TEM Investigation of Carbide Precipitation in Low Carbon Steels Containing Silicon

By Santanu Kr. Ray* and O. N. Mohanty**

The time-temperature range of the formation of metastable and stable carbides and their rate of growth during the ageing of three grades of low carbon steel containing Si in the range from 0.3 to 1.52 mass % have been studied using TEM. In comparison to steels with higher amount of Si (3 mass % and more), stable carbide particles started precipitating quite early during ageing and at lower temperatures in the investigated steels. Thus, inhibition of the transition of metastable to stable carbide was negligible. The growth-rate of carbide particles for the 0.3% Si steel was appreciable; however, the same for the steels with 1.1 and 1.5% Si was slower. These findings together with the observations on sites of nucleation of the carbides have been rationalised on the basis of the role of silicon in modifying the activity coefficient of carbon in ferrite and the stability of the carbides.

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I. Introduction

Carbon being one of the most important elements alloyed with iron, precipitation of carbides from ferrite has been investigated quite extensively. It is possible to retain carbon in supersaturated solid solution when subjected to rapid cooling owing to the continuous decrease of solubility of carbon in ferrite from the eutectoid temperature down to lower temperatures. On raising the supersaturated ferrite to moderate temperatures precipitation of carbide takes place as the system moves towards equilibrium.

A substitutional solute can affect precipitation of carbon from alpha iron by modifying the rate of carbide precipitation, sites of nucleation, type of carbide and the rate of growth of the carbide. For example, the decreased rate of precipitation of carbides in presence of silicon is thought to be responsible for the inhibition of the tempering of martensite in steels containing silicon\(^1\). By stabilising the metastable carbide\(^2\)\(^-\)\(^4\) and by lowering its growth rate\(^5\), silicon when present to the extent of 3 mass % is also known to act as a very effective inhibitor of magnetic ageing\(^6\) in low carbon steels.

II. Experimental

The chemical compositions of the three grades of low carbon steel containing silicon in the range from 0.3 to 1.52 mass % are listed in Table 1. All the steels were of commercial variety. The microstructure in the mill-received condition showed more or less equi-axed grains of ferrite. Specimens from these grades were solution treated at 1023 K for 2.4 ks in vacuum

Table 1 Chemical composition of the investigated steels.

<table>
<thead>
<tr>
<th>Designation</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3Si steel</td>
<td>0.013</td>
<td>0.30</td>
<td>0.25</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>1.1Si steel</td>
<td>0.020</td>
<td>1.11</td>
<td>0.28</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>1.5Si steel</td>
<td>0.015</td>
<td>1.52</td>
<td>0.23</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

* R & D Centre for Iron & Steel, Steel Authority of India Ltd., Ranchi, India.
** Metallurgy Department, Indian Institute of Technology, Kharagpur, India.
(5 × 10^{-3} \text{ Pa}), water quenched, and then isothermally aged at 398, 443, 483, 523 and 573 K for periods varying from 60 s to about 10 Ms. Microstructures of the samples under different heat-treated conditions were observed using a Philips EM-300 unit. Thin foils were prepared by jet polishing of 3 mm dia samples in a solution of 5% perchloric acid and 95% acetic acid at a temperature of about 288 K.

### III. Results

TEM investigation of the aged specimens indicated two types of carbides. Selected area diffraction gave spots only from the ferrite matrix, but no diffraction patterns from the carbides themselves could be obtained. Hence, habit plane determinations has been used to distinguish the two carbides. In the 0.3Si-steel at low ageing temperatures (398 and 443 K), during the early part of ageing the carbides had a \{100\}_a habit plane. They were found to grow on all the three \{100\}_a planes. Figure 1 shows a typical structure containing carbide particles of this type formed after 2.16 ks of ageing at 398 K. Previous work\(^{(8)-(9)}\) on binary Fe-C alloys and unalloyed low carbon steels have indicated that ‘low temperature’ carbide of such a habit is actually \(\varepsilon\)-carbide. 0.3 mass% silicon which is usually present in low carbon steels is unlikely to modify the carbide at low temperatures. In the 0.3Si-steel cementite precipitates could be observed first after about 1.2 Ms at 398 K and after 1.8 ks at 483 K. Cementite could be identified from its \{110\}_a habit\(^{(2)-(10)}\). At 523 K beyond 0.9 ks of ageing only cementite particles could be observed. The typical appearance of cementite particles is shown in Fig. 2, which is the microstructure obtained after 0.9 ks at 523 K.

Two types of carbides, the low temperature one with an \{100\}_a habit and the high temperature one with an \{110\}_a habit, were also observed during ageing of 1.1Si- and 1.5Si-steels. In the absence of diffraction spots from these carbides, exact identification was difficult. In these two steels the low temperature metastable carbide persisted to slightly longer ageing time and higher temperature. The stable carbide with \{110\}_a habit apparently did not precipitate even after about 6 Ms at 398 and 443 K in the 1.5Si-steel and on similar ageing at 398 K in the 1.1Si-steel. However, compared to 3%Si-steels such inhibition of the transition from metastable to stable carbide in these two steels is negligible. Leslie \textit{et al.}\(^{(2)-(4)}\) have earlier reported that in steels containing 3% silicon the metastable carbide with \{100\}_a habit persisted even after prolonged ageing up to 573 K. In sharp contrast to this, in the present 1.5Si-steel the stable carbide started precipitating after about 60 ks at 483 K and in the 1.1Si-steel even at 443 K after about 180 ks. In the
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1.1 Si-steel after 1.5 ks at 523 K (Fig. 3) and in the 1.5 Si-steel after 180 ks at 483 K (Fig. 4), stable high temperature carbide was the only type observed.

In the 0.3 Si-steel at low temperatures carbides formed both in the matrix and on dislocations generated during water quenching, as evident from Fig. 1. In the 1.1 Si and 1.5 Si-steels, however, at lower temperatures carbides were found to precipitate mostly in the matrix. Figure 5 indicates that in the 1.1 Si-steel aged 450 ks at 398 K metastable carbide particles precipitated exclusively in the matrix. Earlier investigations on 3% Si steels\(^2\)–\(^4\) have shown that a large number of precipitates formed in the matrix even at 673 K. In sharp contrast to this, metastable carbide particles in Fe–0.45\% Mn–C alloy\(^4\) and in a commercial steel with 0.17\% P\(^1\) have been reported to have precipitated predominantly on dislocations even at low temperatures.

Different stages of ageing have been characterised by average sizes of the carbide particles. Carbide-size measurements were done using thin foils. Since carbide particles are anisotropic in shape, it is the maximum dimension which is reported. In such estimations, difficulties can arise out of a wide distribution of sizes. In addition, some inaccuracies will crop up when the dimensions of the particles exceed the foil thickness. In order to extract meaningful data in the face of these limitations, the average size was determined making use of a number of particles present at a given condition of ageing.

The rate of growth of the carbide particles with progress of ageing at different temperatures has been determined, and the results for the
three steels are shown in Figs. 6, 7 and 8. The
points appearing at the shortest times are not
intended to indicate the beginning of carbide
precipitation. The rate of growth was much
slower for the 1.1Si and 1.5Si-steels compared
to that with 0.3% Si. In the latter grade after
0.3 ks of ageing at 573 K cementite particles
had an average maximum dimension of about
0.8 μm. After 2.7 ks the particles grew to a
dimension more than 1.4 μm, (Fig. 9). At
523 K the growth was from 0.7 μm after 0.3 ks
to more than 1.55 μm after 7.5 ks. In sharp
contrast to this, in the 1.1Si-steel during 523 K
ageing cementite particles grew from 0.35 μm
after 1.5 ks (Fig. 3) to only about 0.8 μm after
almost 600 ks (Fig. 10). At 573 K after 21.6 ks
the maximum dimension was found to be
slightly more than 0.8 μm and growth appar-
ently ceased beyond that. At 443 K even after
5.4 Ms the average size was only about 0.6 μm
(Fig. 11). In the 1.5Si-steel the rate of growth
IV. Discussion

The carbide particles revealed only two habit planes, \(\{100\}_a\) and \(\{110\}_a\). The nucleation site did not appear to influence the nature of this habit. For a given ageing treatment, the metastable carbides formed on \(\{100\}_a\) and cementite on \(\{110\}_a\) regardless of whether the particles originated at dislocations or within the matrix.

The \(\{100\}_a\) habit is common for precipitates formed at low temperatures in alpha iron. Such a pattern has been observed in Fe–N, Fe–Mo, Fe–W, Fe–Au and Fe–Zn systems. The \(\{100\}_a\) habit is possibly due to the fact that the modulus of elasticity of iron is minimum in [100] direction\(^4\).

Carbon in supersaturated ferrite is unstable with respect to both the stable and the metastable carbides. In principle, any of the two could precipitate from the unstable carbon in supersaturated solid solution at low temperature. However, though the stable carbide has lower chemical free energy, lattice match between the metastable carbide and ferrite is much better. In such a situation, lower interfacial energy predominates at low temperature and initially metastable carbide preferentially nucleates. Due to a higher activation energy involved, the stable carbide has a lower nucleating rate and it nucleates only on prolonged ageing. Carbon concentration in the ferrite matrix in equilibrium with the nuclei of the stable carbide being less than that which is in contact with the metastable ones, precipitates of the latter type dissolve with the appearance of the stable carbide particles. At higher temperatures higher chemical free energy of the metastable carbide nearly rules out its precipitation; the stable carbide is virtually the only type that precipitates.

To rationalise the carbide precipitation behaviour in the presence of a substitutional alloying element, it is essential to know how the element modifies the relative stabilities of carbon in supersaturated ferrite and of the metastable and stable carbides\(^{12}\). For a definite carbon concentration, the stability of carbon in ferrite is reflected through its activity coefficient. Smith found that silicon significantly
increased the activity coefficient of carbon in ferrite \cite{13}, thus its addition accordingly was found to decrease the solubility of carbon \cite{14}\cite{15}. The influence of silicon on the metastable carbide stability does not appear to have been studied. However, with regard to cementite it is broadly recognised that the presence of a substitutional solute having insignificant solubility in the carbide would tend to increase its free energy and consequently lower its stability. Having negligible equilibrium solubility in the stable carbide, silicon is thus expected to preclude its precipitation. To explain the inhibition of metastable to stable carbide in presence of 3 mass\% silicon, it has been pointed out that though the increased activity coefficient of carbon in ferrite in the presence of silicon should have enhanced stable carbide precipitation, its effect in decreasing the stability of the stable carbide acts as the predominant factor\cite{12}. That the effect of a substitutional solute on the carbide stability is a major parameter of consideration in the transition of metastable to stable carbide, is exemplified by the easier transition of \(\varepsilon\)-carbide to cementite in the presence of manganese. The decreased activity coefficient of carbon in this case cannot prevent an early precipitation of cementite since by freely substituting iron in Fe\(_3\)C, manganese increases the stability of cementite. From the time-temperature ranges of existence of the metastable and stable carbides observed in the steels of the present investigation, it is apparent that silicon upto 1.5 mass\% is not very effective in inhibiting stable carbide formation. A possible conclusion that can be drawn from this observation is that, silicon in the said range is not capable of increasing the free energy of stable carbide to an appreciable extent.

Experimental evidences point towards a good correlation between the effect of a substitutional alloying element on the activity of carbon in ferrite on the one hand and the site of carbide precipitation on the other. The elements like silicon which enhance the activity of carbon are also found to elevate the ageing temperature up to which matrix precipitation would persist; and the elements which lower the activity, such as manganese and phosphorus, would tend to foster precipitation on dislocation. This behaviour is rationalised by the fact that the decreased carbon activity would be expected to act in the same way as a lower carbon supersaturation in that, as the temperature would go up, the system would depend more and more on the aid of dislocations for the formation of carbides.

Earlier investigations have shown that in the presence of manganese the growth-rate of carbide particles was much the same as in binary Fe-C alloys\cite{4}. In the presence of 3 mass\% silicon on the other hand, the rate of growth of metastable carbide (the only type observed up to 573 K) was found to be much slower\cite{5}; furthermore, the growth ceased after some time. This led Keh and Leslie\cite{5} to the generalised conclusion that only the substitutional solutes essentially insoluble in carbide could have a discernible effect. Subsequent observation of reduced rate of growth of carbide particles in the presence of aluminium\cite{12}, which has negligible equilibrium solubility in carbide, has lent support to this hypothesis. The diffusivity of a substitutional solute being much slower than that of carbon, necessity of silicon to diffuse out from the growing carbide particles seems to be responsible for the slower rate of growth.

To rationalise the behaviour of silicon, a different mechanism can be thought of. Silicon rejected from the growing carbide particles increases the activity of carbon in their vicinity since silicon increases the activity coefficient of carbon in ferrite. This forces carbon to diffuse up an activity gradient to reach the carbide particles. The earlier observation in case of steels with 3% silicon, which has been confirmed in the present investigation as well for the 1.1Si and 1.5Si-steels, that carbide growth stops after a time is possibly explained by this mechanism. Presumably it also explains the finding of this study that though silicon in the range from 1.1 to 1.5 mass\% could not effectively inhibit stable carbide formation, the growth was nevertheless much slower and ceased beyond some time.

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