

Influence of silicon on cementite precipitation in steels

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The mechanism by which relatively small concentrations of silicon influence the precipitation of cementite from carbon supersaturated austenite and ferrite are investigated. It is found that one condition for the retardation of cementite is that the latter must grow under para-equilibrium conditions, i.e. the silicon must be trapped in the cementite. However, this is not a sufficient condition in that it can only be effective in retarding the transformation rate if the overall driving force for the reaction is not large. It is demonstrated that the experience that silicon retards the tempering of martensite requires the presence of lattice defects which can reduce the amount of carbon available for precipitation and the associated driving force.

Introduction

It has long been known that silicon inhibits the precipitation of cementite; concentrations of ~2 wt-% silicon can change a brittle, cementite rich white cast iron into a ductile graphite rich grey cast iron.¹ In strong steels, the silicon is used to control the tempering of martensite.²⁻⁷ Indeed, this is the basis of the successful aerospace alloy 300M, containing ~1.6 wt-%Si; in this case the rate at which cementite precipitates from supersaturated martensite is significantly reduced when compared with a corresponding steel without the silicon.⁸ Silicon also retards the precipitation of cementite from austenite.⁹⁻¹⁷

These general statements about the retardation of precipitation are only valid when the cementite is forced by circumstances to inherit the silicon concentration of the matrix from which it precipitates. Silicon has a negligible solubility in cementite, which can form rapidly if diffusion permits the silicon to partition into the parent phase during growth. This is only possible when transformation occurs at elevated temperatures. However, the precipitation of cementite during the tempering of martensite or during the formation of bainite is at temperatures where the mobility of substitutional atoms is limited. The silicon must then become trapped in the cementite during its para-equilibrium growth. This dramatically reduces the free energy change associated with precipitation, with a corresponding large reduction in precipitation kinetics.^{18,19}

To summarise, the mechanism by which silicon retards the precipitation of cementite is that the driving force for precipitation is dramatically reduced when the cementite is forced to inherit the silicon present in the

parent phase. Any retardation is therefore prominent at low temperatures where atomic mobility is limited.

There is a need to express this theory into a quantitative framework because in many steel design scenarios, it is necessary to keep the silicon concentration to a minimum. One such case is steels for certain automobile applications where surface quality is reduced by the presence of tenacious silicon containing oxides. The purpose of the present work is to utilise recent theory on the kinetics of precipitation processes^{20,21} to provide a quantitative framework for the formation of cementite from both supersaturated austenite and ferrite, building on previous work which was limited either to equilibrium and para-equilibrium phase diagram calculations¹⁹ or the calculation of interface velocity during the growth of cementite from ferrite.²²

Method

A new method has recently been introduced to model precipitation kinetics, based on Onsager's thermodynamic extremum principle.^{20,21} The total Gibbs free energy G is expressed in terms of a number of state parameters q_i relevant to the precipitation process with $Q=f\{q_i \dots \dot{q}_i\}$. The evolution of the system is described by a set of linear equations derived from the relation $\partial G/\partial q_i \propto \partial Q/\partial \dot{q}_i$. The Gibbs free energies are calculated using the standard CALPHAD method and associated thermodynamic data. The thermodynamic data of the ferrite, austenite and cementite phases are taken from the compilation of assessments published by Lee.²³ In addition, the C-Si interaction energy in cementite was taken to be 250 kJ mol⁻¹, according to the suggested value given by Ghosh and Olson.²² The rate of dissipation Q is for precipitation kinetics expressed in terms of the migration of interfaces and associated diffusion processes. Soft impingement is accounted for using a mean field approximation and hard impingement is neglected, so the method is limited to the case of small precipitate fractions, which is a good approximation for the present study. The framework of the model is

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convenient for multicomponent, multiphase systems and the complete method has been implemented in the software MatCalc, version 5.21.1; the database provided with this version also contains the thermodynamic information used in the present study.

The kinetic calculations assume nucleation on dislocations with the density of dislocations assumed to be 10^{12} m^{-2} when precipitation occurs from austenite and 10^{16} m^{-2} for precipitation from martensite.

Interfacial energy

Interfacial energies are calculated from information on the enthalpy of solution using a generalised broken bond analysis.²⁴ Accordingly, the part of the interfacial energy per unit area γ_I , coming from chemical interaction of atoms across the interface, can be expressed as

$$\gamma_I = \frac{n_S z_{S,\text{eff}}}{N z_{L,\text{eff}}} \Delta E_{\text{sol}}$$

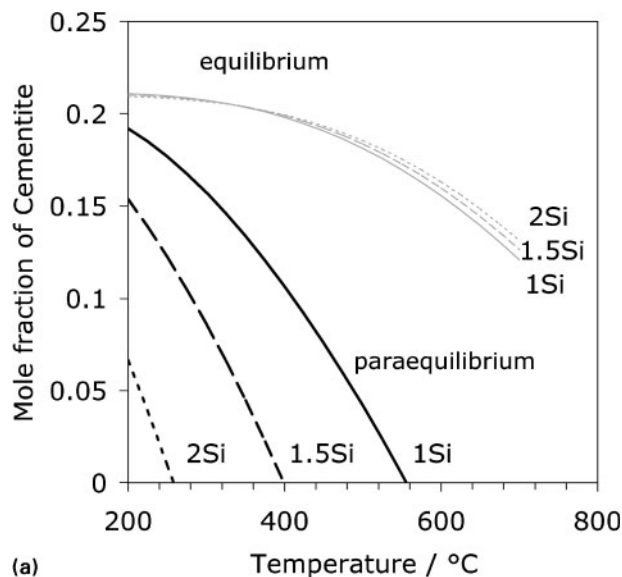
where n_S is the number of atoms at the interface per unit area, $z_{S,\text{eff}}$ the number of broken atomic bonds across the interface, $z_{L,\text{eff}}$ the effective coordination number of the crystal system, N the Avogadro constant and ΔE_{sol} the enthalpy of solution for the precipitate in the surrounding matrix. ΔE_{sol} is a quantity, which is fully determined by the thermodynamic information stored in the independent databases. The mean effective structural factor $z_{S,\text{eff}}/z_{L,\text{eff}}$ for a body centred cubic structure has been determined in Ref. 24 to be 0.328.

Precipitation from austenite

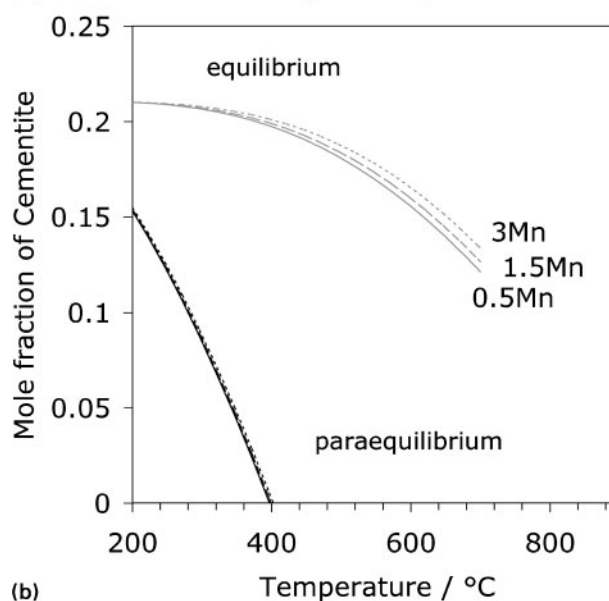
There is an important class of strong steels which exploit silicon to prevent the precipitation of cementite during the bainite transformation – this causes the residual austenite to become enriched with carbon and hence to be retained in the final microstructure; the subject has been reviewed.^{25–28} The typical composition of this austenite is Fe–1.2C–1.5Mn–Si (wt-%) and the silicon concentration must be such as to prevent the decomposition of the austenite into a mixture of cementite and ferrite during the course of the routine heat-treatment used to produce the steel. It is this austenite composition that forms the basis of the calculations presented in this section.

Figure 1a illustrates the calculated influence of silicon on the fraction of cementite as a function of temperature. Whereas the equilibrium fractions are hardly influenced by silicon, there are dramatic changes for the para-equilibrium condition in which the silicon is trapped inside the cementite lattice; in contrast, under equilibrium conditions the solubility of silicon in cementite is negligible so its concentration hardly affects the phase fraction. These interpretations are consistent with the data presented in Fig. 1b which shows the influence of manganese on the precipitation of cementite from supersaturated austenite.

Time temperature precipitation diagrams for para-equilibrium are plotted in Fig. 2; the transformation temperature range of interest from the point of view of bainitic steels is between about 300–400°C. In the particular case of TRIP assisted steels of the kind typical in the automobile industries,^{26,27} the time periods are minutes or less, making it difficult to avoid cementite precipitation at low silicon concentrations. The reason



(a)



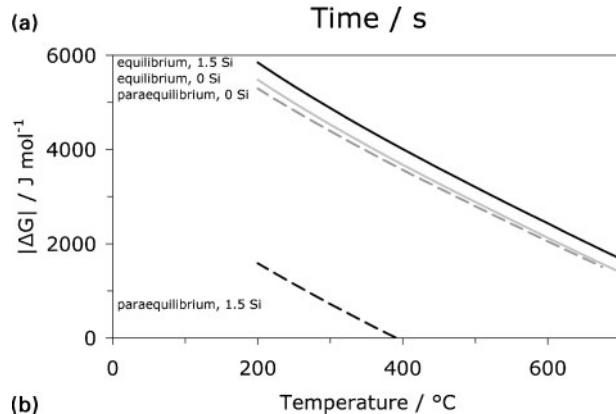
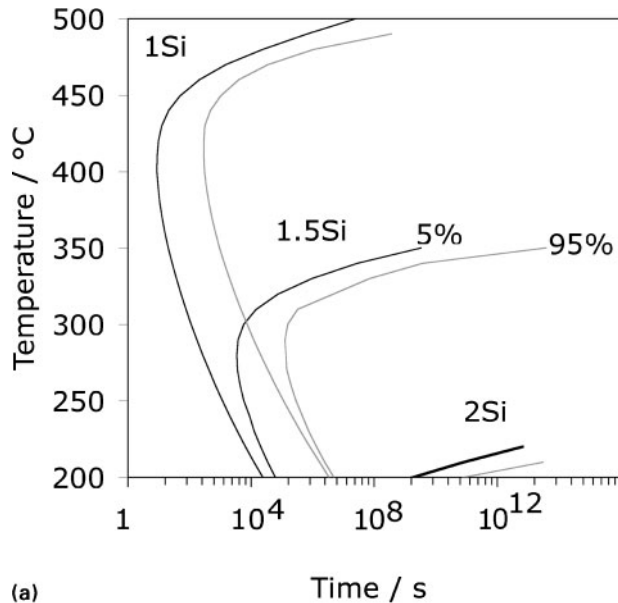
(b)

a variation of Si concentration; b variation of Mn concentration

1 Calculated phase fraction of cementite in equilibrium or para-equilibrium with austenite, in system Fe–Si–Mn–C with base composition Fe–1.2C–1.5Mn–1.5Si (wt-%)

why silicon has such a large influence on the para-equilibrium precipitation of cementite from austenite is understood from Fig. 2b which illustrates the dramatic reduction in $|\Delta G|$ when the silicon is trapped in the cementite structure. ΔG is the free energy change associated with the formation of a minute quantity of product phase such that it hardly affects the composition of the remaining parent phase, and the composition of the product phase is that which ensures that $|\Delta G|$ is maximised, as illustrated and described in detail in Fig. 6.2b of Ref. 25.

There are limited experimental data available for appropriate comparison with the present work, since practical TRIP assisted steels always have a high silicon concentration. However, Jacques and co-workers²⁹ deliberately designed both low and high silicon TRIP assisted steels and reported experimental data for comparison against theory. The chemical compositions



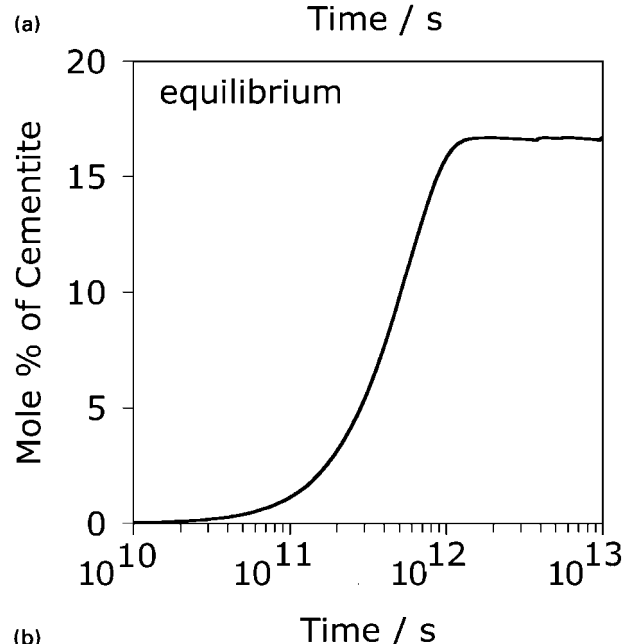
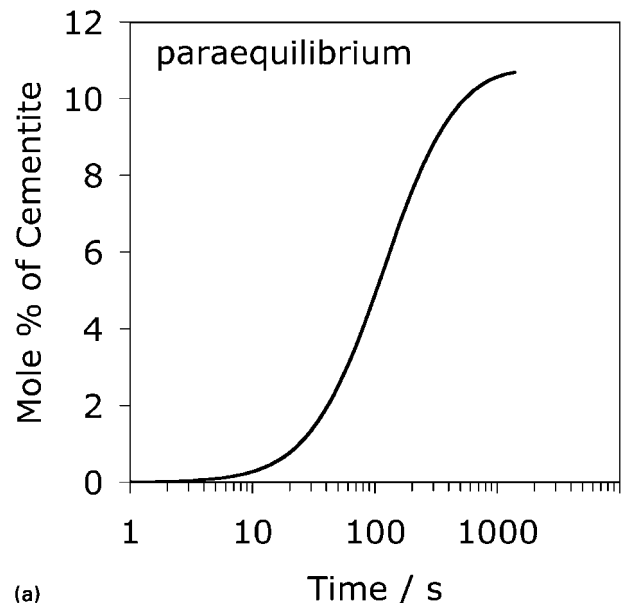
2 **a** time temperature precipitation diagram for para-equilibrium cementite in system Fe-Si-Mn-C with base composition Fe-1.2C-1.5Mn-1.5Si (percentages represent portion of cementite precipitation that is completed) and **b** magnitude of free energy change accompanying $\gamma \rightarrow \gamma + \theta$ reaction for both equilibrium and para-equilibrium conditions as function of silicon concentration of austenite

of the two steels are Fe-0.16C-0.38Si-1.3Mn and Fe-0.29C-1.41Si-1.42Mn respectively, and the carbon concentrations of the retained austenite were reported to be ~0.8 and 1.0 wt-% respectively. Transmission electron microscopy on a sample which was transformed at 370°C for 3 min revealed cementite precipitation from the austenite between the bainitic ferrite platelets, consisted with the calculations illustrated in Fig. 3a. Note that the calculations must use the carbon concentration of the retained austenite rather than the average concentration of the steel.¹

In contrast, Jacques et al. did not find any cementite in the high silicon alloy treated at 360°C for time periods up to 4000 s. The authors' calculations show that para-equilibrium precipitation in the austenite (1 wt-%C) is thermodynamically impossible at that temperature, and equilibrium precipitation would take an unrealistically long time to occur as shown in Fig. 3b.

Precipitation from ferrite

The so called '4340' steel with a chemical composition Fe-0.4C-0.7Mn-0.28Si-0.8Cr-1.8Ni-0.25Mo (wt-%) is



3 **a** para-equilibrium cementite precipitation from austenite containing Fe-0.8C-0.38Si-1.3Mn (wt-%) held at 370°C and **b** equilibrium cementite precipitation from austenite containing Fe-1.0C-1.41Si-1.42Mn (wt-%) held at 360°C

a high quality and strong steel used for making components such as gears, shafts, piston rods, gun barrels, etc. It is used in the quenched and tempered condition, but to avoid the 350°C tempered martensite embrittlement³⁰ it is somewhat over tempered at 425°C for 1 h, giving a yield strength of 1350 MPa.

Tempered martensite embrittlement is associated with the formation of coarse cementite in a matrix which has a strength that does not allow this coarse cementite to be tolerated. It manifests as a minimum in a plot of toughness versus tempering temperature when the latter is 350°C. To avoid this difficulty, another variant, '300M' has been developed with essentially the same composition but with the silicon concentration boosted to 1.6 wt-% to retard tempering so that minimum in toughness is shifted to higher tempering temperatures, therefore, 300M can be tempered at just 315°C without embrittlement, leading to a much greater strength in excess of 1650 MPa.

The experimental evidence therefore shows clearly that silicon retards the para-equilibrium precipitation of cementite from carbon supersaturated ferrite. The calculations by Ghosh and Olson²² suggest, however, that precipitation is too rapid to have a perceptible effect. Calculations have been conducted by the authors specifically for 4340 and 300M steels where the experimental evidence is strong for retardation of cementite. The calculations confirm that the cementite precipitates incredibly and rapidly during tempering at 315°C, the 0.43 wt-%C steel with little meaningful difference between the silicon rich 300M and low silicon 4340 steels (Fig. 4a). This is inconsistent with the widely accepted tempering kinetics of these steels.

Figure 4a also shows that a significant influence of silicon in retarding tempering only occurs when the carbon concentration is substantially reduced. The reason for this becomes clear in Fig. 4b, where it is seen that even at the lowest of carbon concentrations, the driving force for precipitation in the silicon rich steel remains large, a reflection of the fact that the solubility of carbon in ferrite in equilibrium or para-equilibrium with cementite is negligible at the tempering temperature of 315°C.

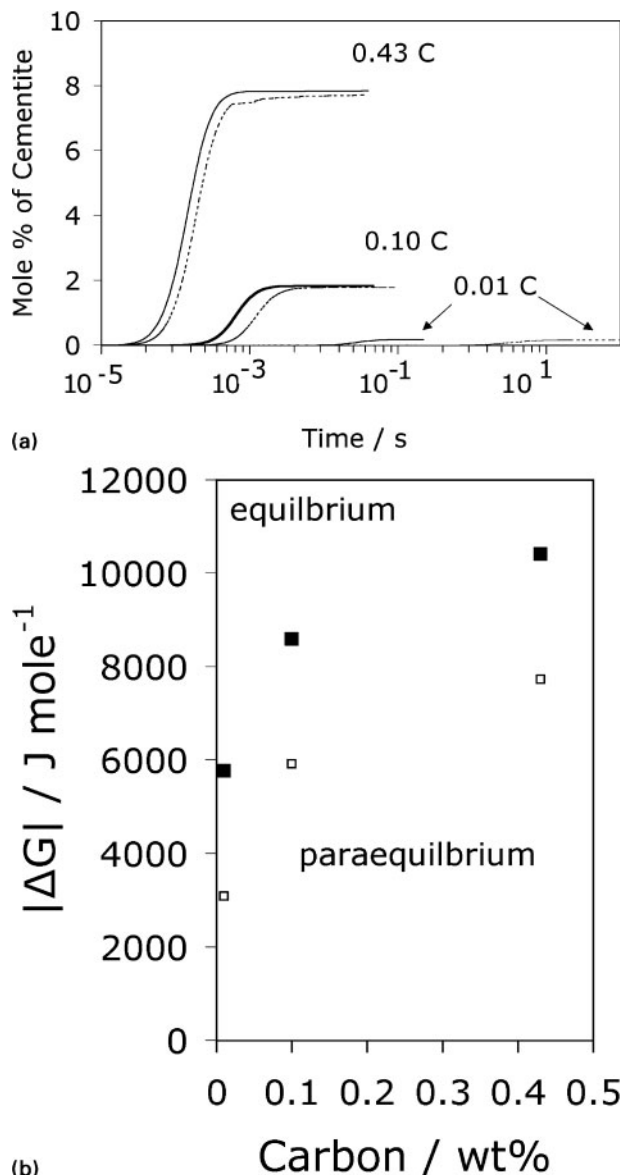
One probable explanation of the discrepancy between both the authors' and Ghosh and Olson's calculations and experimental observations on the tempering of martensite comes from some classic work by Kalish and Cohen.³¹ They proposed that in the presence of dislocations, carbon prefers to be segregated to dislocations rather than precipitate as cementite or ϵ carbide. Although they did not consider other defects, such as the high density of interfaces present in the microstructure of martensite, these would also be expected to tie up the carbon that is normally available for precipitation and thus further support the authors' argument.

The defects can effectively be thought of as a separate phase which is a greater attractor for carbon than cementite. In these circumstances, the carbon available for precipitation as cementite is reduced. The rate of precipitation then depends on the 'dissolution' of the defects during annealing, making carbon available for cementite formation. This must greatly retard tempering kinetics and, because of the reduced carbon concentration in the perfect lattice, lead to a smaller driving force for precipitation and hence a larger difference between the silicon rich and silicon poor steels.

It is relevant and interesting that other work has demonstrated a direct relationship between the carbon content of lath martensite and its dislocation density.³² In the case of bainite, there is direct evidence from atom probe experiments of a substantial excess of carbon locked in the dislocations in the bainitic ferrite,^{33,34} with X-ray evidence to show that the excess becomes relieved as the dislocation density is reduced by tempering.³⁵ A paper just published strongly reinforces this theory in that it shows that ~90% of the carbon atoms in a silicon rich martensitic steel were trapped in Cottrell atmospheres in the vicinity of the dislocation cores in dislocation tangles in the martensite matrix after cooling at 560 K s⁻¹ and aging at 22°C.³⁶

Conclusions

It is found that the impressive retardation of cementite precipitation in austenite, caused by the addition of a



4 a kinetics of para-equilibrium cementite precipitation at 315°C, from supersaturated 4340 (continuous curves) and 300M (dotted curves) steels as function of carbon concentration and b magnitude of ΔG for $\alpha \rightarrow \alpha + \theta$ reaction at 315°C

small concentration of silicon, can be explained by the fact that the cementite, when it forms under para-equilibrium conditions, traps the silicon as it grows. The resulting reduction in the free energy change of the reaction slows down the kinetics of precipitation. Equilibrium growth of cementite in which silicon is partitioned into the austenite does not significantly influence precipitation kinetics; it follows that elevated temperature transformations involving cementite, such as the diffusional formation of pearlite, are also not particularly affected by the addition of small concentrations of silicon.

In some cases, the precipitation of para-equilibrium cementite from austenite becomes impossible because of a lack of a driving force for precipitation. The cementite can then only form with the partitioning of silicon, which may take an inordinately long time.

The present study also reveals that silicon is ineffective in retarding the precipitation of cementite if the

parent phase is highly supersaturated with carbon. This is because the driving force for the reaction is large even for para-equilibrium precipitation. Consistent with previous work,²² and under the assumption that all the carbon is available for precipitation, the calculations indicate that silicon has a negligible effect in slowing the formation of cementite in typical tempered martensite, in spite of the fact that experience suggests otherwise. It is proposed that this is because the carbon in the martensite is trapped at dislocations and other defects, so that the rate controlling factor in the precipitation process is the elimination of defects so that the trapped carbon becomes available for cementite formation.

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