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Effects of carbon and nitrogen concentrations on precipitation sequence during tempering of martensitic steels investigated by advanced experimental methods and modeling

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Abstract

Advanced characterization techniques and modeling are used to get new insight on the microstructural evolutions occurring during the tempering of low-alloyed steels with initial martensitic microstructure. Tempering temperatures from 150°C to 600°C, are considered to make vary the metallurgical phenomena activated, from carbon segregation to defects to precipitation of different types of carbides (transition, cementite, alloyed). A large range of carbon compositions, from 0.1 to 0.7 wt.% are investigated, with the same main experimental technique: in situ HEXRD at synchrotron beamlines, with complementary post mortem fine-scale characterizations by TEM and 3D-APT. In the middle of this range (~0.3wt.%), the usual sequence is observed: successive precipitation of transition and cementite carbides. New observations concern the carbon concentrations outside this range. For high carbon concentrations (~0.6wt.%), the same sequence occurs but the martensite/ferrite matrix remains highly supersaturated in carbon compared to equilibrium, for a long time and even after the precipitation of cementite. For low carbon concentrations (~0.1wt.%) most of the carbon starts to segregate at defects (dislocations, lath boundaries). This enters in competition with the transition carbides which are almost fully hindered, whereas cementite precipitates afterwards. Two previous models from literature are combined to predict the concomitant kinetics of carbon segregation and precipitation. Segregation puts the transition carbides at a disadvantage with cementite and for this reason, the latter precipitates earlier than usually reported. The effects of nitrogen enrichment (up to ~0.4 wt.%N, context of carbonitriding thermochemical treatments) in austenite domain of stability (before the martensitic quench) are also investigated. In low-alloyed steel considered (23MnCrMo5), nitrides are formed upon enrichment (CrN, MnSiN₂). This has a strong impact on the precipitation sequence, compared to model systems previously investigated (Fe-N, Fe-C-N).

Introduction

Many steel products, including recently developed 3rd generation AHSS, contain martensite, and thermal treatments of tempering may be applied to improve ductility: the steel is submitted to heating up to temperature from about 150°C to 600°C, depending on the microstructures and properties looked after. The sequence of microstructural evolutions occurring upon tempering are well established (e.g. [1]). The carbon first segregates at defects (dislocations, lath boundaries), then it precipitates to form transition carbides, cementite carbides and secondary carbides, in the case of alloys containing carbide-forming elements (Mo, Cr, V...). In addition, retained austenite, if present in the initial martensitic microstructure, may decompose to ferrite and cementite. Dislocations recovery also occurs if the temperature is high enough. Recent development of experimental techniques provides new insight on the microstructural evolutions during tempering of steels.

This contribution summarizes several studies addressing these microstructural evolutions by using advanced characterization techniques at different scales: in situ High-Energy X-Ray Diffraction experiments at synchrotron beamlines, 3D atom probe tomography (APT) and High-Resolution Transmission Electron Microscopy (TEM). In a steel with higher carbon concentration (0.67wt.%C), the distribution of the carbon inside the microstructure will be monitored with precision, allowing to establish the precipitation kinetics and to show that the microstructure may stay out of thermodynamic equilibrium even after tempering for long time and at high temperature [2]. In a series of steels with lower carbon content (0.1-0.3wt.%C), a significant proportion of the carbon will segregate to defects and perturbate the usual sequence. This will be studied both by experiments and modeling [3]. In the context of

thermochemical treatments of carbonitriding followed by tempering, another study addressing the effects of an enrichment in nitrogen on the precipitation sequence in a low-alloy steel will be presented. So far, mostly model systems such as Fe-N of Fe-C-N have been considered (e.g. [4]). The precipitation sequence needs to be studied in low-alloyed steels containing nitride-forming elements such as Cr, Mn or Si.

Monitoring the distribution of carbon by in situ HEXRD (high-carbon steel)

The microstructural evolutions upon tempering of a nanobainitic steel (Fe-0.67C-1.7Cr-1.67Si-1.0Mo-0.5V, wt.%) with additions of Mo and V have been studied² in order to develop a new class of alloys combining nanobainite microstructure with secondary precipitation (alloyed carbides containing Mo and V), for applications at temperatures up to 250°C. This paper summarizes one part of this study, focusing on the possibilities given by in situ HEXRD experiments at synchrotron beamlines to investigate carbides precipitation, austenite decomposition and carbon redistribution inside the microstructure.

Tempering treatments consist of continuous heating at 1°C/s from room temperature to 1000°C. Three initial microstructures were produced by austenitizing at 1150°C followed by gas quench, then quench in liquid nitrogen to form martensite (LNM), or gas quench to room temperature (RTM), or bainite transformation at 250°C for 20 h (NB, nanobainite). The initial fraction of retained austenite is equal to 7%, 21% and 32% respectively, according to XRD. Figure 1 shows XRD diffractograms focusing on an angular window containing diffraction peaks of all carbides. In all three microstructures, the precipitation sequence of transition carbides (TCs) followed by cementite and alloyed carbides (MC) is put into evidence. The diffraction peaks of the carbides are clearly defined, thanks to the high flux and the high energy of the beam, and this allowed to quantify the fraction of carbides. The precipitation kinetics established in situ by HEXRD were in good agreement with dilatometry experiments. Thanks to the analysis of the cell parameters, the distribution of the carbon among the carbides, the bainitic ferrite, the martensite and the austenite could be established with precision. For instance, the NB microstructure shows less transition carbides than LNM and RTM, because of the higher fraction of retained austenite, and because some carbon partitioned to the latter phase during the bainite transformation [5]. Full analysis of these experiments is presented in [2].

Several deviations from thermodynamic equilibrium have been observed upon tempering. First, the austenite remains stable for a long time: several hours of isothermal holding at 650°C and 700°C and even longer time at lower temperature. This has been ascribed to Mo and V which would reduce ferrite/austenite interface mobilities by solute drag, or to the pinning of these interfaces by carbides.

Other deviation from equilibrium regards the supersaturation of the carbon in solid solution inside the martensite or the bainitic ferrite. Figure 1b shows the evolution of the c/a ratio of the quadratic cell of the martensite/bainitic ferrite for all three initial microstructures. It remains significantly higher than 1 up to high temperatures, showing that the crystallographic structure remains tetragonal. In agreement with other studies (e.g. [6]), it suggests that carbon may remain in supersaturation in the matrix, despite the heating up to high temperatures (enhancing carbon diffusion) and the formation of the transition and cementite carbides.

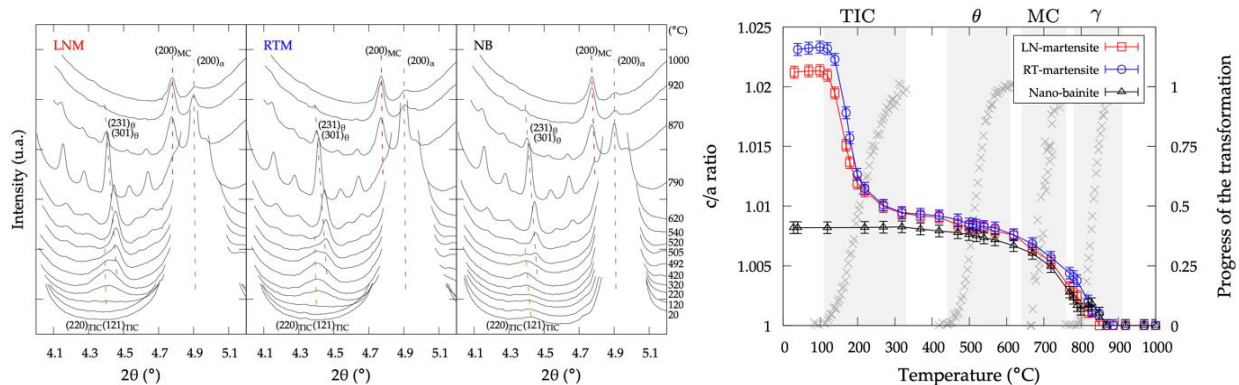


Figure 1: a) Reduced angular windows of experimental 1D diffractograms displaying the phase transformations during continuous heating at 1°C/s for LNM, RTM and NB microstructures (temperatures are indicated at the right). Orange, blue, red and green dotted lines correspond respectively to transition-iron- carbides, cementite, MC carbides and martensite/bainitic ferrite. b) Tetragonal ratio (c/a) evolution of martensite/bainitic ferrite during the continuous heating treatment at 1°C/s for the three initial microstructures. The grey curves represent the precipitation kinetics (progress of the transformation) extracted from dilatometry for LNM microstructure, and grey areas are the temperature ranges of each precipitation kinetics.

Competition between carbon segregation and carbides precipitation (low-carbon steels)

The consequences of carbon segregation at defects on the sequence of precipitation in low-C steels (0.1, 0.2 and 0.3w.%C) have been investigated with experimental characterizations at several scales (APT, HEXRD, TEM) and by the modeling of all mechanisms involved (carbon segregation, carbides nucleation, growth and coarsening). Tempering treatments consist of heating from room temperature at 10°C/s and isothermal holds at 300°C and 400°C. Before tempering, austenitization followed by water quench was applied to samples with dimensions 10x4x1.5 mm cut out cold rolled plates of low-alloyed steels (with Mn and Cr as main alloying elements).

APT observations show that the segregation of the carbon at the defects already starts during the water quench. Figure 2a shows the reconstruction of an APT tip from 0.2C steel sample, after austenitization, quench into water and aging for several months at room temperature. The carbon is segregated to dislocations and the carbon concentration in the Cottrell atmospheres is about 10at.%, in agreement with previous studies (e.g. [7]). This means that most part of the carbon is segregated in this steel, according to mass balance and knowing the dislocation density, which was established by XRD using the modified Williamson-Hall method [8].

The consequences of carbon segregation to defects on carbides precipitation sequence were investigated experimentally by in situ HEXRD experiments. Figure 2b shows a series of diffractograms obtained upon heating at 10°C/s for the 0.3C steel. The carbides are more difficult to detect than in the higher-C, steel mentioned above (Figure 1). Except cementite in 0.3C steel, the fraction of the carbides could not be quantified due to their low size and low fraction. Nevertheless, the temperature domains at which the respective transition and cementite carbides are detected could be estimated. In 0.1C steel, the transition carbides are almost fully suppressed. In 0.2C steel, their fraction is low, whereas they are clearly detected in 0.3C steel. The low fraction of the TCs in lower-C steels is ascribed, in first analysis, to the competition with the segregation of carbon. Contrary to the TCs, the sequence of nucleation, growth and coarsening of cementite is not influenced by the segregation of carbon, according to HEXRD experiments and to measurements of the cementite carbides sizes on the basis of TEM micrographs.

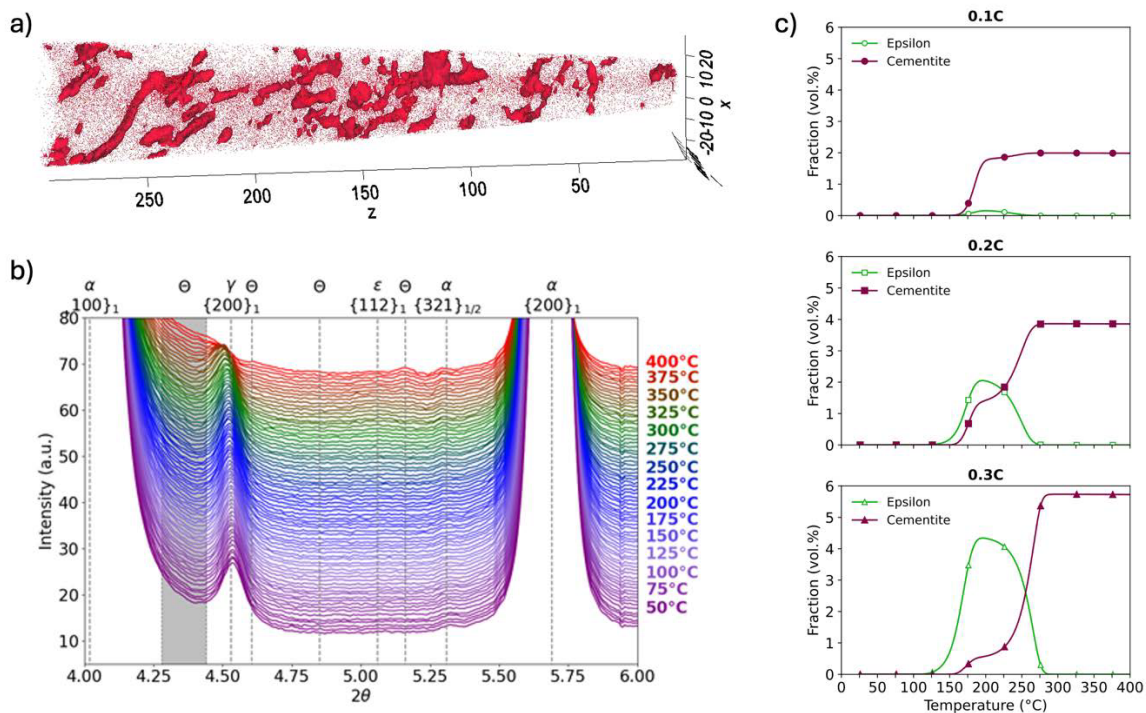


Figure 2: a) Reconstruction of an APT tip of a water-quenched 0.2C sample with several linear segregations corresponding to Cottrell atmospheres at dislocations. 4 at.% carbon isosurfaces are shown, and the axes are in nanometers. b) Diffractograms obtained by in situ HEXRD during continuous heating at 10°C/s up to 400°C of the 0.3C steel. c) Simulation results of the evolutions of the carbides' fractions upon heating at 10°C/s up to 400°C for the 0.1C, 0.2C and 0.3C steels.

A modeling study was done to investigate further the sequence of precipitation. Indeed, the experiments only gave a partial view of it, because of the low detectability of the carbides. A new mean-field and physically based model has been introduced to address specifically the impact of the segregation on the precipitation of the carbides. This model combines two previous ones, addressing respectively the segregation of the carbon at dislocations [9] and the precipitation of the transition and cementite carbides [2].

The segregation model allows to predict the kinetics of carbon segregation to dislocations. Its main parameters are the dislocation density, the diffusion coefficient of carbon and the trapping energy of the carbon at the dislocation. It predicts the carbon concentration inside the Cottrell atmospheres and inside the remainder of the matrix, as a function of time and temperature. The simulations confirm that the segregation of carbon already starts during the quench into water. The segregation strengthens during aging at room temperature and during the first stage of heating, upon tempering.

The consequence of segregation is to make the distribution of carbon heterogeneous, with carbon-rich Cottrell atmospheres surrounded by a matrix poor in carbon. A previous nucleation-growth-coarsening model has been modified to evaluate the consequences of these heterogeneities on the precipitation of the carbides. Based on previous studies, it is assumed that the TCs nucleate homogeneously inside the matrix, and the cementite heterogeneously at the dislocations. (Note that other mechanisms for the formation of the TCs are possible according to literature, as discussed in [3]). According to the kinetic simulations, the depletion of the matrix hinders the formation of the TCs, whereas the enrichment in the Cottrell atmospheres enhances the cementite carbides. This puts the TCs at a disadvantage compared to cementite.

The simulations also show that the effect of segregation is stronger for decreasing steel carbon content. Figure 2c shows the evolutions of TCs and cementite fraction as a function of temperature upon heating at 10°C/s in 0.1, 0.2 and 0.3C steels. In agreement with the experiments, the TCs are almost fully suppressed in 0.1C steel, mitigated in 0.2C steel, while a significant fraction is formed in 0.3C steel. In latter steel, the usual precipitation sequence is retrieved, with TCs followed by cementite. But in 0.1C and 0.2C steels, due to the mitigation of the TCs, the cementite is predicted to form at lower temperatures than usually reported. In 0.2C steel, it also forms concomitantly with the TCs, instead of sequentially.

From these simulations, it comes out that the mitigation of the TCs and the modified sequences do not come directly from the competition segregation / precipitation, as was suggested by the experiments, but from the heterogeneities in carbon that are produced inside the microstructure, and mostly before the precipitation of the carbides.

Effects of nitrogen on precipitation sequence

The effects of an enrichment in carbon and nitrogen, up to 0.6wt.%C and 0.5wt.%N, on the precipitation sequence upon tempering of a low-alloy 23MnCrMo5 steel have been investigated by combining TEM observations, dilatometry and in situ HEXRD experiments. Tempering treatments consist of continuous heating at 1°C/s from room temperature followed by isothermal holding at 160°C (representative of industrial treatment) and up to 500°C. Tempering is preceded by austenitization at 900°C followed by quench into cold oil (OQ) or water (WQ).

Figure 3 shows TEM characterizations of a 0.4wt.%C-0.5wt.%N steel after austenitization and OQ. The as-quenched microstructure consists of a martensitic matrix with CrN and MnSiN₂ nitrides. Both precipitates show a large distribution of sizes, from a few tens of nm to about 1 μm. The largest nitrides tend to be located at prior austenite grain boundaries and tend to show a faceted morphology, instead of a more globular one for the smaller nitrides. Some VN and AlN nitrides with sizes between 50 and 100 nm and agglomerated with the CrN nitrides were also detected. These observations in as-quenched state agree with previous studies [10,11]. It is thought that the CrN and MnSiN₂ nitrides are formed during the enrichment treatment of carbonitriding at 900°C.

New observation from High Resolution TEM is the presence of Fe₁₆N₂ nitrides inside the matrix (Figure 3). According to HEXRD experiment (not shown here), epsilon transition carbides are also present in the as-quenched microstructure. So far, Fe₁₆N₂ nitrides have not yet been detected by HEXRD and epsilon nitrides have not been detected by TEM. Nevertheless, these observations show that the martensitic matrix underwent significant self-tempering during the oil quench.

The presence of Fe₁₆N₂ nitrides precipitated homogeneously inside the matrix shows that some nitrogen remains inside the matrix after the carbonitriding treatment at 900°C (i.e. CrN and MnSiN₂ nitrides did not consume all the nitrogen). However, despite the presence of nitrogen inside the matrix, the sequence of precipitation observed upon tempering essentially corresponds to the usual one associated with the precipitation of the carbon: precipitation of transition carbides followed by cementite with, besides, the decomposition of retained austenite. (The corresponding TEM and HEXRD experiments are not presented here). CrN and MnSiN₂ nitrides only undergo small variations of their morphology and fraction.

Surprisingly the Fe₁₆N₂ nitrides are still observed after significant tempering: 1h at 160°C or even 1h at 300°C. No Fe₄N nitrides have been observed so far, as one might have expected from the precipitation sequences established in model Fe-N and Fe-C-N steels [4]. Put together, these experimental results suggest that the precipitation of CrN and MnSiN₂ nitrides at high temperature during the carbonitriding treatment strongly depletes the matrix in nitrogen, which then mostly undergoes redistribution of carbon upon tempering. However, further tempering experiments are planned with samples having higher concentration in nitrogen than in previous experiments (about 0.5wt.%N instead of 0.2wt.%N). More characterization techniques (APT, TKD, in situ TEM, ASTAR...) will also be used for complementary observations.

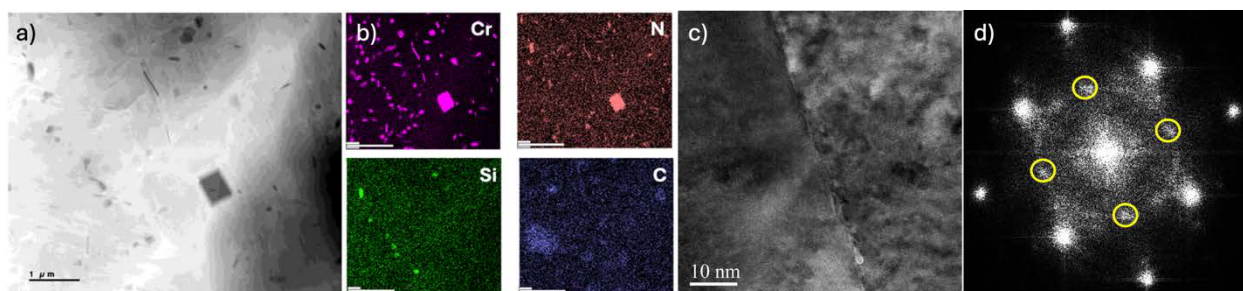


Figure 3. TEM observation of the microstructure after carbonitriding at 900°C (0.4wt.%C, 0.5wt.%N) following by quench into oil. a) STEM (nitrides in dark contrast); b) EDX maps corresponding to a) showing CrN and MnSiN₂ nitrides; c) Bright-Field HRTEM micrograph; d) FFT (right-hand grain in d), some Fe₁₆N₂ spots are circled.

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