On the Influence of Carbide Formation Upon the Growth Kinetics of Proeutectoid Ferrite in Fe-C-X Alloys

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In the preceding paper, the growth kinetics of grain boundary ferrite allotriomorphs in Fe-C-Si, Fe-C-Mn, Fe-C-Ni, and Fe-C-Cr alloys are reported to be best described by the paraequilibrium model. Significant differences are still observed, however, between the experimentally measured kinetics and those calculated from this model. A TEM study was conducted on these alloys to ascertain whether any of these differences could be attributed to carbide precipitation. In the Fe-C-Mn and Fe-C-Cr alloys, where the measured growth kinetics are low, carbides precipitate on dislocations within the ferrite and are effectively absent, respectively; hence carbide precipitation cannot be responsible for the deviations in these alloys. In the low Ni, Fe-C-Ni alloy, where calculated and measured kinetics agree, carbide precipitation was again found on dislocations in the ferrite. Faster than calculated growth kinetics in the Fe-C-Si and the high Ni, Fe-C-Ni alloys, on the other hand, are attributed in part to carbide precipitation at austenite:ferrite boundaries.

In an accompanying paper, Bradley and Aaronson\(^1\) (BA) report measurements of the thickening and lengthening kinetics of grain boundary ferrite allotriomorphs as a function of isothermal reaction temperature in single Fe-C-Si, Fe-C-Mn, and Fe-C-Cr alloys and in two Fe-C-Ni alloys. The ability of three models: a) local equilibrium with bulk partition of alloying element,\(^2\)-\(^10\) b) local equilibrium with localized pileup but no bulk partition of alloying element,\(^10\)-\(^14\) and c) paraequilibrium,\(^14\)-\(^18\) to account for these data is quantitatively examined. Although it is concluded that the paraequilibrium model best explains the data, significant discrepancies remain between calculated and measured growth kinetics even for this model. While good agreement is obtained for the low Ni, Fe-C-Ni alloy, growth faster than calculated is found for the Fe-C-Si and the high Ni, Fe-C-Ni alloys and slower than calculated for the Fe-C-Mn and Fe-C-Cr alloys. Although several explanations are considered by BA, an obvious one, clearly in need of experimental testing, is that of carbide precipitation at austenite:ferrite boundaries. This can occur either as interphase boundary carbide precipitation on planar or on (apparently) curved austenite:ferrite boundaries, or as pearlite-like fibrous carbide precipitation.\(^19\)-\(^20\) Such precipitation might slow down the growth of ferrite by pinning the austenite:ferrite boundaries.\(^21\) Alternatively, these carbides could increase the growth kinetics of mobile areas of the austenite:ferrite boundaries by steepening the carbon concentration gradient in austenite driving their growth. Accordingly, the present investigation was undertaken to study this question in the BA alloys within the temperature-time envelopes employed for the growth kinetics studies. The observations reported here also supplement the literature on carbide precipitation per se in Fe-C-X alloys. With the exception of Cr, the alloying elements used are not strong carbide-formers and their effects upon the formation of carbides in association with proeutectoid ferrite have not been as intensively studied.

**EXPERIMENTAL PROCEDURE**

The composition of the alloys used in this investigation are given in Table I of BA.\(^1\) The same heat treatment procedure was utilized. Somewhat larger specimens, \(0.013 \times 0.013 \times 0.0025 \text{ m}\), were employed to facilitate transmission electron microscopy (TEM) studies. These specimens were chemically thinned to ca. \(7 \times 10^{-5} \text{ m}\) using a solution described by Plichta et al.\(^22\) Discs \(3 \times 10^{-3} \text{ m}\) in diameter punched from the specimens were thinned to perforation with a Fischione twin jet electropolisher using an electrolyte consisting of \(2.5 \times 10^{-4} \text{ m}^3\) glacial acetic acid, \(7.5 \times 10^{-2} \text{ kg} \text{ anhydrous sodium chromate}, \(2.5 \times 10^{-2} \text{ kg} \text{ chromic oxide} \text{ and } 10^{-2} \text{ m}^3\) water at room temperature under a potential of ca. 60 volts. The thinned discs were examined with Philips EM301G and JEOL 100CX electron microscopes. Ferrite containing areas were examined in each specimen until the various types of observation had been repeated with sufficient frequency to assure the investigators that a representative proportion of the specimen had been examined.
RESULTS

Fe-0.13 pct C-2.99 pct Cr. Previous TEM studies of carbide formation in Fe-C-Cr alloys have been mainly in alloys whose chromium content exceeds the 3 pct used in this study. A variety of carbide morphologies was found in association with ferrite including interphase boundary carbides, fibrous carbides and also idiomorphs at ferrite:ferrite grain boundaries. The type of carbide formed was dependent upon composition; $M_2C_3, M_7C_3$, and $M_3C$ were identified.

The TTT-curve for the initiation of the proeutectoid ferrite reaction in this alloy, reproduced in Fig. 1(a) from the work of Aaronson and Domian, exhibits a bay, the deepest portion of which is at ca. 600 °C. Specimens were isothermally reacted at 700, 650, and 600 °C. Optical microscopy revealed (Fig. 2(a)) that ferrite grows along austenite grain boundaries at all three temperatures. The ferrite is blocky in appearance at 700 °C but becomes more ragged at lower temperatures. TEM studies showed that, within the reaction time ranges employed by BA, all ferrite examined appeared to be free of carbides (Fig. 3). Some exceedingly fine precipitates may have been present on dislocations, though this observation could not be confirmed. However, it is quite certain that neither interphase boundary nor fibrous carbides appeared in any of the ferrite observed.

Fe-0.12 pct C-3.08 pct Mn. No previous TEM studies of carbide precipitation in association with ferrite appear to have been reported in Fe-C-Mn alloys. The TTT-curve for the beginning of austenite decomposition in this alloy is given in Fig. 1(b). Optical microscopy showed that proeutectoid ferrite morphology evolved progressively from predominantly grain boundary allotriomorphs at 650 °C to blockier allotriomorphs with some secondary sawteeth at 600 °C (Fig. 2(b)), and secondary sideplates at almost all grain boundaries at 550 °C. TEM revealed carbides only at 600 °C (Fig. 4(a)). Imaging the carbides in dark field clearly showed them to lie on dislocations (Fig. 4(b)). At 650 and 550 °C, no carbides were seen in any of the ferrite examined.

Fe-0.11 pct C-3.28 pct Ni. Chilton and Speich observed cementite precipitation on dislocations within the ferrite as well as interphase boundary precipitation of carbides in several Fe-C-Ni alloys. The TTT-curve for the alloy used in this study is given in Fig. 1(c). Optical microscopy showed a blocky allotriomorphic microstructure with secondary sawteeth at 715 °C (Fig. 2(c)); secondary sideplates began to develop at 650 °C. At 715 °C, TEM showed carbide precipitation as an allotriomorph-like morphology nucleated on dislocations (Fig. 5). Dark-field observations demonstrated that the carbides in a given ferrite grain can take up at least three different orientations when precipitated on dislocations (Figs. 5(b) through (d)). At 650 °C, ferrite free of carbide precipitation was observed as well as precipitation on dislocations.

Fe-0.40 pct C-1.73 pct Si. No prior TEM investigations of carbide precipitation in hypoeutectoid Fe-C-Si alloys have been located. The TTT-curve for this alloy is given in Fig. 1(d). Microstructures at two

Fig. 1—TTT-diagrams for initiation of transformation in: (a) Fe-0.13 pct C-2.99 pct Cr, (b) Fe-0.12 pct C-3.08 pct Mn, (c) Fe-0.11 pct C-3.28 pct Ni, and (d) Fe-0.40 pct C-1.73 pct Si.