Thermodynamic Modeling of Metastable and Transition Carbides in the Fe-C System

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The tempering of martensitic Fe-C steels involves the evolution of metastable and transition carbides, which play a crucial role in determining the mechanical properties of the material. Accurate thermodynamic descriptions of these carbides are essential for modeling their precipitation behavior during tempering and autotempering. Naraghi et al. [1] made a first attempt to model the thermodynamic stability of metastable and transition carbides by using the CALPHAD method, and in particular, they elegantly treated carbon ordering in martensite with a two sublattice order/disorder model. However, according to their description, all transition carbides appear stable relative to cementite and ferrite at certain ranges of temperatures. This is in sharp contradiction to experimental observations [2]. Therefore, a revision of Naraghi et al.'s work is necessary.

In this study, we present a revised thermodynamic description of these transition carbides, η -Fe₂C and χ -Fe₅C₂, using the CALPHAD approach. Prior assessments, such as those by Naraghi et al., have treated carbon ordering in martensite using a two-sublattice order/disorder model but overestimated the stability of transition carbides relative to cementite (θ -Fe₃C) and ferrite (α). To address these discrepancies, we incorporate long-term isothermal tempering experimental data [2] and density functional theory (DFT) calculations [3] to refine the Gibbs energy functions of transition carbides.

Our revised model demonstrates that η -Fe₂C and χ -Fe₅C₂ are transient phases rather than stable equilibrium phases in the Fe-C system. The calculated phase diagram now aligns more closely with experimental observations, ensuring a more accurate representation of the carbide precipitation sequence during steel tempering. Furthermore, improvements in the description of $\alpha/\alpha^{\prime\prime}$ -ordering have been made by integrating recent ab initio results, enhancing the predictive capability of the thermodynamic framework.

The updated Fe-C phase diagram, obtained from our new thermodynamic descriptions, is presented in Fig. 1. These findings highlight the necessity of refining thermodynamic assessments using both experimental observations and first-principles calculations to achieve realistic modeling of phase equilibria. The revised model has significant implications for the development of advanced steels, as it enables better control over the microstructural evolution during processing. Future work will focus on integrating kinetic simulations to further elucidate the temporal evolution of carbide phases under different tempering conditions.



Figure 1. The revised Fe-C phase diagram with all metastable and transition carbides as well as the metastable miscibility gap for the α/α "-ordering (in dashed line)

References

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Biographical Note

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