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Eutectoids with cementite as the major constituent in Fe–C–M alloys

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ABSTRACT

The addition of a third element to hypereutectoid Fe–C alloys may cause inclusions of a minor constituent in the precipitate of cementite from austenite even if the initial austenite is supersaturated only with cementite. Cementite will often become the major constituent of this kind of microstructure. For Fe–C–Cu alloys this has been explained as the result of precipitation from supersaturated cementite. An alternative mechanism could be that the mixture of cementite and a minor constituent forms by simultaneous and cooperative growth of the two phases, i.e., by a reaction that may be regarded as eutectoid. This mechanism has already been applied to explain the occurrence of eutectoid colonies with cementite as the major constituent and a minor constituent for which there was no supersaturation initially.

This phenomenon has been observed in hypereutectoid ternary Fe–C alloys with Al, Mn or Si. The necessary requirements on the ordinary isothermal phase diagram are now examined with a graphical method based on the slopes of tie-lines. It predicts the phenomenon in all cases where it has been observed, including Fe–C–Cu and not in the Fe–C–Ni and Fe–C–Cr systems where it has not been observed. The requirements become more evident when the calculated phase equilibria are plotted as an isothermal phase diagram with the alloy content as a function of the carbon activity instead of carbon content. Finally, a comparison is made with bainite in Fe–C alloys where ferrite is the major and cementite the minor constituent. The same two explanations have been proposed for that case.

1. Introduction

Wasynczuk et al. [1], Fourlaris and Baker [2] and Khalid et al. [3–5] independently reported that grain boundary and Widmanstätten precipitates of cementite and pearlitic cementite can contain very fine inclusions in hypereutectoid steels alloyed with Cu and heat treated isothermally from an austenitic condition. They concluded that the particles are Cu-rich and belong to the very wide miscibility gap in the fcc phase of the binary Fe–Cu phase diagram. Figs. 1 and 2, reproduced from Khalid et al. [4], show an acicular unit of precipitated cementite but with an internal structure reminiscent of the result of general precipitation from a supersaturated solution when the driving force for nucleation is high. They proposed that cementite had first precipitated with the initial content of substitutional alloying elements in solid solution and Cu had later precipitated inside the cementite. However, a midrib free of fine inclusions was also noticed. They concluded that this thin unit of cementite had formed as a primary Widmanstätten plate but they did not explain why it did not later precipitate fine Cu particles. An alternative mechanism could be that the Cu particles form directly during the sideways growth of the cementite plate, i.e., under cooperation with cementite, but not during the initial edgewise growth of the thin plate of cementite. The necessary conditions for the precipitation of such two-phase units from austenite in the austenite + cementite phase field of ternary Fe–C–M alloys will now be examined and applied to some other cases where cementite precipitates together with a second phase and becomes the major constituent in a eutectoid microstructure.

2. Characteristics of eutectoid reactions

When a binary phase diagram predicts that a phase should transform to two new phases then it also indicates that the components should partition between the new phases during growth. Cooperative growth is promoted by the formation of two-phase colonies for which the growth front offers short diffusion distances. The resulting microstructures are well-known from solidification of eutectic alloys but they are called eutectoid when formed in a solid parent phase. That term is usually applied to eutectic-like colonies formed below a three-phase equilibrium which is invariant in a binary system under constant pressure and temperature but monovariant in ternary systems. A requirement is that the ordinary isothermal phase diagram resembles those of eutectic systems. However, Uhrenius and Hillert [6] demonstrated that a eutectic-like microstructure could form by heating the intermetallic phase in a peritectic system. They also presented several eutectic-like microstructures

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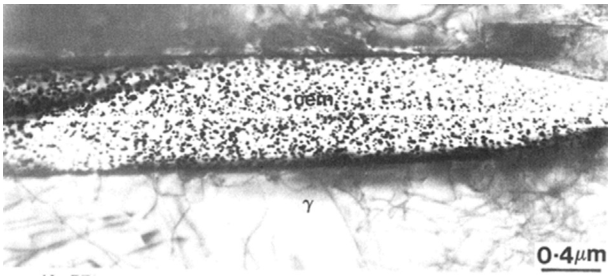

Fig. 1. Cementite plate with inclusions identified as Cu-rich particles, formed isothermally at 500 °C in an Fe–0.83C–9.70Mn–2.57Cu (mass%) alloy. Bright-field transmission electron micrograph. The white horizontal midrib without inclusions is identified as a primary Widmanstätten plate of cementite.
From Khalid et al. [4].

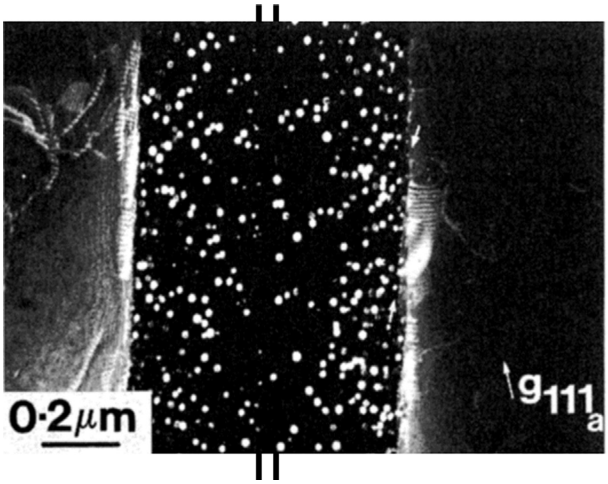

Fig. 2. Similar to Fig. 1 but dark-field transmission electron micrograph. The black vertical band without inclusions is identified as a primary Widmanstätten plate of cementite.
From Khalid et al. [4].

formed in the solid state of Fe–C–M alloys without a strict connection to cooling of the material. In particular, they demonstrated how such microstructures could form when alloyed steels were carburized. They suggested that the term eutectoid should be used for all eutectic-like microstructures of two new phases formed simultaneously, regardless of the experimental conditions and the type of phase diagram. This definition of the term eutectoid was applied in the present work. As an introduction, some characteristics of the eutectoid reaction to pearlite in Fe–C alloys will first be described and the similarities and differences of the formation of eutectoids with a high fraction of cementite in ternary Fe–C–M systems will be emphasized.

In the formation of pearlite in binary Fe–C alloys there are two transport processes, short-range diffusion, by which carbon is partitioned between the two eutectoid phases, and long-range flow of heat to remove the heat of reaction from the growing colonies. That heat is positive when the enthalpy of the eutectoid, i.e., its heat content, is lower than for austenite. The growth rate is mainly limited by the short-range diffusion of carbon because heat conduction is much faster. The temperature remains approximately constant as long as the parent austenite acts as an effective thermostat and growth rate and coarseness will then remain constant. As the heat of reaction will gradually heat up the austenite, growth rate will decrease and coarseness will increase due to the decreasing driving force at the higher temperature. The colonies will eventually obtain a divergent appearance if the reaction heat cannot be removed from the system by external cooling.

In the process of a eutectoid reaction in a ternary Fe–C–M alloy there are two new transport processes, short-range diffusion of the alloying element, M, by which it is partitioned, and long-range diffusion of carbon from the bulk of the parent austenite and to the growing colonies. The diffusivity of M is much lower than of C and it will now limit the growth rate. The long-range diffusion of carbon is slower than the loss of heat and it will gradually decrease the carbon activity of the system while the temperature increase is negligible. This will result in the divergent appearance of the eutectoid. The mechanisms of the eutectoid reaction in the binary and ternary systems are thus closely related, the rate of partitioning being governed by diffusion of carbon or the alloying element and the decisive long-range transport being concerned with heat or carbon.

The present discussion will concern the formation of eutectoid microstructures in Fe–C–M alloys by the transformation of austenite situated in the austenite(γ) + cementite(θ) phase field. Normally one would expect only cementite to precipitate but with a sufficient alloying addition it may happen that a ferrite(α) + cementite(θ) eutectoid forms, i.e., some kind of pearlite, but often with α as the minor constituent. That may not be surprising since α should not form at all according to the phase diagram. The interesting question is whether and when a third phase, e.g. α, may appear as a eutectoid constituent together with cementite. The answer is based on the fact that any two phases may form as a eutectoid colony if each constituent can promote the growth of the other one. The first part of the present work focuses on the characteristics of the isothermal Fe–C–M phase diagram that make this possible and it will be shown that the critical feature is the shape of the tie-triangle for the three phases involved but also the slopes of the tie-lines that form the tie-triangle.

Lamellar α + cementite eutectoids are often considered as pearlite even if they differ from pearlite formed in binary Fe–C alloys. At considerable alloy contents the growth rate slows down and the fraction of cementite changes due to the necessity of the alloying element to partition between the two eutectoid phases. The fact that an alloying element may partition between ferrite and cementite in pearlite was observed by Kuo and Hultgren [7]. They isolated pearlitic cementite electrolytically and analyzed it chemically, often finding contents of the alloying elements much different from those of the steel. Hultgren called this reaction product orthopearlite and today it is often regarded as partitioned pearlite. The α + θ eutectoids that are discussed in the present work may thus be regarded as orthopearlite or partitioned pearlite.

3. Local equilibrium at the eutectoid growth front

The present discussion will be based on the simplifying assumption that the growing phases in a eutectoid colony obtain alloy contents expected from local equilibrium of each eutectoid phase in contact with the parent austenite(γ) at the growth front but subject to the carbon activity in the bulk of γ due to the comparatively rapid long-range diffusion of carbon. One can calculate the carbon activity for any alloy in a state of pure γ and then plot a corresponding isoactivity line in the phase diagram, extending over various phase fields where any point could represent supersaturated γ. This has been done in the schematic Fe–C–M phase diagram in Fig. 3. It is plotted with composition variables defined as $u_j = x_j/(x_{Fe} + x_M)$. The cross represents supersaturated γ in the γ + θ(cementite) phase field and it may precipitate θ. The parent γ would adjust its composition in contact with θ and, according to the local equilibrium assumption, that composition can be found on the intersection of the isoactivity line for carbon in the parent γ and the solubility limit for θ in γ, the point marked γ/θ. That γ phase can precipitate the third phase, φ, and adjust its composition to the point marked γ/φ which is on the solubility limit for φ in γ. From the intersections of an isoactivity line for carbon in γ with the solubility limits in γ for the