A Kinetic and Electronmicroscopic Study of Transformations in Continuously Cooled Fe–15%Ni Alloys

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Koistinen and Marburger's equation relating volume fraction of athermal martensite to temperature has been applied to diffusional transformation dilatometry data obtained on continuous cooling Fe–15%Ni alloys. After austenitising for 1 h at 1 000°C and cooling at 50 K/min (0.83 K/s), grain boundary nucleated massive ferrite was observed which developed into Widmanstätten ferrite with a ferrite habit plane of $\{110\}_b$ for temperatures between 372°C and 352°C. On cooling at 44 K/s from 1 000°C bainitic ferrite was observed for temperatures below 360°C. There was some retained austenite in this bainitic structure giving a ferrite habit plane of $\{110\}_b$ parallel to the austenite plane $\{111\}_f$. Cooling at the same rate, 44 K/s from 1 200°C gave lath martensite below the M_s of 261°C with a ferrite habit plane of $\{112\}_b$. Superlattice spots corresponding to the DO₃ or B2 structure were observed in electron diffraction patterns on cooling at 50 K/min (0.83 K/s) and 44 K/s from 1 000°C.

KEY WORDS: Fe–15%Ni; Koistinen and Marburger's analysis; continuous cooling; dilatometry; massive ferrite; Widmanstätten ferrite; bainitic ferrite; lath martensite; crystallography; ordering; DO₃ or B2 structure.

1. Introduction

Normally the crystallography of transformations in quenched specimens is studied without reference to the thermal history of the specimens during quenching. However, different types of transformations may occur at different temperatures during cooling producing mixed morphologies. The work in this paper describes the morphology of massive ferrite^{1–3)} (α_q) and the crystallography of Widmanstätten ferrite^{3,4)} (α_w), bainitic ferrite^{5–8)} (α_B), and lath (massive) martensite^{9,10)} (α_m). The nomenclature in brackets is due to Araki *et al.*¹¹⁾ These microstructures were observed in Fe–15%Ni alloys under different austenitising conditions and cooling conditions. Thermal history during cooling was characterised by an expression based on Koistinen and Marburger's (K-M) equation for athermal martensite¹²⁾ as described in the next two paragraphs.

K-M found that the volume fraction of athermal martensite, y varied with temperature T below the martensite start temperature M_s , according to the equation:

$$\ln(1-y) = (M_s - T) \dots \dots \dots (1)$$

Thus $-\ln(1-y)$ varies linearly with temperature T .

This equation was later derived from first principles by Magee¹³⁾ who showed that:

$$\alpha = \bar{V} \phi \Delta S_v^{\gamma \rightarrow \alpha} \dots \dots \dots (2)$$

where $\bar{V}$ =average volume of each newly formed plate of martensite. ϕ =proportionality constant relating the change

in chemical driving force $d\Delta G_v^{\gamma \rightarrow \alpha}$ /unit volume of martensite for austenite to martensite transformation during a temperature drop dT , to the increase in number of new plates of martensite per unit volume of austenite, dN . $\Delta S_v^{\gamma \rightarrow \alpha}$ =entropy change for austenite to martensite transformation/unit volume of martensite. This is assumed to be constant over the temperature range M_s to M_f , where M_f =martensite finish temperature.

Recently it has been found that K-M's equation can be applied to dilatometric data obtained on continuously cooling specimens undergoing diffusional transformations.^{3,14)}

Figure 1 for example shows the dilatation curve for a

Fig. 1. Dilatometry curve for a 0.13% C HSLA steel, cooled at 1 K/s, after Medina *et al.*¹⁵⁾

Fig. 2. Koistinen and Marburger's (K-M) analysis of Fig. 1; $-\ln(1-y)$ versus temperature; where y =volume fraction transformed. After Wilson and Medina.¹⁴⁾

0.13% C high strength low alloy (HSLA) steel obtained during cooling at 1 K/s,¹⁵⁾ while Fig. 2, show plots of $-\ln(1-y)$ vs. temperature derived from Fig. 1.¹⁴⁾ It will be seen in Fig. 2 that there are a number of straight lines of increasing slope and that the intersections of these lines define temperatures in good agreement with the temperatures of transformation points on the dilatometric curve, Fig. 1.

Transformations in Fe-15%Ni occur at a slower rate than in pure iron, and the effects of cooling rate on transformation temperatures in this alloy are well established, Fig. 3.⁸⁾ It was therefore decided to study transformations in Fe-15%Ni by dilatometry and K-M analysis. The crystallography of the transformations of the same specimens could then be further investigated by subsequent transmission electron microscopy (TEM).

Tsuzaki *et al.*^{16,17)} have commented on the isothermal character of transformations in an Fe-15%Ni alloy. These authors found isothermal transformation at temperatures below what they say is the athermal M_s of $397 \pm 5^\circ\text{C}$, with a maximum isothermal rate at 380°C . The carbon content of Tsuzaki *et al.*'s alloy was 0.0017% compared with 0.01% C in the alloy studied by Wilson *et al.*^{6,8)} This difference in carbon content may therefore account for the slight discrepancy in transformation temperature between the two alloys. The depression of transformation temperature to a plateau of 350°C with increasing cooling rate, Fig. 3⁸⁾ is direct evidence of an isothermal component to the transformation in Fe-15%Ni. Nevertheless the present authors maintain that the transformation in this alloy is bainitic at this temperature even if the carbon content is lowered to 0.0017% C. The debate is akin to that argued for the B_s being $\sim 700^\circ\text{C}$ and M_s of lath martensite, $545 \pm 5^\circ\text{C}$ at higher cooling rates in pure iron.^{6,18-21)}

Cantor and his co-workers²⁴⁻²⁶⁾ have observed what is clearly twinned martensite in splat quenched Fe-5%Ni and Fe-10%Ni alloys. In melt spun Fe-Ni alloys Hayzelden and Cantor²⁷⁾ found massive ferrite in concentrations upto 25% Ni, rather than massive (lath) martensite¹⁰⁾ in conventionally cooled material. Massive ferrite is thought to form due to the enhanced nucleation rate at the many austenite grain boundaries and grain corners in the very fine austenite grains of size $3 \mu\text{m}$. The fine austenite grains arise from the

Fig. 3. Variation of transformation temperature with cooling rate in Fe-15%Ni, taken from Wilson *et al.*⁸⁾

very fast solidification encountered in melt spinning.

2. Experimental Procedure

Fe-15%Ni alloys were manufactured by tungsten arc button melting using Japanese electrolytic iron, carbonyl nickel shot and pure graphite. They were then hand forged at 1050°C to an 8 mm diameter slug and after homogenising swaged to 5.1 mm diameter rod. Two series of alloys were made which received slightly different homogenising treatments:

- Series A Fe-14.53 $\pm$ 0.3%Ni, 0.01 $\pm$ 0.005%C, sealed under vacuum in silica. Capsule cooled in air after homogenising for 4 d at 1150°C and after normalising for 35 min at 900°C .
- Series B Fe-15 $\pm$ 0.5%Ni, 0.01 $\pm$ 0.005%C, sealed under vacuum in silica. Capsule cooled in air after homogenising for 24 h at 1250°C and after normalising for 1 h at 900°C .

The composition of the alloys are in mass%. Inaccuracies in composition arose due to the limited amount of material available for analysis. Dilatometer specimens, 5 mm diameter $\times$ 10 mm were machined from the swaged rod and tested in an MMC quenching dilatometer at Corus, Swinden Technology Centre, Rotherham. Austenitising treatments, cooling conditions and transformation temperatures are given in the results part of the paper.

Cylinders 3 mm diameter $\times$ 10 mm long were carefully machined from the dilatometer specimens. Discs for TEM were cut from these 3 mm diameter cylinders, ground down on emery papers to 50–100 μm thickness, and jet polished in an electrolyte consisting of 420 ml ethanol, 120 ml glycerol and 60 ml perchloric acid at -40°C . Such foils were examined in a JEOL 3010 electron microscope operated at 300 kV with a double tilting stage. The rotation angle between the image and the diffraction pattern was controlled within $\pm 0.25^\circ$. The interfaces between the transformation products and the matrix were observed at the edge on condition as far as possible. *i.e.* the thickness fringes due to the boundaries were made as thin as possible by tilting the specimen. Thus, the normals to the interfaces provided the habit plane normals of Widmanstätten ferrite, bainite and

Fig. 4. Dilatation curves for alloys analysed in this investigation.

Fig. 5. K-M analysis of run No. 22, showing grain boundary massive ferrite forming between 386°C and 372°C, and Widmanstätten ferrite between 372°C and 352°C.

martensite. Optical micrographs were taken on a Zeiss microscope. Following Tsuzaki *et al.*,¹⁷⁾ specimens were etched for 2–3 s in water diluted aqueous ferric chloride.

3. Experimental Results

Figure 4 shows the dilatometer curves obtained on cooling the two alloys, whereas Figs. 5 to 7 show the K-M analyses of these dilatometer curves. A description of the runs carried out on the dilatometer now follows together with an account of the microstructure observed by TEM. The following nomenclature was used for transformation temperatures; α_s , W_s and B_s are the start temperature for the austenite to ferrite transformation, to Widmanstätten ferrite and to bainite respectively. The temperature γ_s is the start temperature for the reverse transformation to austenite. Percentages in brackets after the transformation points give the amounts of transformed product at the commencement of that particular type of reaction.

3.1. Run No. 22. Alloy Series B. Fe-15±0.5%Ni, 0.01±0.005%C

Figure 5 shows the analysis of the dilatometric curve for run No. 22 heated at 50 K/min under vacuum, and after holding for 1 h at 1000°C cooled at 50 K/min $\gamma_s(0\%) = 620^\circ\text{C}$, $\alpha_s(0\%) = 386^\circ\text{C}$, $W_s(11\%) = 372^\circ\text{C}$, $B_s(87\%) =$

Fig. 6. K-M analysis of run No. 23, showing bainitic ferrite forming between 315°C and 234°C.

Fig. 7. K-M analysis of run No. 24, showing lath martensite forming between 261°C and 232°C.

352°C, and $T_0 = 1/2(\alpha_s + \gamma_s) = 503^\circ\text{C}$.

The microstructure consisted of mainly Widmanstätten ferrite and some grain boundary massive ferrite. A lath structure is evident in the specimens taken from run No. 22, Fig. 8(a) and Fig. 9(a). The lath width is $\sim 0.7 \mu\text{m}$ and the dislocation density reduced compared with figures of bainitic ferrite and lath martensite, to be discussed later. These ferrite laths form between 372°C and 352°C, and are thought to be Widmanstätten ferrite rather than bainitic ferrite because of the reduced dislocation density and the high temperatures during transformation. Electron diffraction patterns in Fig. 8(b) and Figs. 9(b) and 9(c) in conjunction

Fig. 8. Widmanstätten ferrite in specimen from run No. 22, cooled at 50 K/min, (0.83 K/s). Temperature range 372°C to 352°C.
(a) Bright field image and (b) electron diffraction pattern of Fig. 8(a).

Fig. 9. Another area of Widmanstätten ferrite in specimen from run No. 22, cooled 50 K/min, (0.83 K/s). The temperature range was from 372°C to 352°C.
(a) Bright field image, (b) electron diffraction pattern of Fig. 9(a), and (c) analysis of electron diffraction pattern of Fig. 9(b), note presence of superlattice spots.

Fig. 10. Typical optical micrograph of specimen from run No. 22.

Fig. 11. Massive ferrite around prior austenite grain boundaries taken from specimen of run No. 22, cooled at 50 K/min, (0.83 K/s). Temperature range 386°C to 372°C.
(a) Bright field image and (b) electron diffraction of pattern Fig. 11(a) showing slight misorientation between grains.

with the TEM micrographs indicate a $\{110\}_b$ ferrite habit for the laths in agreement with King and Bell's study of Widmanstätten ferrite in Fe-0.47% C.²⁸⁾

(* In this paper the suffix b refers to bcc *i.e.* ferrite, α ; likewise f refers to fcc, *i.e.* austenite, γ .)

Note the existence of strong superlattice spots in the diffraction pattern of Fig. 9. A typical optical micrograph of this structure is shown in **Fig. 10**. It is difficult to reveal the ferrite and Widmanstätten ferrite interfaces by conventional etching techniques because of the low carbon content of the alloys.

Specimens from this run, (No. 22) also frequently showed areas of massive ferrite around prior austenite grain boundaries, **Fig. 11**. The electron diffraction pattern in Fig. 11(b) indicates the significant misorientation $\pm 7^\circ$ about a common $\langle 111 \rangle_b$ close-packed direction between massive ferrite grains. This grain boundary ferrite may be compared with the areas of massive ferrite seen by Chong *et al.*³⁾ in furnace cooled Fe-9%Ni. Grain boundary ferrite forms heterogeneously at a high temperature on prior austenite grain

Fig. 12. Typical optical micrograph of specimen from run No. 23.

Fig. 13. Bainitic ferrite taken from specimen from run No. 23, cooled at 44 K/s. Temperature range 315°C to 234°C. (a) Bright field image and (b) electron diffraction pattern taken from area in Fig. 13(a).

boundaries. This ferrite subsequently develops into Widmanstätten ferrite within the austenite grains with tent relief on prepolished surfaces.^{3,4,29–37} Similar structures were observed by Bodnar and Hansen^{36,37} in a 0.18%C–1.1%Mn steel. As long ago as 1979, Entin and his co-workers³⁸ describe “Widmanstätten ferrite crystals, mainly observed inside the grains, with a network of polyhedral ferrite crystals in the boundary zone, the formation of which does not involve the development of micro-relief” in 0.03% C low alloy steels. These workers³⁸ also observed it was easier to obtain Widmanstätten ferrite with high austenitising temperatures for long periods, an effect also observed by Chong in Fe–9%Ni³⁹ and Bodnar and Hansen^{36,37} in their steels.

3.2. Run No. 23. Alloy Series A. Fe–14.53±0.2%Ni, 0.01±0.005%C

Figure 6 shows the analysis of the dilatometer curve for run No. 23 heated at 50 K/min, and after holding for 1 h at 1 000°C cooled at 44 K/s. $\gamma_s(0\%)=583^\circ\text{C}$, $\alpha_s(0\%)=360^\circ\text{C}$, and $B_s(15\%)=315^\circ\text{C}$ respectively. The microstructure was

Fig. 14. Another area of bainitic ferrite, taken from specimen of run No. 23, cooled at 44 K/s. Temperature range 315°C to 234°C.

(a) Bright field image, (b) electron diffraction pattern of area in Fig. 14(a), sheet 5, Analysis of electron diffraction pattern of area in Fig. 14(a), (c) analysis of electron diffraction pattern in Fig. 14(b); note presence of superlattice spots.

mainly bainitic ferrite. This is probably due to the finer austenite grain size compared with that in run No. 24 where the austenitising temperature was 1 200°C. An optical micrograph of the structure is shown in Fig. 12. As can be seen in Figs. 13, 14, and 15 the interfaces between the bainitic laths and the matrix (which often decomposed into martensite during the subsequent cooling) were very straight and the habit planes were parallel to the $\{110\}_b$ ferrite plane. The smoothness of the interfaces may arise from the diffusional modification of the lath surfaces after the ferrite lath formation. In the case of Fig. 13, the habit plane can be slightly rotated about the $[112]_b$ ferrite direction from the $(110)_b$ ferrite plane. In Fig. 14 the habit plane can also be slightly rotated about the $[1\bar{1}0]_b$ ferrite direction from the $(110)_b$ ferrite plane. However, in both cases, the normals to the interface traces coincide with the $[110]_b$ ferrite direction. Thus the ferrite habit plane of this structure is exactly $(110)_b$, within an error of 1° . Ohmori *et al.*^{40,41} reported a common ferrite habit plane of $\{110\}_b$ with a long axis parallel to the $\langle 111 \rangle_b$ ferrite direction for bainites in Ni–Cr–Mo steels containing 0.12–0.22% C. They christened these bainites B-I, B-II and B-III. Bainite B-I is one form of upper bainite forming at a relatively high temperature and is similar to bainitic ferrite described here with a lath morphology and retained austenite between the laths. In B-II bainite the austenite is sufficiently enriched in carbon to precipitate cementite between the laths. B-III bainite forms at temperatures just above M_s . The cementite is pre-

Fig. 15. Area of bainitic ferrite showing retained austenite, taken from specimen from run No. 23, cooled at 44 K/s. Temperature range was from 315°C to 234°C. (a) Dark field image using the $(200)_f$ reflection, (b) electron diffraction pattern of area in Fig. 15(a) and (c), analysis of diffraction pattern in Fig. 15(b); note presence of superlattice spots.

cipitated at a constant angle within the laths, similar to lower bainite^{42,43} although in the latter case plates of bainite were reported rather than laths.⁴²

The existence of a bainitic transformation in low interstitial alloys was first suggested independently by Goodenow and Hehemann,⁵ and Wilson.^{6,19} The bainitic structure in very low-carbon alloys has since been reported in various literatures.^{44–53} Wilson *et al.*⁸ reported a tentative ferrite habit plane of $\{112\}_b$ for bainitic ferrite in Fe–15%Ni. However this was only a cursory TEM analysis with three traces, and was not very accurate.

It is also of interest that the superlattice spots similar to a DO_3 or B2 structure were recognised in the case of the $\langle 100 \rangle_b$ ferrite zone in Figs. 14(b) and 14(c) and Figs. 15(b) and 15(c). The intensity of these spots was not as great as those obtained in Fig. 9(b) of run No. 22. It appears that their intensity increased with decreasing cooling rate.

Additional evidence showing that Figs. 13(a), 14(a) and 15(a) are bainitic is the existence of retained austenite in this structure. Gilbert and Owen⁵⁴ reported retained austenite in Fe–15%Ni at 5500 K/s which according to Fig. 3, is bainitic at this cooling rate (the same alloy was used for determining Fig. 3 as that used by Gilbert and Owen). In the case of martensite observed in run No. 24, to be discussed later, the retained austenite layers could never be observed

Fig. 16. Optical micrograph of specimen from run No. 24.

at the interfaces between the martensite laths. It is thought that in the case of bainite, partition of carbon atoms occurred between the ferrite and the austenite matrix,^{55,56} thus stabilising the interlath austenite. An example is shown in Fig. 15(a). The dark field image using the $(002)_f$ austenite reflection revealed that an austenite layer exists between the ferrite laths. The orientation relationship between the ferrite (suffix b) and the austenite (suffix f) is given as:

$$\begin{aligned} (011)_b // (111)_f \\ [100]_b // [\bar{1}10]_f \\ [01\bar{1}]_b // [11\bar{2}]_f \end{aligned}$$

This is the Nishiyama–Wassermann relationship.⁵⁷ However, since the mutual rotation of $\pm 7^\circ$ about the $[011]_b // [111]_f$ axis can be allowed, this pattern cannot be separated from the Kurdjumov–Sachs relationship.⁵⁸

$$\begin{aligned} (011)_b // (111)_f \\ [11\bar{1}]_b // [10\bar{1}]_f \\ [2\bar{1}1]_b // [1\bar{2}1]_f \end{aligned}$$

3.3. Run No. 24 Alloy Series A. Fe–14.43±0.2%Ni, 0.01±0.005%C

Figure 7 shows the analysis of the dilatometric curve for run No. 24 heated at 50 K/min after holding for 0.5 h at 1200°C cooled at 44 K/s. $\gamma_s(0\%)=579^\circ\text{C}$, $\alpha_s(0\%)=285^\circ\text{C}$ and $M_s(40\%)=261^\circ\text{C}$, respectively. Bainitic ferrite is thought to form between 285°C and 261°C. The microstructure was mainly lath martensite, no retained austenite was observed. An optical micrograph of the specimen from run No. 24 is shown in Fig. 16. In this case the transformation products were lath-like and were highly dislocated. The laths were aligned in parallel fashion but the interfaces between them are not so straight, such a structure being often encountered in martensite; Figs. 17 and 18. Because of this and the fact that the specimen is cooled from a high austenitising temperature, the authors believe this structure to be martensite. Martensite is more easily obtained on quenching from a high temperature.^{38,39,59} The habit plane, or at least the broad face of laths of this martensite was close to the ferrite plane $\{112\}_b$, Figs. 17 and 18. In some regions, A and B in Fig. 17(a) parallel laths were twin-related as can be seen in Figs. 17(b) and 17(c) its schematic representation Fig. 17(d) and tracing of laths Fig. 17(e). Thus

Fig. 17. Lath martensite taken from specimen from run No. 24, cooled at 44 K/s. Temperature range was from 285°C to 232°C. (a) Bright field image, (b) electron diffraction pattern of area A in Fig. 17(a), (c) electron diffraction pattern of area A and B in Fig. 17(a), (d) analysis of diffraction patterns from areas A and B, and (e) part tracing of Fig. 17(a), showing location of diffraction patterns, *i.e.* within each circle. See text for further discussion.

the diffraction pattern in Fig. 17(b) was from area A *i.e.* lath M1. The diffraction pattern in Fig. 17(c) was from areas A and B *i.e.* laths M1, T1, M2 and T2. Laths M1 and T1 are twin related, as are T1/M2 and M2/T2. Laths M1, M2, and M3 are in the same orientation and T1 and T2 are also in the same orientation. Thus the relative orientations are given by:

$$\begin{aligned} [11\bar{1}]_{\text{matrix}}/[11\bar{1}]_{\text{twin}} \\ [101]_{\text{matrix}}/[101]_{\text{twin}} \\ (\bar{1}21)_{\text{matrix}}/(\bar{1}2\bar{1})_{\text{twin}} \quad \text{close to habit plane} \end{aligned}$$

The detail of this orientation relationship will be discussed later. The observation that the habit plane is $\{112\}_b$, requires some justification since the boundary of the laths was observed to be wavy. In Fig. 17(e) the lath boundaries

Fig. 18. Lath martensite taken from specimen from run No. 24, cooled at 44 K/s. Temperature range was from 285°C to 232°C. (a) Bright field image and (b) electron diffraction pattern of area in Fig. 18(a).

were slightly wavy in the direction $[111]_m/[111]_t$. However in the direction normal to the photograph the interface is rather straight and the thickness of the boundary < 8.6 nm (*i.e.* < 0.5 nm at $\times 58000$). Even if the foil is assumed to be as thin as 100 nm the deviation of the M1/T1 interface from the incident beam direction will be less than $8.6/100$ radians *i.e.* 5° . Thus the habit plane of the martensite of $\{112\}_b$ is thought to be accurate to less than 5° . Rao and Thomas⁶⁰ also observed twin related laths with a $(112)_b$ habit occasionally in quenched 0.3% C iron alloys and more extensively in a quenched Fe-4%Cr-0.4%C alloy and concluded that these laths obeyed the Bain relationship. However, this relationship should be treated with caution since some ambiguity exists in the analysis of their diffraction patterns similar to those described above.

There is possibly an area of twinned martensite, marked C in Fig. 17(a). It is possible from the K-M analysis, Fig. 7 that this martensite forms at 232°C (85%). This point is discussed further in Sec. 4.1.

4. Discussion

4.1. Transformation Temperatures

Kaufman and Cohen⁶¹ showed that for athermal, non thermoelastic martensitic transformations;

$$T_0 = 1/2 (M_s + A_s) \quad \dots\dots\dots (3)$$

where A_s is the temperature of transformation of martensite to austenite by reverse shear. At a later date, Wilson^{6,62} found that for the bainitic transformation in Fe-15%Ni and the massive transformation in alloys containing less than 10% Ni:

$$T_0 = 1/2 (\alpha_s + \gamma_s) \quad \dots\dots\dots (4)$$

Strictly speaking this only applies to transformations occur-

ring athermally. In fact it was found that there was good agreement between theoretical values of T_0 defined by the condition $\Delta G_{\gamma-\alpha}^{\gamma-\alpha}=0$ and those given by Eq. (4) using values of α_s and γ_s obtained at the same heating and cooling rate. In the case of run No. 22 $T_0=1/2(\alpha_s+\gamma_s)=503^\circ\text{C}$ while the recent thermodynamic analysis of Borgenstam and Hillert²³⁾ gave a value of 488°C at 15% Ni. The significance of these values of T_0 is that all the transformations, namely massive ferrite, Widmanstätten ferrite, bainitic ferrite, lath martensite and twinned martensite, occur below T_0 with sufficient chemical driving force $\Delta G^{\gamma-\alpha}$ to drive these composition invariant transformations. However the transformation temperatures are such that they occur in the two phase field, *i.e.* outside the single phase region to give supersaturated ferrite, the reaction to $(\alpha+\gamma)$ being far too sluggish.^{63,64)} This is in agreement with the work of Massalski⁶⁵⁾ who found the massive transformation occurred in an Fe–9.1%Ni outside the retrograde single phase region on quenching. Chong *et al.*³⁾ also reported massive ferrite forming in an Fe–9.14%Ni alloy in the temperature range 575°C to 558°C , also in the two phase region. In the case of alloy B, run No. 22, the formation of massive ferrite is thought to occur between 386°C and 372°C , while Widmanstätten ferrite forms between 372°C and the B_s of 352°C . However in the latter case Aaronson *et al.*⁶⁶⁾ reports $W_s(\alpha_w)$ for Widmanstätten ferrite to be above T_0 , but below A_{e3} in Fe–C alloys, as does Enomoto⁶⁷⁾ in Fe–0.108%C–Si and Fe–0.108%C–Mn alloys. Bhadeshia^{32,68)} presents impressive calculations showing that W_s depends on the degree of undercooling below A_{e3} and not T_0 . In all these cases T_0 was calculated from theory and not experimental determinations as carried out here, and therefore maybe questionable. Ohmori *et al.*^{33,69)} reports W_s to be below T_0 in Si–Mn steels containing upto 0.58% C. Clearly further theoretical and experimental work is required in this area.

The B_s of 352°C in alloy B is in good agreement with the plateau value of 350°C found in Ref. 8), Fig. 3 for Fe–15%Ni. However the B_s of 315°C in alloy A observed in run 23 is considerably lower than 350°C . The reason for this is not known but could be due to a higher carbon content in alloy A compared with alloy B. The B_s temperature is very sensitive to residual carbon levels,^{21,70,71)} $\sim 11\,000\text{ K}/\%\text{C}$, whereas the M_s for lath martensite and the M_s for twinned martensite are relatively insensitive; $\sim 380\text{ K}/\%\text{C}$ and $\sim 206\text{ K}/\%\text{C}$ respectively.⁷²⁾ It is not clear what is happening between 360°C and the B_s of 315°C , and it will require further work to clarify what mode of transformation is occurring in this temperature interval.

It is possible that the change in slope at 234°C and 232°C of the K–M plots for runs No. 23 and 24, Figs. 6 and 7 represent the M_s for twinned martensite. The collected data for transformation temperatures in Fe–Ni alloys by Zhao,⁷³⁾ gives a value of $233\pm 10^\circ\text{C}$ for M_s of twinned martensite in Fe–15%Ni. However, there is considerable recalescence $\sim 22\text{ K}$ in the thermal arrest accompanying the formation of twinned martensite.⁶²⁾ This is due to the large latent heat of the transformation⁷⁴⁾ to twinned martensite and thus one might expect a more definite change in slope of the K–M plot. More work is therefore required to establish the M_s of twinned martensite in Fe–15%Ni.

4.2. Crystallography and Morphology of Massive Ferrite and Widmanstätten Ferrite

The observation of grain boundary nucleated ferrite developing into Widmanstätten ferrite at high temperatures in run No. 22 is in agreement with previous work on Fe–7.4%Cr–1.8%Ni,⁵⁰⁾ on a 0.23% C low alloy steel,³³⁾ on an Fe–9%Ni alloy³⁾ and on a 0.18%C–1.1%Mn steel.^{36,37)} As stated previously the ferrite habit plane of $(110)_b$ for Widmanstätten ferrite is in agreement with the observations of King and Bell²⁸⁾ on a Fe–0.47%C alloy. Indeed as noted by Ohmori⁵³⁾ the crystallography of Widmanstätten ferrite, upper bainite (presumably bainitic ferrite for $C<0.01\%$) and lath martensite are similar and only differ in respect of lath width and dislocation density and mode of nucleation. The low dislocation density of dislocations in Widmanstätten ferrite are also consistent with the work of Ricks *et al.*⁵⁰⁾

4.3. Crystallography of Bainitic Ferrite

Araki and co-workers^{51,52)} have proposed a crystallographic model for bainite formation involving an invariant line and approximate austenite habit plane of $\{111\}_f$ equivalent to $\{101\}_b$ ferrite plane. This is roughly in agreement with the habit plane found here. Christian⁷⁵⁾ has commented on the validity of applying an invariant line strain to the bainitic transformation. Bainitic ferrite is thought to be similar to upper bainite with austenite trapped between the laths rather than cementite.⁴¹⁾ The laths have an austenite growth direction close to $\langle 110 \rangle_f$ and an austenite habit plane near $\{111\}_f$. This type of habit cannot be obtained directly from the phenomenological theories of Bowles–Mackenzie⁷⁶⁾ assuming a common $\langle 110 \rangle_f$ direction lattice invariant shears. However, there is some evidence that bainitic ferrite forms by the coalescence of needlelike ferrite sub-units. These are elongated in a $\langle 110 \rangle_f // \langle 111 \rangle_b$ lattice invariant shear direction on the $\{111\}_f$ austenite slip planes forming a slip band. These leads to the formation of bainitic ferrite with the $\langle 110 \rangle_f \{111\}_f$ habit. This in turn nucleates another bainitic lath.⁴¹⁾ This model is probably the most appropriate to the present results on Fe–15%Ni alloys.

4.4. Crystallography of Lath Martensite

As mentioned previously the lath martensite obtained here, below 285°C , had a ferrite habit plane of $\sim (112)_b$ in agreement with Rao and Thomas⁶⁰⁾ for twinned related laths in a quenched 0.3% C alloy and an Fe–4%Cr–0.4%C alloy. However in work on a quenched 0.1% C, 2% Si iron alloy and a 0.3% C, 3% Cr, 2% Mn, 0.5% Mo steel Kelly *et al.*⁷⁷⁾ obtained a different result using a precision diffraction technique involving Kikuchi line patterns. In this case adjacent laths were found to have different variants of the Greninger–Troiano relationship⁷⁸⁾ which could be mistaken for a twin relationship. The austenite habit plane in Kelly *et al.*'s alloys was $(557)_f$ approximately 10° from the austenite plane $(111)_f$ which is parallel to the ferrite plane $(101)_b$.

Owen and his co-workers^{79,80)} studying iron–nickel alloys with a steep composition gradient and using two and three surface analysis report a habit plane within 3° of $\{111\}_f$ parallel to $\{110\}_b$ and an orientation relationship near to that of and Nishiyama.⁵⁷⁾ In the same paper, Schoen *et al.*⁸⁰⁾ also summarise that all the previous determinations of the

habit plane of lath martensite lie within 12° of $\{111\}_f$. These workers⁸⁰⁾ obtained good agreement with crystallographic theories of martensite formation using two lattice invariant shears occurring by slip. Bryans *et al.*⁸³⁾ report a habit close to $\{111\}_f$ in high Ni iron alloys. Marder and Krauss⁸⁴⁾ also reported a $\{557\}_f$ habit plane in Fe–0.2% C, Fe–0.6% C and Fe–12% Ni, as did Sandvik and Wayman in an Fe–20% Ni–6% Mn alloy.⁸⁵⁾ This $\{557\}_f$ habit is also predicted using two lattice invariant shears occurring by slip.^{85,86)} The formation of lath martensite with these $\{111\}_f$ to $\{557\}_f$ habit planes could be explained in a similar fashion described above for bainitic ferrite.⁸⁷⁾

However it should be noted that the habit plane, at least the broad face, of the present lath martensite is far from $\{110\}_b/\{111\}_f$ and close to $\{112\}_b$. In the theory of martensite crystallography,⁷⁶⁾ this $\{112\}_b$ ferrite plane should lie within a stereographic triangle consisting of the $(010)_f$, the $(011)_f$ and the $(111)_f/(011)_b$ when the following Kurdjumov–Sachs relationship holds:

$$\begin{aligned} (111)_f/(011)_b \\ [10\bar{1}]_f/[11\bar{1}]_b \\ [1\bar{2}1]_f/[2\bar{1}1]_b \end{aligned}$$

Considering both martensite laths formed from the same austenite grain and above condition, the following relationship will be deduced by assuming the Kurdjumov–Sachs orientation relationship:⁵⁸⁾

$$\begin{aligned} [11\bar{1}]_{\text{matrix}}/[11\bar{1}]_{\text{twin}}/[10\bar{1}]_f \\ (011)_{\text{matrix}}/[0\bar{1}\bar{1}]_{\text{twin}}/(111)_f \\ [2\bar{1}1]_{\text{matrix}}/[2\bar{1}1]_{\text{twin}}/[1\bar{2}1]_f \\ (\bar{1}21)_{\text{matrix}}/(\bar{1}2\bar{1})_{\text{twin}}/\sim(131)_f \quad \text{close to habit plane} \end{aligned}$$

4.5. Kinetics of Transformations

Run No. 22 gave a value of -0.094 K^{-1} for the parameter in Eq. (1) for Widmanstätten ferrite, which may be compared with the value of -0.083 K^{-1} obtained for the same reaction in Fe–9% Ni.³⁾ Bainitic ferrite gave an average value for α of -0.031 K^{-1} from Figs. 5 and 6 while lath martensite a value of -0.052 K^{-1} from run No. 24. This latter value may be compared with -0.011 K^{-1} for twinned martensite in plain carbon steels.¹²⁾

The fact that lath martensite grows comparatively slowly⁸⁸⁾ ~ 0.07 to 0.4 mm/s ^{89,90)} has led to the suggestion that the rate of growth of lath martensite is controlled by the rate of movement by slip of the lattice invariant shears.⁹¹⁾ In contrast the rate of growth twinned martensite is very rapid⁸⁸⁾ $\sim 1000 \text{ m/s}$,^{92,93)} so in this case the rate of movement of the lattice invariant shear by twinning may control the speed of formation of this type of martensite.⁹¹⁾

4.6. Superlattice Spots

Superlattice spots were observed in the $\langle 100 \rangle_b$ ferrite zone in Figs. 9(a) and 9(b), Figs. 14(b) and 14(c) and Figs. 15(b) and 15(c). Their intensity increased with decreasing cooling rate. Thus such an ordering may be an indication that bainite formed *via* short range diffusion while keeping atomic-site correspondence between it and the austenite matrix. Although far from the composition of Fe₃Ni or FeNi it is possible that the ordered electron spots are due to

formation of either of these phases in Fe–15% Ni. The FeNi and Fe₃Ni phases are not present on the Fe–Ni phase equilibrium diagram.⁹⁴⁾ However a number of workers have proposed the existence of ordered structures based on Fe₃Ni and FeNi corresponding to the DO₃ or B2 crystal structure.⁹⁴⁾ As remarked by Swartzendruber *et al.*⁹⁴⁾ it is possible that these phases are metastable. Ohmori⁹⁵⁾ also found superlattice electron diffraction spots in Fe–9Ni–0.8C martensites tempered at 100°C .

5. Summary

Transformations in low carbon Fe–15% Ni alloys obtained under continuous cooling conditions have been examined by application of Koistinen and Marburger's equation for athermal martensite¹²⁾ to dilatometric data and by transmission electron microscopy.

(1) At slow cooling rates, 50 K/min, (0.83 K/s) grain boundary nucleated massive ferrite was observed between 386°C and 372°C , which developed into Widmanstätten ferrite, with a $(110)_b$ ferrite habit plane, between 372°C and the B_s of 352°C .

(2) On cooling from a low austenitising temperature (1000°C) at 44 K/s, bainitic ferrite with a $\{110\}_b$ ferrite habit, accurate to $\pm 1^\circ$, was obtained. There was retained austenite between the laths giving a habit plane in the austenite of $\{111\}_f$ with either a Nishiyama–Wassermann orientation relationship⁵⁷⁾ or a Kurdjumov–Sachs⁵⁸⁾ relationship. The diffraction conditions were such that it was not possible to distinguish between these two relationships. The dislocation density was higher than that observed for Widmanstätten ferrite, but lower than that for lath martensite. The phenomenological crystallographic theory⁴¹⁾ was thought to apply to this structure. It was possible that twinned martensite formed at $233 \pm 3^\circ\text{C}$ and below at this cooling rate.

(3) On cooling at the same rate, 44 K/s, from a higher austenitising temperature, 1200°C , lath martensite formed with an M_s of 261°C . This M_s is in agreement with a previous determination of $260 \pm 20^\circ\text{C}$, Fig. 3.⁸⁾ Areas of twinned martensite were also observed, C, Fig. 17(a) and are thought to form at $233 \pm 3^\circ\text{C}$ and below. No. retained austenite was observed in this specimen and the ferrite habit plane was $\{112\}_b$, within 5° , in agreement with the earlier work of Rao and Thomas.⁶⁰⁾

(4) Superlattice spots observed in the $\langle 100 \rangle_b$ ferrite zone in runs No. 22 and 23 were thought to arise from a DO₃ or B2 structure due to possible congruent ordering of Ni atoms in forming Fe₃Ni or FeNi.

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