more enriched in carbon and therefore have a higher driving force for cementite precipitation [14].

There is no partitioning of substitutional solutes across the bainitic ferrite–austenite interface during the bainite reaction,

---

[*] *Corresponding author*. Tel.: +34 91 5538900; fax: +34 91 5347425.

1044-5803/$ – see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.matchar.2013.11.013

in spite of the requirements of equilibrium [15,16]. Thus, given the opportunity, substitutional elements are expected to redistribute approaching equilibrium phase boundary as the bainite structure is tempered. Field ion microscopy and 1D atom probe revealed that when a mixture of bainitic ferrite and austenite is tempered at low temperature, the substitutional solutes partition before the austenite begins to decompose [17]. More recently, the compositional analysis of the austenite–bainitic ferrite interface by atom probe tomography (APT) [18] revealed chromium spikes at the austenite/bainitic ferrite interface indicating that negligible partitioning local equilibrium was reached. However, the retained austenite decomposed during tempering before equilibrium was reached at the interface.

It has long been known that cementite precipitation due to the decomposition of the residual austenite occurs at the austenite–bainitic ferrite interface. Hot-stage transmission electron microscopy (TEM) examination [19] of the precipitation events during tempering of an aggregate of retained austenite and bainitic ferrite formed at 350 °C for 205 min in medium carbon high silicon steel, revealed that the majority of carbides formed at the austenite–bainitic ferrite interface and then grew into the austenite, so that the process of austenite decomposition can be described as interphase precipitation. Subsequently, the boundary pulled away from the line of carbides and this sequence continued repeatedly until the austenite had fully decomposed. In general, due to the thickness of the austenite film, only one or two lines of carbide were observed before austenite decomposition was completed [19]. That is the reason why a typical appearance of interphase precipitation in rows [20,21] is not observed at the nanoscale.

Austenite decomposition can also occur after the upper bainite transformation during an extensive aging, with a much longer time than is necessary to complete the bainite reaction. It is generally accepted that interlath carbide precipitation is a secondary event involving the diffusional decomposition of the carbon enriched austenite after bainitic ferrite formation. Shackleton and Kelly [22] performed a systematic study of the crystallography of carbide precipitation in bainite. They found that the orientation relationships for interlath cementite in upper bainite were mainly constrained from the austenite. The observed α/θ relationships were derived assuming that the cementite precipitates from austenite with the Pitsch γ/θ relationship [23] and allowing the ferrite to be a variant of the Kurdjumov and Sachs α/γ relationship [24]. More recently, the following three-phase orientation relationship,

$$(111)_\gamma || (011)_\alpha || (\bar{1}03)_\theta \text{and} [\bar{1}01]_\gamma || [\bar{1}\bar{1}1]_\alpha || [010]_\theta \tag{1}$$

was considered in upper bainite structure of a Fe–Ni–C alloy [25], where the interlath cementite clearly nucleates at the austenite–ferrite boundary.

In the present work, the onset of interphase carbide precipitation due to the decomposition of the retained austenite was analyzed by the complementary techniques of high-resolution TEM (HRTEM) and APT in tempered nanostructured bainitic steels containing significant (20–40%) amounts of unstable austenite. The results have provided new experimental evidence on the crystallographic orientation relationships and solute distribution among the three phases (ferrite, austenite, and cementite) involved.

2. Material and Methods

The chemical compositions of the studied steels are given in Table 1. The alloys were supplied after casting, rolling, and a homogenization heat treatment at 1200 ºC for 72 h. Specimens were austenitized at 1000 ºC for 15 min and then isothermally transformed at 200 ºC for 240 h before quenching into water. The microstructure thus obtained was tempered at temperatures below 400 ºC for different times. Previous X-ray diffraction (XRD) results suggest that the austenite should be fully decomposed after tempering at 450 ºC for 30 min [26]. Details on the processing, heat treatments, and preliminary microstructural characterization of nanostructured bainitic steels are reported elsewhere [5,10,27].

Specimens for TEM were sliced from 3 mm diameter rods of tempered material, mechanically thinned to 0.06 mm, and then twin-jet electropolished to perforation with a mixture of 5% perchloric acid, 25% glycerol, and 70% ethanol at −5 °C at 40 V. The samples were examined on a Philips Tecnai F30 field emission gun (FEG) TEM operated at 300 keV.

APT specimens were cut from the tempered material and electropolished by standard micropolishing methods [28]. APT analyses were performed in the Cameca laser-assisted local electrode atom probe (LEAP 4000X HR), which was operated in voltage pulsed mode with a specimen temperature of 50 K, a pulse repetition rate of 200 kHz, and a pulse fraction of 0.2. The large field of view and rapid analysis capability of this instrument facilitated the analysis at an atomic scale of the nucleation of interphase carbides in steels. The solute distribution across the interphase interfaces was determined with proximity histograms [29]. The main advantages of this method are that it can accommodate the curvature of non-planar interfaces and enables solute profiles to be obtained that are normal to the interface.

3. Results and Discussion

The initial microstructure of the steels studied consists of ~40 nm-thick plates of bainitic ferrite and 20–40% austenite, depending on the carbon and silicon content (Table 1) [30]. Retained austenite is enriched in carbon to 5–12 at.%, depending on its morphology and size. Nanoscale austenite

Table 1 – Chemical composition of nanocrystalline bainitic steels. The balance is Fe.

Steel	C	Si	Mn	Mo	Cr	V
Steel1:						
wt.%	1.0	1.5	1.9	0.3	1.3	0.1
at.%	4.3	2.8	1.8	0.1	1.3	0.1
Steel2:						
wt.%	0.8	2.2	2.0	0.3	1.4	0.1
at.%	3.5	4.1	2.0	0.2	1.4	0.1