Importance of Microstructure on Precipitation in Tempering of Martensitic Steels

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Abstract. Precipitation hardening is one of most effective strengthening mechanisms in steels, and much research has been performed in the past. To evaluate the contribution of precipitates, the quantitative features of precipitates including mean size and particle size distribution etc., are vital and needed. However, the predictive modeling of precipitation is still a challenge so far, especially on a quantitative level. Thus, in the present work, precipitation of carbides after tempering of martensitic Fe-Cr-C alloys, consisting of hierarchically arranged substructures within the prior-austenite grains, namely packets and blocks of individual laths, up to 1000h has been investigated. Experimental measurements using electron microscopy and modeling using a Langer-Schwartz theory with the Kampmann-Wagner -Numerical (KWN) method have been conducted. The importance of a proper definition of the initial microstructure for predictive modeling is discussed, in terms of the comparison of calculated and experimental results.
1. Introduction

Since precipitation hardening is one of the most strengthening mechanisms in metallic alloys, further understanding and modelling of precipitation behavior has attractive numerous attentions in the past decades [1-4]. Martensitic steels have been widely used in many industrial fields such as tool steel, after subjected to heating treatment e.g. tempering to improve its toughness or/and strength [1]. During tempering, release of internal stresses generated from the martensitic transformation, diffusion of saturated solid solution atoms and annihilation of dislocations together with movement of various boundaries cause softening of steels [5]. While, dispersion precipitates form in the matrix as carbide-formed alloying elements added and strengthen the steels after tempering. To evaluate the contribution of precipitates on the strength, parameters like size, volume fraction, size distribution etc of the precipitates are needed [6-8]. By measuring and controlling these precipitation parameters, it is possible to tune and optimize properties of the steels, not only the mechanical properties such as strength and ductility but also creep resistance, wear resistance and degradation properties [8]. However, due to their very fine size and variation with the tempering conditions, quantitative parameters only from the experimental investigations using transmission electron microscopy (TEM), atom probe tomography (APT) and small-angle scattering (SAS) are always time-consuming and costly [9-11]. With recent progresses in both theoretical and experimental analysis of steels, inspired by the trends in materials design towards integrated computational materials engineering (ICME) [7], modelling to predict e.g. the mechanical property evolution from the microstructural evolution during tempering is becoming more tractable. This can provide an efficient way for a new alloy design and process optimization. Further improvements of the predictive capabilities of models correlating microstructure with nucleation, growth and coarsening mechanism of precipitates depend on an improved understanding of the microstructure and chemical composition evolution, as well as implies the control mechanism of precipitation at the interface of matrix/precipitates [12,13].

The purpose of the present work is to investigate the microstructure evolution and precipitation behavior in a Fe–0.15C–1Cr model alloy tempered at 700 °C. This alloy was chosen since it provides an excellent model for systems where it is necessary to handle diffusion of both interstitial elements and substitutional elements simultaneously. Meanwhile, the Langer–Schwartz–Kampmann–Wagner (LSKW) modeling [14-15] scheme as implemented in TC-PRISMA for predictive modeling of precipitation is assessed by comparing with experimental results from TEM analysis on carbon extraction replica samples and thin-foil samples.

2. Experimental procedures

The chemical composition of the investigated alloy is given in table 1. An isopleth phase diagram for Fe–0.14 wt% C–xCr and for the investigated steel, calculated using Thermo-Calc [16] and the TCFE12 database [17] are shown in figure 1. It can be seen in figure 1 that for the alloy the stable phases at 700 °C are ferrite, cementite(M2C) and M2C3, and that below 524°C ferrite and M2C are the stable phases. It should be noted that the chemical composition of the present alloy is located nearby the border of ferrite and M2C two-phase region, and contains a very small fraction of M2C3 (0.0017 V.%) at equilibrium accordingly.

Small specimens (10×10×1 mm3) were austenitized at 1100 °C for10 min and quenched in brine. For the as-quenched specimen, figure 2 shows a fully lath martensite as observed in low carbon low alloy steels. The as-quenched samples were thereafter tempered at 700 °C for 5 s, 5 min, 30 min, 5 h, 100 h and 1000 h in the Sn-Bi metal bath (5 s and 5 min), a tube furnace with Ar gas (30 min) and in evacuated quartz tubes (5, 100 and 1000 h). To study the as-quenched microstructure and its evolution during tempering, an optical microscope(OM), a JEOL JEM-2100F microscope operating at 200 kV and a JEOL JSM-7800F FESEM scanning electron microscope (SEM) equipped with an electron backscatter diffraction (EBSD) detector and electron channeling contrast imaging (ECCI) detector operated 15 kV were applied. TEM thin-foil and carbon extraction replicas were prepared for identification and quantification of precipitates. Quantification of the precipitates was performed in a scanning transmission
electron microscope (STEM). For each tempered sample, approximately 1000 precipitates were imaged from several random regions and their mean size was calculated.

Table 1. Nominal chemical composition of the investigated alloy (in wt. %).

| Alloy      | C  | Cr  | Si  | Mn | S  | Al | Cu  | Ni |
|-----------|----|-----|-----|----|----|----|-----|----|
| 0.14C-0.98Cr | 0.14 | 0.983 | 0.021 | 0.07 | 0.06 | 0.014 | 0.011 | 0.017 |

Figure 1. isopleth phase diagram for Fe–0.14 wt% C–xCr and for 0.14C–98Cr steel

Figure 2. LOM microstructure of the as-quenched specimen

3. Modeling
In the present study the precipitation module (TC-PRISMA) as implemented in the Thermo-Calc software was used for modeling the precipitation during tempering. The details of the models can be found in [3] but for the convenience of the reader a short overview will now be given. All models assume that the particles are spherical with no diffusions inside them. Different types of growth models are implemented, for example, simplified, advanced, Para equilibrium and Neglect partitioning local equilibrium (NPLE). The difference between each model exists in the tie-line taken and the interface condition. In the simplified treatment a constant tie-line taken across the bulk composition is assumed, whereas for the advanced treatment a new tie-line is determined at each time step [16]. In the present work the Para and simplified treatment are used for quantitative predictions and comparison with experiments, to generate a better understanding of the operating growth mechanism. The thermodynamic and kinetic data for the simulations were taken from the TCFE12 and MOBFE7 databases. As
mentioned earlier, M$\textsubscript{3}$C and M$\textsubscript{7}$C$_3$ are stable carbides at 700°C, thus both precipitates are included in the modeling. The interfacial energy between the precipitates and the matrix is critical for quantitative predictions and here the interfacial energy ($\sigma_c$) calculated based on a Becker’s model $^{[18]}$ in combination with the thermodynamic data from TCFE12 was adopted directly, that are 0.22019J/m$^2$ for M$\textsubscript{3}$C and 0.29691J/m$^2$ for M$\textsubscript{7}$C$_3$, respectively. Furthermore, the number of potential nucleation sites as another critical parameters is selected as the dislocation density 2.13×10$^{15}$ m$^{-2}$ in the martensitic structure since most nucleation events occur at dislocations $^{[10]}$.

4. Results and discussion

The stability diagram of the investigated steel is presented in figure 3. In addition to the austenite and ferrite phases, the equilibrium carbides, M$\textsubscript{3}$C, M$\textsubscript{7}$C$_3$ and M$_{3}$C$_{2}$, are represented in the temperature range of 500 ~ 900°C. By which, the relative stability of all carbides is possible to calculate when these stable carbides are suspended. The dashed line in figure 3 show the metastable diagram after the stable carbides are suspended. Furthermore, it is shown that M$\textsubscript{3}$C carbides are not stable at temperatures higher than 782 °C and that M$_{7}$C$_{3}$ carbides are not expected to be observed, as they are only stable at temperatures below 702 °C.

![Figure 3](image_url)

Figure 3. The stability diagram of 0.14C-0.98Cr steel

The tempered microstructure of specimens at 700°C for 5s up to 1000 h are presented in figure 4. After tempering for 5s, lath martensite is similar to that in the as-quenched one, with features of long and thin lath with straight boundaries. Noted that, plenty of carbides, showing as black or white points due to channeling contrast, are clear seen at intra- and inter-lath. This is consistent with the TEM observation (figure 5(a)). With the prolonged tempering, the width of lath as well as the size of precipitates are increased gradually, see figure 4 (b–f) and figure 5(b). After tempered for 1000 h, large carbides are most located at various grain boundaries. Meanwhile, the specimen still keeps its hierarchical structure, i.e. lath, sub-/block packet, even after 1000 h, see figure 4(h). Interestingly, fine elongated ferrite with equivalent circle diameter (ECD) of 1.9±0.5 µm was reserved after such long time tempering, see figure 4 (f, g, h), which provide one simple way to obtain fine grain size microstructure only by quenching and tempering, as reported earlier $^{[10]}$. During tempering, migration of high angle grain boundaries is pinned by the formed carbides, result in a slow movement of grain boundaries and coarsening rate of substructure. This type information of microstructure evolution together with its pinning effect are important to acquire as the mechanical property modelling aims to consider the grain boundary strengthening as an important factor.

Figure 5 shows the typical TEM microstructure for thin foils and carbon replicas. After identified by selected area diffraction patterns (SADPs) by TEM, not shown here, all the
precipitates in the present steels are M$_3$C, no other carbides are found, although M$_7$C$_3$ carbides are expected to form. The absence of M$_7$C$_3$ carbides in the present work maybe mainly due to: 1) their very small volume fraction or 2) uncertainty of the database, the chemical composition is located nearby the region with only M$_3$C carbides as the stable carbide at 700°C.

Figure 4. ECC images of as-quenched specimens after tempering at 700°C for: (a) 5s; (b) 5 min; (c) 30 min; (d) 5h; (e) 100 h; (f) 1000 h; OM (g) and IPF (h) maps for 1000 h

Figure 5. Typical TEM for thin foil and carbon replicas samples: (a) 5s; (b) 30 min
The mean radius and volume fraction of $\text{M}_3\text{C}$ from TC-Prisma simulations and experiments are presented in figure 6. For the simulations, both simplified and PARA growth models are plotted to give insight of growth mechanism. The mean radius of $\text{M}_3\text{C}$ increases from 25±5 nm at 5 s to 682 ±45 nm at 1000 h, while the volume fraction keeps constant at the range of 0.015±0.04 v.% indicating a coarsening stage even after 5 s at 700 °C. It is clearly that the volume fraction of carbides can be predicted very well using both growth models with default input data from misstructure and chemical composition. However, the PARA growth model significantly overestimates but the Simplified growth model underestimate the mean radius of $\text{M}_3\text{C}$ carbides, especially at the very earlier stage, see figure 6. In general, there is no Cr diffusion occurs at the nucleation of $\text{M}_3\text{C}$ carbides, which is more like the PARA condition [10,11]. As the tempering continuous Cr starts to partitioning to $\text{M}_3\text{C}$ carbides from the matrix, that is why the agreement between the calculated values by Simplified growth model and experiments is good at the late stage. Other parameters as input data should be considered for a better agreement, such as grain boundaries as active nucleation sites. As seen from figure 4 and figure 5, in addition to at dislocations the precipitates are also nucleated at various boundaries. Furthermore, carbon trapped by dislocation or others defects are need to escape first prior to form $\text{M}_3\text{C}$, this could delay the start point of PARA growth model [19]. At the other hand, a higher number of nucleation sites refine the mean size of precipitates at a given volume fraction. Thereafter, to improve the predictive modelling of precipitation quantitative data of such as various boundaries and carbon suggestion etc., are needed.

![Figure 6](image)

**Figure 6.** Comparison of calculation and experiments for (a) Mean radius and (b) Volume fraction of carbide evolution during tempering

5. **Summary**

The precipitation behavior in a 0.14C-0.98Cr steel during tempering at 700°C for 5 s up to 1000 h has been investigated together with microstructure evolution. Only $\text{M}_3\text{C}$ carbides is observed through the tempering, and forms at both intra- and inter-lath. The mean radius of $\text{M}_3\text{C}$ increases from 25±5 nm at 5 s to 682 ±45 nm at 1000 h, while the volume fraction keeps constant at the range of 0.015±0.04 v.%. By comparison, the PARA growth model significantly overestimates but the simplified growth model underestimate the mean radius of $\text{M}_3\text{C}$ carbides, especially at the very earlier stage.

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