A study of carbide dissolution in bearing steels using computational thermodynamics and kinetics

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Abstract. This paper provides a study of carbide dissolution during heating of bearing steel using computational thermodynamics and kinetics. 100Cr6 steel was used for the experimental work and calculations using the Thermo-Calc and DICTRA. Carbide dissolution was calculated at different full and intercritical austenitization temperatures from 840 to 1200 °C. The calculations also give the distribution of the alloying elements at carbide and austenite phase boundaries. In experimental work, SEM was used to study microstructures. SEM micrographs were evaluated with line intercept technique and carbide size and quantity were determined. The experimental results were compared with calculations providing good correlation.

1 Introduction
Traditional production cycle of bearing steels include intercritical austenitization to avoid grain coarsening and cracks formed during quenching. However, intercritical austenitization causes to remaining coarse spherical carbides in the final microstructure of bearing parts. It is well known that carbide size and dispersion determine the lifetime of bearings, because coarse carbides providing appropriate nucleation sites for crack propagation and growth [1-3].

In the last decade, a number of researchers have studied computational thermodynamics and kinetics mainly concerned with carbide formation and dissolution in bearing steels. Luzginova et al. [4] studied cementite spheroidization under occurrence of divorced eutectoid transformation reaction. They calculated the time dependence of the cementite fraction and the cementite particle spacing at the different austenitization temperatures with DICTRA. Following the spheroidization, growth of cementite in ferrite was also investigated by Song et al. [5]. According to their DICTRA simulations during cementite precipitation in ferrite, Cr and Mn were partitioned under non-partitioning local equilibrium (NPLE) mode. Si cannot be dissolved in cementite and resulted spikes in Si profile due to local equilibrium (LE). Recently, the carbide dissolution of a bearing steel during the intercritical austenitization was studied by Zhang et al. [6]. They have reported that austenite growth controlled by the diffusion of C during the initial step without redistribution of Cr. In second step, when the carbon content reaches the iso-activity in austenite, the dissolution mechanism becomes partitioning local equilibrium (PLE) mode controlled by the diffusion of Cr. In work by Zhao et al. [7], the cementite dissolution was simulated using MTData software. A cementite radius of 1.88 μm was assumed. Volume fraction of cementite was calculated as a function of time at 860 °C and compared to results from dilatometry and microscopy. It was found that the cementite dissolution is rapid at the initial time and then slow down depending on C and Cr at the interface between austenite and cementite phases. Epp et al. [8] also tried to simulate cementite dissolution using ThermoCalc calculation and in situ X-ray measurements. Cementite content was calculated as 17 wt-% and
measured as 16.3 wt-% using XRD. However, the complete dissolution was not reached at 900 °C after 42 min as predicted at the equilibrium state.

In the present investigation, the carbide dissolution was investigated at different austenitizing temperatures below and above the A_{cm} temperature. Spheroidizing heat treatment has been applied to obtain the initial microstructure. The spheroidizing annealed samples were then austenitized by holding at different temperatures between 840 and 1200 °C. Carbide dissolution has been also calculated using Thermo-Calc and DICTRA software in order to evaluate microstructural variations resulting from different heat-treatment conditions.

2 Experimental

The chemical composition of bearing steel is presented in Table 1. Heat treatments, computational simulation, microstructural characterization and image analyses were done to investigate carbide dissolving behavior.

| Table 1. Chemical Composition (in Mass Percent) |
|-----------------------------------------------|
| C    | Si    | Mn | P   | S    | Cr | Ni | Al | Cu | Ti |
| 0.965 | 0.261 | 0.29 | 0.0167 | 0.0128 | 1.47 | 0.0474 | 0.0261 | 0.0755 | 0.0063 |

In order to establish intercritical and full austenization temperatures, the phase diagrams were calculated using ThermoCalc software [9] and TCFE6 database [10] for steel alloys. According to calculations in Fig 1, cementite phase should be dissolved at temperatures above 901.72 °C. Thus, temperatures of 915, 1050, 1100 and 1200 °C were selected in experimental work.

Dissolution behavior of carbides was simulated using DICTRA software [11] and MOBFE2 kinetic database [12] for different temperatures. To create a model for simulation initial structure with spherical carbides was evaluated to determine carbide size and quantity as shown in Fig 2. SEM micrographs of spheroidized specimens were analyzed with line intercept method, average radius was determined. To determine the quantity of carbides in matrix at the equilibrium condition thermodynamic calculations was used. Calculations offer 14.3 volume-% of cementite phase at 720 °C for spheroidization.

Figure 1. Calculated (a) isopleth and (b) phase amounts for 0.965 C-0.261 Si-0.29 Mn-1.47 Cr-0.0474 Ni steel using Thermo-Calc.
The microstructures of the samples were examined by scanning electron microscopy (SEM) using secondary electron imaging on a JSM-6060 SEM. The samples were first mechanically polished using 3 µm diamond solution, and then etched using 3% Nital at room temperature. SEM images were evaluated with the line intercept method to determine average radius of carbides and size distribution.

3 Results
Commercially production cycle of bearing steels includes spheroidization for reducing hardness before cold rolling. In spheroidization treatment, specimens were kept at 800 °C for 120 minutes and cooled to 720 °C with cooling rate of 15 K/h and followed by air cooling to room temperature. Fig 3 presents typical microstructure of the sample after spheroidization treatment. Microstructure is consisted of spheroidal carbides in ferritic matrix. An image analysis software was employed which measured diameter of each particle. Due to the particles of bimodal size distribution with overlapped peaks, two different average particle sizes can be determined. The histogram shows a rather broad particle size distribution of 700–1700 nm with an average value of 976 nm. During the dissolution of carbides, coarser carbides are dissolved at the final stage of heat treatment. Thus, in our calculations, only coarser carbides were taken into account.

Figure 2. Model for DICTRA calculations.

Figure 3. SEM micrograph of spheroidal carbides in ferritic matrix and particle size distribution.
According to the study on carbide dissolution in bearing steels by Kang et al, smaller precipitates tend to dissolve faster than larger particles and the dissolution is diffusion controlled. Thus, DICTRA calculations were applied to larger particles of carbides at different austenitizing temperatures. The simulation begins with a cementite particle with radius of 488 nm surrounded by an austenite grain with radius of 1018 nm. The chemical composition of cementite and austenite calculated at spheroidization temperature of 720 °C using ThermoCalc, as given in Table 2. The radius of cementite obtained from DICTRA simulations were plotted in Figure 4. The results indicate that intercritical austenization treatments should give a small decrease of particle size at 840 and 915 °C. However, at temperatures above 1050 °C, all particles can be dissolved completely.

**Table 2.** Calculated chemical compositions of phases at 720 °C using ThermoCalc.

| Phase   | C      | Mn     | Si     | Cr     |
|---------|--------|--------|--------|--------|
| Ferrite | 0.0132143 | 0.165904 | 0.290496 | 0.245577 |
| Cementite | 6.73324 | 1.4147 | 4.7234 × 10^{-11} | 8.52682 |

but not asked by DICTRA

**Figure 4.** Dissolution of cementite particles at different austenitizing temperatures.

Following the spheroidization treatment, specimens were reheated to 915 °C and 1050 °C. In Fig 5a, it seems that an annealing at 915 °C for 10 min was not enough for complete dissolution of cementite particles. Mostly finer carbides with diameter <500 nm were dissolved compare to the carbide distribution of conventional spheroidization as given in Fig 3. The complete dissolution of carbides was observed after heat treatment at 1050 °C for 15 min as shown in Fig 5b.
4 Discussions

In this work, cementite dissolution at full and intercritical austenitizing temperatures in 100Cr6 steel is experimentally measured using scanning electron microscopy of heat treated samples and simulated by ThermoCalc and DICTRA software. According to calculations and experimental studies, following conclusions are as follows.

Both experimental measurements and simulations reveal that the cementite dissolution is slow at the intercritical austenitizing temperatures. The complete dissolution of cementite can only be attained at higher austenitizing temperatures.

The kinetic simulations indicated that the dissolution of cementite at temperatures above 1050 °C should be finished after a couple of minutes. According to thermodynamical calculations, cementite should be dissolved temperatures above 901.72 °C. However, SEM observations revealed that holding at 915 °C for 10 min was not enough for complete dissolution of cementite. Kinetic calculations also showed that a longer duration than 1000 s should be needed for complete dissolution of cementite.

Figure 5. SEM micrograph of samples annealed at a) 915 °C/10 min (with particle size distribution) and b) 1050 °C /15 min prior to a water quench.

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