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THE ISOTHERMAL DECOMPOSITION OF IRON-NITROGEN AUSTENITE

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Introduction

Nitrogen, like carbon, forms an interstitial solid solution in gamma iron and the eutectoid section of the iron-nitrogen phase diagram can be seen in Fig. 1. The co-ordinates of the eutectoid point are 2.35 wt%N at 591°C and the associated phases are ferrite containing 0.1 wt%N, and the face centred cubic nitride Fe_4N, containing 5.3 wt%N. It is the purpose of this paper to discuss the experimental results of various kinetic, morphological and crystallographic studies of the isothermal decomposition of the metastable austenite at temperatures below 591°C and above the M_S temperature (2). Preliminary investigations by the authors (3) have indicated that the transformation products formed in the higher temperature ranges are various forms of iron-nitrogen pearlite, while the lower temperature product is iron-nitrogen bainite. As with the iron carbon system, there is a transition region where both pearlite and bainite can form simultaneously and the temperature and composition dependence for this transition is represented in Fig.1.

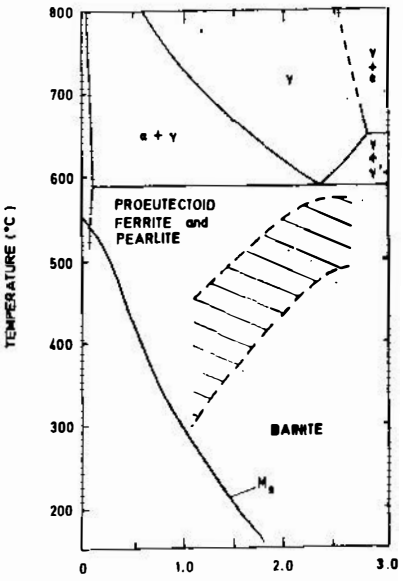

Fig. 1. The eutectoid section of the Fe-N phase diagram together with the temperature composition regions in which proeutectoid ferrite, pearlite and bainite are dominant. The variation of M_S with composition is also shown.

Preparation of Alloys

The series of iron-nitrogen alloys needed for the present studies of the decomposition of the metastable austenite were prepared in the form of thin sheet for optical and electron metallography and in the form of wire for

kinetic and structural analysis. These alloys containing up to 2.7 wt%N were produced from Johnson Matthey pure iron by nitriding with ammonia/hydrogen mixtures into the gamma phase field at temperatures between 650 and 740°C. (4).

General Isothermal Reaction Kinetics

The changes in electrical resistance accompanying the isothermal decomposition of austenite were measured at intervals of 20°C in the range 200°C to 585°C, for a series of alloys containing 0.8, 1.1, 1.3, 1.5, 1.9, 2.4 and 2.6 wt%N. These changes amounted to a decrease in resistance of about 30% to 50% of the initial value and they come to a definite end point. It was therefore possible to express the reaction in terms of the volume fraction of austenite transformed. T.T.T. diagrams derived from such data were found to be of the classical C-curve form observed for numerous reactions (5). At temperatures above the nose of the C curve, where the rate of reaction is increasing with decreasing temperature, the kinetics are necessarily complicated by the separation of pro-eutectoid constituents before the formation of pearlite. Therefore no further resistivity experiments were carried out where iron-nitrogen pearlite can form.

Iron-Nitrogen Pearlite

In 1905 when inhomogeneous alloys of iron-nitrogen were slowly cooled, a lamellar micro-structure was observed by Braune (6), after whom Fry (7) in 1923 named the product braunite. In the present optical metallographic studies, iron-nitrogen pearlite or braunite was found to have two basic nodular morphologies. These nodules could have either a lamellar structure in which case they resembled iron-carbon pearlite, or were granular, in which case the Fe_4N nitride in the ferrite matrix could not be resolved by optical metallography. Furthermore, the lamellar pearlite was only observed within 30°C of the eutectoid temperature. In the optical metallograph shown in Fig.2, which is of a eutectoid alloy fully transformed at 585°C, the lamellar pearlite accounts for only 20% of the

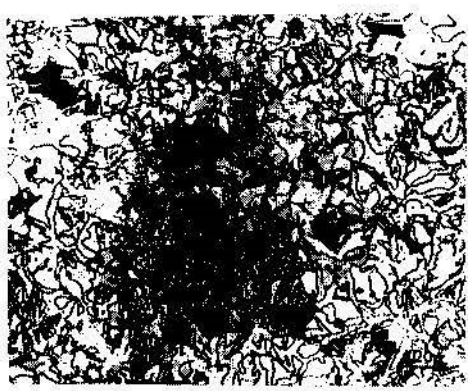

Fig.2.

Micrograph of an Fe-2.4 wt%N alloy fully transformed to granular and lamellar pearlite at 585°C.

transformation product, the rest is granular pearlite. Thin film electron microscopy studies enabled the fine structure of the granular pearlite to be resolved, and in Fig.3 the morphology of the Fe_4N nitride particles in a ferrite matrix can be observed. Analysis of the diffraction patterns of several such areas of granular pearlite showed that there was no consistent orientation relationship between the ferrite and the parent austenite, Fig.5.

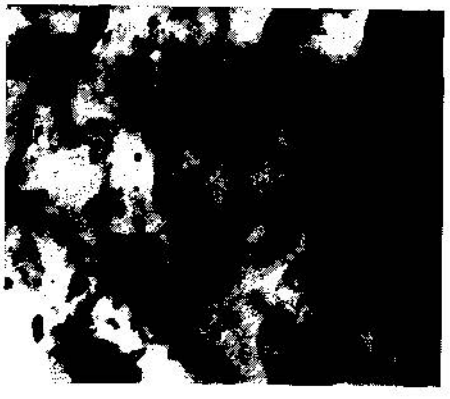

FIG. 3.

Transmission electron micrograph of granular pearlite in an Fe-1.1 wt%N alloy fully transformed at 310°C.

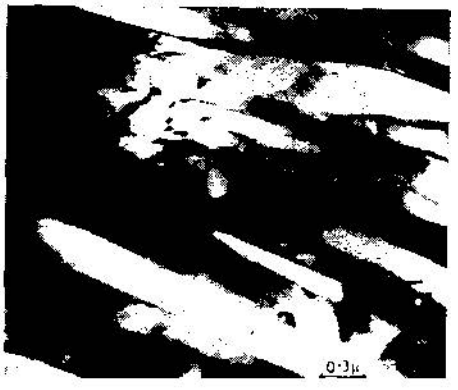

FIG. 4.

Bright field electron micrograph lamellar pearlite in an Fe-2.4 wt%N alloy fully transformed at 580°C.

However it was found that the crystal lattices of the face centred cubic nitride and the austenite were always parallel; this being due to the similarity of their crystal structures and lattice parameters (5). Electron diffraction analysis of lamellar structures, such as in Fig.4, showed that the Fe_4N and the austenite matrix were again in the parallel cube orientation. In the case of the lamellar pearlite, however, the orientations of both face centred cubic lattices with the ferrite were always within an 11° region of the Bain correspondence (8). These orientation results are summarized in the sterographic unit triangle in Fig.5.

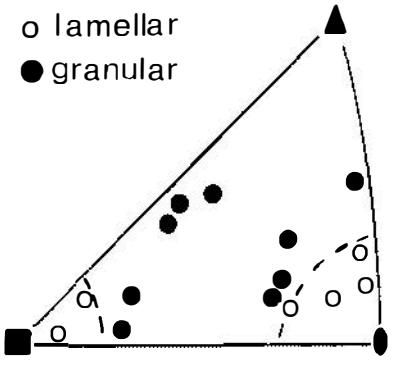

FIG. 5.

Orientation relationships between pearlitic ferrite and the austenite matrix; positions of <001> ferrite poles with reference to a unit triangle of the austenite lattice.

Iron-Nitrogen Bainite

Analysis of the kinetics of the formation of bainite, as derived from the resistivity measurements, showed that a single isokinetic reaction mechanism was operative over the temperature range 200-350°C (3). The present optical metallographic studies over the same temperature and composition range were able to confirm the kinetic results, in that only a single reaction product was observed and that this resembled upper bainite in the iron-carbon system. A transition was found to occur from this product being completely grain boundary nucleated at compositions up to 1.9 wt%N (Fig.6), to it being predominantely intra granular nucleated at compositions in excess of 2.4 wt%N (Fig.7). Optical metallographic techniques were unable to resolve

FIG. 6.
Micrograph of an Fe-1.8 wt%N alloy partially reacted at 310°C. Shows only grain boundary bainite.

FIG. 7.
Micrograph of an Fe-2.4 wt%N alloy partially reacted at 310°C. Shows both grain boundary and intragranular nucleated bainite.

individual phases of nitride and ferrite, except at early stages of transformation in alloys of low nitrogen content. However, the two phases were resolvable using thin foil transmission electron microscopy. It was observed that the ferrite was always the leading phase and that the nitride formed some distance behind the growth front at the boundaries of the ferrite crystals. However the extent by which the ferrite formation led the nitride was found to decrease as the nitrogen content increased. These features are illustrated in Fig.8 for a 2.4 wt%N alloy partially reacted at 450°C. The lattice orientation relationships between the ferrite of the bainitic product and the parent austenite, as derived from electron diffraction studies, are summarised in Fig.9, where it can be seen that

all the orientations lie within 11^{o} of the Bain relationship; this being the same relationship as was observed with the lamellar pearlite.

FIG. 8.

Transmission electron micrograph of an Fe-2.4 wt%N alloy partially reacted at $450^{o}C$ showing the structure of the grain boundary bainite.

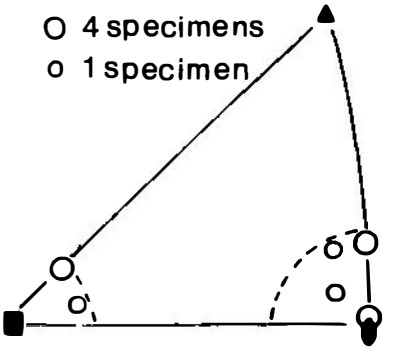

FIG. 9.

Summary of the orientation relationships between bainitic ferrite and the austenite matrix; unit triangle of the austenite lattice.

During the formation of bainite in the lower nitrogen alloys it has been shown, as in Fig.8, that ferrite is the leading phase and the formation of nitride some distance behind the growth front, is considered to be a secondary process. The rate of growth of the ferrite, which is essentially free of nitrogen, is limited by the rate at which nitrogen can be removed from the leading edge and will depend on the diffusivity of nitrogen in austenite in the interface. If lattice and boundary diffusion occur simultaneously in the interface during the growth of iron-nitrogen bainite, then the contribution made by boundary diffusion should be a function of the ferrite/austenite interfacial area. In practice the extent by which ferrite formation leads nitride precipitation is found to decrease as the nitrogen content of the alloy is increased and is not detectible in thin foils of partially reacted Fe-2.6 wt%N alloys. Consequently the contribution by boundary diffusion should diminish and become negligible in the most concentrated alloys. Since the activation energy for boundary diffusion in semi or incoherent interfaces is less than for lattice diffusion (9) then the value of the overall activation energy for bainite formation should be low in the more dilute alloys and approach that for lattice

diffusion of nitrogen in austenite, 30 Kcals/mole (10), in the 2.6 wt%N alloy. There is always some uncertainty in the significance of overall activation energies when the exact nature of the thermally activated processes contributing to the temperature dependency of the reaction rate are unknown. However, using the technique of Hillert (11) in conjunction with the resistivity data, it was found that the overall activation energy for the transformation to bainite increased uniformly from 20 Kcals/mole at 1.1 wt%N to 30 Kcals/mole at 2.6 wt%N, thus supporting the ideas discussed above.

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DISCUSSION :

R.D. Doherty : 1) May we see the electron microscope picture of the "branched" growing in the centre of grains in Fe - 1.9% Nitrogen?

2) Why do you think these structures formed in this way ?

T. Bell : A complete answer to the above questions may be found in reference 3 to the present paper.

H. Jones : What was the morphology of the granular pearlite ? Did the orientation of the nitride phase vary within a nodule ?

T. Bell : As discussed in the paper the granular pearlite has a nodular morphology. There was no consistent orientation relationship between the ferrite and nitride of the granular morphology.

N.J. Grant : Can you give further detail on the preparation of your high nitrogen alloys?

T. Bell : The alloys were prepared by nitriding into the gamma phase field using controlled mixtures of NH_3/H_2. Reference 4 in present paper gives full details.

N.J. Grant : It should be possible to produce high N_2-Iron alloys by pressurization techniques which could be splat cooled to room temperature.