Phase evolution and carbon redistribution during continuous tempering of martensite studied with high resolution techniques

Annika Vieweg [a,*], Erwin Povoden-Karadeniz [b], Gerald Ressel [a], Petri Prevedel [a], Tomasz Wojcik [b], Francisca Mendez-Martin [c], Andreas Stark [e], Jozef Keckes [d], Ernst Kozeschnik [b]

[a] Materials Center Leoben Forschung GmbH, Roseggerstrasse 12, A-8700 Leoben, Austria
[b] Institute of Materials Science and Technology, TU Wien, Getreidemarkt 9, 1060 Wien, Austria
[c] Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Franz Josef Strasse 18, 8700 Leoben, Austria
[d] Department of Materials Physics and Erich Schmid Institute of Materials Science, Montanuniversität Leoben, Jahnstraße 12, 8700 Leoben, Austria
[e] Helmholtz Zentrum Geesthacht, Institute of Materials Research, Max Planck Straße 1, 21502 Geesthacht, Germany

HIGHLIGHTS

- Carbon redistribution is essential during tempering of a steel to decrease hardness and distortions within the martensitic matrix.
- High resolution techniques, such as atom probe tomography, as well as in-situ synchrotron radiation were used.
- Position of carbon within the martensitic microstructure, as well as crystal structures of carbides are analyzed in-situ.
- A non-stochiometric epsilon carbide phase is found, nucleating from clusters at dislocations within the martensitic laths.

GRAPHICAL ABSTRACT
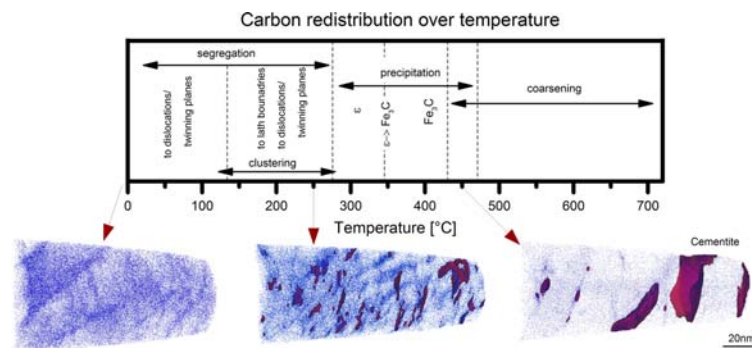
ARTICLE INFO

ABSTRACT

Using high resolution techniques, such as, 3D atom probe tomography, transmission electron microscopy and synchrotron radiation, the continuous tempering process of a 50CrMo4 steel is analyzed. Differences of continuous heating compared to isothermal holding at certain tempering temperatures are discussed. Focus is laid on in-depth characterization of phase development and carbon redistribution effects, such as, segregation and clustering. The results of this work suggest that segregation is the dominant effect at low temperatures ($<150\,°C$), while cluster formation within these segregated areas is prominent at intermediate temperatures (150–250 °C). Epsilon carbide is formed during continuous heating with off-stoichiometric chemical composition (270–350 °C). It transforms finally into cementite ($T > 350\,°C$).

© 2017 Elsevier Ltd. All rights reserved.

---

* Corresponding author.
 E-mail address: annika.vieweg@mcl.at (A. Vieweg).

1. Introduction

Tempering of martensite is a common heat treatment for controlling the hardness and toughness properties of structural steels. Tempering decreases the hardness of the martensitic matrix and increases toughness. The different phenomena occurring during tempering have been widely discussed [1–8]. They can be categorized into the four stages of tempering [2,4,9]. The first stage of tempering is described through epsilon carbide precipitation and occurs in a temperature range from 50 to 250 °C. Following this stage, retained austenite decomposes into bainite (230–320 °C) [2]. The third and fourth stages of tempering describe the continuous carbide evolution: cementite forms from epsilon carbides (200–350 °C) and secondary hardening carbides can occur between 500 and 650 °C.

Alternatively, the whole tempering process can be described through a sequence of redistribution processes of carbon within the complex microstructure. A zeroth stage of tempering at low temperatures, which describes clustering and segregation of carbon, has been proposed and discussed in this context [10–16].

Clusters are considered to represent Fe-C nano-agglomerates that appear randomly distributed within the polycrystalline microstructure, due to long-range interaction between the carbon atoms [17]. While, in earlier studies, these clusters were considered to have a crystal structure, sometimes described as tetragonal Fe_4C [16,18–20], recent studies based on atom probe tomography (APT) suggest a classification of clusters rather by a carbon concentration threshold in the order of 12–14 at.% C [8,21]. The term segregation is used to describe the enrichment of carbon at lattice defects, which is a rather prominent effect below 200 °C. Even at room temperature, the attraction of carbon to dislocations is an important mechanism for the evolution of C during tempering [2,12,22]. Segregation of C to dislocations can be classified as Cottrell atmospheres, where the carbon concentration is typically around 6–8 at.% [23,24].

In addition to clustering and segregation, precipitation of hexagonal epsilon carbide, $Fe_{2.4}C$, [25,26] is often observed in the early stages of tempering [2,11]. The formation of epsilon carbide is C diffusion-controlled and the precipitates mostly occur as a subgrain boundary film, precipitating along the $(101)_M$ planes in the $\langle 100 \rangle_M$ direction to the matrix [27–29]. The chemical composition of epsilon carbide is subject of discussion. While early studies suspect of stoichiometric carbon concentrations of 8–9 at.% carbon [29], recent experiments indicate a stoichiometric composition of 30 at.% C [30] for the epsilon carbide.

This diversity of carbon-related mechanisms gives rise to numerous still open questions within this field of research: 1) each of the above mentioned publications focused either on segregation or clustering, and did not discuss the question, which of these phenomena is dominant, 2) the chemical composition of epsilon carbide and clusters have been discussed but different compositions are claimed, and 3) the above presented investigation focuses on the evolution of carbon segregation and precipitation as well as carbide compositions after a tempering procedure at a certain temperature and time. No in-situ analyses have been conducted to observe the precipitation mechanisms and chemical compositions, though. Caballero et al. [21] and Clarke et al. [8] used atom probe tomography to analyze the chemical composition of clusters and carbides, but these studies were conducted after long holding times (up to 2 h) at various tempering temperatures. Beneteau et al. [7] used synchrotron radiation to evaluate the tetragonality of martensite in-situ during heating but did not account for phase changes and chemical compositions. Additionally, the influences of retained austenite, if present, are mostly neglected in the studies listed above.

In the present study, the redistribution of carbon in the course of a continuous fast tempering process with 10 K/s, representing a typical inductive heating process used in industry, is characterized by a combination of high resolution experimental techniques. High energy X-ray diffraction (HEXRD) is used in-situ to examine the phase fractions and distortion within the material during heating in addition to a

dilatometry signal. The microstructures are analyzed through interrupted quenching in the course of the tempering process from different temperatures and the carbon distribution is examined by means of transmission electron microscopy (TEM) and 3D atom probe tomography (3D-APT).

Through the combination of these high-resolution techniques, the dynamics and interaction of carbon clustering, segregation and precipitation within a 50CrMo4 steel during tempering is analyzed and discussed in detail and, therefore, the understanding of the processes is enhanced. Additionally, the work is complemented by a discussion of the interaction and kinetics of clustering, segregation and precipitation processes.

2. Experimental

The steel investigated in this study is a 50CrMo4 steel with the chemical composition as listed in Table 1.

For the dilatometer experiments, cylindrical samples with a diameter of 4 mm and a length of 10 mm were manufactured at half radius of a rolled material. Samples were austenitized at 850 °C for 20 min and subsequently quenched at a rate of 280 K/s. To analyze the complete tempering process, the samples were heated to 700 °C with 10 K/s directly after quenching, held there for 1 min and cooled to room temperature with 10 K/s. The martensite start temperature of this steel, $M_s = 270$ °C, was already evaluated in earlier studies [31]. To study different tempering states, samples were heated to specific temperatures (150, 200, 250, and 320 °C) with 10 K/s and directly quenched to room temperature with the same quenching rate (280 K/s). These samples were subsequently analyzed by TEM, APT and Vickers hardness testing (HV1).

For in-situ phase analysis, HEXRD measurements were conducted at the HEMS beamline (P07) at Petra III [32], where a Bähr DIL805A was placed into the beam [33]. For these measurements, the as-quenched martensitic microstructure was placed within the dilatometer at the beamline. In order to penetrate the 4 mm thick samples, high energy X-rays were used with a photon energy of 87.1 keV, corresponding to a wavelength of 0.14235 Å. The beam size was 0.7×0.7 mm. The resulting diffraction rings were recorded with a Perkin Elmer XRD1621 flat panel detector with a frame rate of 5 Hz and an exposure time of 0.2 s. To evaluate phase fractions and full width half maximum (FWHM) values, selected peaks of the phases were fitted using a Pseudo Voigt fit function. For every phase, a characteristic peak was chosen, which had little or no adjacent peaks of other phases, to minimize the effect of overlapping signals. For ferrite/bcc (space group: I m − 3 m), this was the {200} peak, for austenite/fcc (space group: F m − 3 m) the {200} peak, for cementite/Fe_3C (space group: P n m a) the {301} peak and for the epsilon carbide/hcp (space group: P 63 2 2) the {112} peak. The ferrite peak is representing the martensitic matrix, since the martensite is identical with the ferritic matrix, despite the fact that it is supersaturated with carbon and exhibiting tetragonal distortion. Phase fractions are not evaluated quantitatively, but the ratios of the peak area of a certain phase to the sum of all peak areas is depicted in style of ASTM-E973-13 [34].

The TEM analysis was carried out on a FEI Tecnai F20, equipped with a field emission gun at an accelerating voltage of 200 kV. The samples were electrochemically etched on a Struers Tenupol 5, using a 7% solution of perchloric acid at temperatures around − 10 °C.

The 3D–APT measurements were carried out at a LEAP™ System 3000XHR in voltage mode at a temperature of 60 K with a pulse

Table 1
Chemical composition of the 50CrMo4 steel used in this study.

	C	Mn	Cr	Mo	Si	P	S	Fe
wt%	0.49	0.71	1.05	0.18	0.27	0.016	0.010	bal.
at.%	2.23	0.71	1.10	0.10	0.53	0.028	0.017	bal.