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Atomic and nanoscale chemical and structural changes in quenched and tempered 4340 steel

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Abstract

Atom probe tomography and transmission electron microscopy (TEM) have been used to determine the location and distribution of carbon and alloying elements associated with the complex structural changes that occur at the atomic and nanoscale in 4340 steel after quenching to martensite and tempering at 325, 450 or 575 °C. Tempering at 325 °C resulted in carbide formation without partitioning of chromium, manganese, molybdenum, aluminum, nickel or phosphorus, but with early-stage silicon rejection from the carbide. TEM verified the presence of cementite and the Bagaryatsky orientation relationship with the tempered martensite matrix and detected complex precipitate structures. Tempering at 450 or 575 °C developed concentrations of all alloying elements at ferrite–cementite interfaces: chromium, manganese and molybdenum partitioned into the cementite, and silicon, aluminum, nickel and phosphorus were clearly rejected from the cementite. These results provide direct evidence for staged cementite growth, where early-stage growth likely occurs under paraequilibrium conditions, followed by initial silicon redistribution and subsequent alloying element redistribution during late-stage growth. Tempering at 575 °C induced spheroidization of the cementite, loss of the Bagaryatsky orientation relationship, and phosphorus concentrations at Cottrell atmospheres within the cementite and at ferrite–cementite interfaces, correlating with early observations of the retardation of spheroidization by phosphorus.

Keywords: Steel; Tempering; Martensite; Atom probe tomography (APT); Transmission electron microscopy (TEM)

1. Introduction

Low-alloy, medium-carbon steels are austenitized, quenched to martensite and tempered at various temperatures to provide beneficial combinations of strength, toughness and fracture resistance. These steels are alloyed with substitutional alloying elements, such as chromium (Cr), manganese (Mn), molybdenum (Mo) and nickel (Ni), to provide good hardenability, i.e. depth of hardening, and resistance to softening during tempering. Although some alloy carbides may be retained, austenitizing is designed to dissolve all carbon and other alloying elements into the face-centered cubic crystal structure of the austenite. As a result, the martensite, formed by the diffusionless shear transformation of the austenite, is supersaturated with carbon and other alloying elements compared to their equilibrium concentrations in ferrite-cementite microstructures. These supersaturations are relieved by the precipitation of a variety of carbide types and morphologies during tempering [1].

It is well known that the alloying elements in steels retard softening during tempering, and Grange et al. [2] have quantitatively documented the effects of various

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elements in steels in retaining the hardness of as-quenched structures as a function of element content and tempering temperature. However, the mechanisms of alloying element redistribution as the saturation in martensite is relieved are only now beginning to be characterized by virtue of recent developments in atom probe tomography (APT).

At low tempering temperatures, carbon is mobile, but the diffusivity of the substitutional elements is too low to significantly influence the microstructure and substructure of the martensite [1,3]. Therefore, carbon plays a dominant role in the chemical and structural changes that occur, permitting the achievement of high strengths and moderate toughness after tempering below ~250 °C [1,3–5]. At tempering temperatures above 250 °C, the replacement of transition carbides and low-carbon martensite by cementite and ferrite occurs [1,6–9]. Higher tempering temperatures (>425 °C) provide sufficient thermal energy for substitutional elements to be mobile and influence structural coarsening, resulting in microstructures that exhibit combinations of high toughness and moderate strengths [1,4,5].

Babu et al. reported early-stage cementite growth under paraequilibrium conditions (i.e. dependent only upon carbon diffusion) in an Fe–C–Si–Mn steel after tempering at lower temperatures, whereas higher tempering temperatures and longer times resulted in Si and Mn partitioning [10]. Zhu et al. have shown no partitioning of Cr, Mo, Mn or Ni with the initiation of Si partitioning after tempering 4340 steel at 300, 350 or 400 °C for 1 h [11]. Tempering at 400 °C for 10 h resulted in significant Cr and Mn partitioning within the cementite and the rejection of Si and Ni [11]. The purpose of this study was to systematically evaluate the redistribution of interstitial and substitutional elements and the subtle structural changes that occur in 4340 steel at the atomic and nanoscale after quenching and tempering between 325 and 575 °C for 2 h using APT and transmission electron microscopy (TEM).

2. Experimental procedure

Aircraft-quality 4340 steel was used for this study; the composition of this steel in wt.% and at.% is provided in Table 1. Nominally 6.35 mm thick plate was austenitized under vacuum for 30 min at 845 °C, oil quenched, and tempered in air at 325 or 450 °C or under vacuum at 575 °C for 2 h. A sample was also encapsulated in quartz under ultra-high-purity argon, austenitized for 30 min at 845 °C, and then ice-water quenched for microstructural comparison with the oil-quenched condition.

APT was performed using a local electrode atom probe (Cameca Instruments Inc. LEAP® 4000X HR). Sections were machined from quenched and tempered steel plate and mechanically ground to a thickness of ~0.25 mm. Abrasive wire-cutting, followed by mechanical grinding, was then used to fabricate specimen blanks with a square cross-section, nominally 0.25 × 0.25 mm.

Specimen blanks were electropolished into sharp needles by a two-stage double-layer and micropolishing technique [12]. The electrolytes used were 25% perchloric acid (70%) in glacial acetic acid for rough polishing and 2% perchloric acid in 2-butoxyethanol for final polishing [12]. Focused ion beam (FIB) annular milling was then performed in an FEI Nova 200 instrument to sharpen each needle for APT. For the LEAP analyses, the specimen temperature was 50 K and the specimens were run in voltage mode. A pulse fraction of 0.2 and pulse repetition rate of 200 kHz were used.

TEM specimens were prepared by two different methods: electropolishing and FIB milling. The electropolishing solution used was 95% glacial acetic acid with 5% perchloric acid. Polishing was performed at room temperature in a Fishione automatic polisher at a potential of 25–30 V. The FIB foil preparation was performed in an FEI DB235 dual-beam FIB equipped with an Omniprobe nanomanipulator for foil extraction. TEM analysis was performed in an FEI TF30 Tecnai instrument operating at 300 kV.

3. Results

3.1. As-quenched martensitic microstructure

Oil quenching of the 4340 steel produced a lath martensitic microstructure. Martensite crystals contain dislocation densities as high as 10^{12} cm^{-2}, resulting from the lattice invariant deformation component of the diffusionless martensitic phase transformation [13]. Fine twins were also observed in some laths, as shown in the bright-field TEM images in Fig. 1.

Nanoscale, plate-like precipitates were also revealed by TEM, as shown in Fig. 2a. Selected-area diffraction (Fig. 2b) suggests that these precipitates are ε′ (also referred to as η) transition carbide [9,14,15]. Three reflections, labeled as A, B and C, are highlighted in Fig. 2b. Position A corresponds to a d-spacing of ~0.20 nm, consistent with $\{0\,2\,1\}_{\varepsilon'}$ planes. Position B corresponds to superlattice reflections from the ordered ε′ carbide and position C results from double diffraction between $\{0\,2\,1\}_{\varepsilon'}$ carbide and $\{1\,1\,0\}_{\alpha}$ martensite reflections. The pattern is consistent with two variants of the following orientation relationship [15]:

Table 1
4340 steel composition.

	C	Mn	Si	Ni	Cr	Mo	Cu	P	S
wt.%	0.42	0.78	0.26	1.78	0.83	0.24	0.03	0.010	0.003
at.%	1.92	0.78	0.51	1.67	0.88	0.14	0.03	0.018	0.005