Effect of Continuous Cooling on the Morphology and Kinetics of Pearlite

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The effect of variations in cooling rate on the morphology and kinetics of pearlite was studied and was contrasted with the isothermal and isovelocity modes of transformation. It was found that continuous cooling suppresses the pearlite transformation to a lower reaction temperature where finer nodule diameters and interlamellar spacings are produced. Growth rates in continuous cooling were in agreement with those for the isovelocity and isothermal transformations, the rate-controlling process for growth in the temperature range studied being volume diffusion in all three cases. The relationship between interlamellar spacing and undercooling was found to be $S\Delta T = 8.02 \times 10^4$ Å K, regardless of the mode of transformation.

THE morphology and kinetics of pearlite is well established in the literature and has been carefully reviewed in several papers.[1,2] Growth-rate measurements and interlamellar spacing on both pure Fe-C alloys and ternary alloys have been made for isothermally produced pearlite.[3,4] Recently, pearlite transformed through a steep temperature gradient has produced bidirectional pearlite, *i.e.*, pearlite colonies that are ±45° to the growth axes,[5] and a morphological study of the substructure has been reported.[6] Kinetic studies of this type of transformation have been conducted and have shown that the two modes of growth, *i.e.*, isothermal and isovelocity, can be interrelated.[7,8] A critical appraisal of these two modes of transformation has also been recently reported in the literature.[9]

On the other hand, the effect of continuous cooling on the morphology and kinetics of the pearlite transformation, though of considerable practical importance, has received little attention in the literature. The effect of cooling rate on the partial transformation to pearlite in low-carbon steel has been studied,[10] but the kinetics of the transformation have not been investigated because of the experimental difficulties involved. Recently, a hot-stage cinephotomicrography technique has been developed that allows for the *in situ* study of pearlite growth during cooling.[11] The present paper describes the results of this hot-stage technique in the study of the morphology and kinetics of pearlite transformed by continuous cooling.

EXPERIMENTAL PROCEDURE

Samples of an Fe-0.81 C binary alloy* were austenitized at 1010°C for 2 min in the hot-stage microscope and cooled at various rates up to 10,000°C/min. Detailed discussion of the hot-stage technique was given in previous papers.[12,13] Nodule-diameter measurements were made on five separate planes of polish for each specimen, and at least thirty measurements were made for each cooling rate. Difficulties were encountered in obtaining the true nodule diameter, because pearlite nodules, as defined by Hull and Mehl,[14] vary in size for a given condition, depending on which nodule nucleated first, and a plane of polish will not be able to cut all the nodules in a population precisely at the true diameter of the nodule (sphere). Because of these difficulties, nodule size was treated as a "pearlite grain size," and measurements were made by the linear intercept method as in the case of any other grain size. Two-stage cellulose acetate-carbon replicas, shadowed with gold-palladium at 20°, were used to measure the minimum interlamellar spacing, S_{min}. Over 200 grids at 10,000 times magnification were scanned, and twenty minimum spacing fields were taken for each condition. The minimum spacing within these twenty fields was measured as S_{min}.

By direct thermal analysis cooling rates were determined as the slope of the cooling curve from 721°C to the transformation arrest. As expected, at the faster cooling rates the transformation arrests were seen as a sharp deflection in the cooling curve whereas at the slower cooling rates the transformation took place over a range of temperature, *e.g.*, up to 45°C. The hot-stage cinephotomicrography technique allows for the growth-rate measurement of individual nodules *in situ*, *i.e.*, as they grow during cooling.

*0.81 C, <0.01 Mn, <0.002 P, 0.005 S, <0.01 Si, 0.02 Ni, <0.01 Cr, <0.002 Mo, <0.001 Cu, 0.002 V, <0.005 Al, <0.002 Sn, 0.001 Ti.

RESULTS

A comparison of the pearlite transformation, as depicted by the isothermal diagram[4] and the continuous cooling diagram, is made in Fig. 1. Note that continuous cooling greatly suppresses the start of the pearlite transformation to lower temperatures. At the lower temperatures, transformation occurs so quickly, on the order of one second, that it is difficult to plot these results on the continuous cooling curve, Fig. 1. Thus, a plot of transformation temperature *vs* time for transformation ($P_s - P_f$) is shown in Fig. 2.

The results of the quantitative metallographic measurements made on average nodule diameter, N_d, and minimum interlamellar spacing, S_{min}, are shown in Figs. 3 and 4. The effect of cooling rate on N_d and S_{min} is seen in Fig. 3 where, as expected, increased cooling rate decreases both morphological parameters. The effect of transformation temperature on nodule diameter and minimum interlamellar spacing

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is plotted in Fig. 4, and, as in the isothermal studies,[3,4] lower transformation temperatures decrease both N_d and S_{min} with an apparent leveling or limiting value for each. Apparently, the minimum interlamellar spacing is directly related to nodule diameter, since the ratio N_d/S_{min} is fairly constant over the range of transformation temperatures, Fig. 5. Thus, a direct relationship exists between the average nodule diameter, N_d, and the minimum interlamellar spacing, S_{min}, for pearlite of eutectoid composition.

A comparison of the isothermal data[4] and the continuous cooling data of interlamellar spacing *vs* undercooling below 727°C is shown in Fig. 6. Brown and Ridley's data show the expected slope from the Zener relationship[16] of −1. A least-squares fit of the continuous cooling data gives a slope of −0.909, a close value, considering the experimental problem of determining the reaction temperature during continuous cooling. The reaction temperature is difficult to determine because of the recalescence associated with the high cooling rates. Also superimposed on the graph are the isothermal data of Williams and Glover.[15] The scatter in these results is quite similar to that of the continuous cooling data, and it is seen that all the data fit within a band with a slope close to Zener's theoretical value of −1. Thus, the continuous cooling and isothermal modes of transformation give the same relationship for interlamellar spacing, even though the reaction temperatures are generally lower for the continuous cooling data.

A plot of the reciprocal interlamellar spacing as a

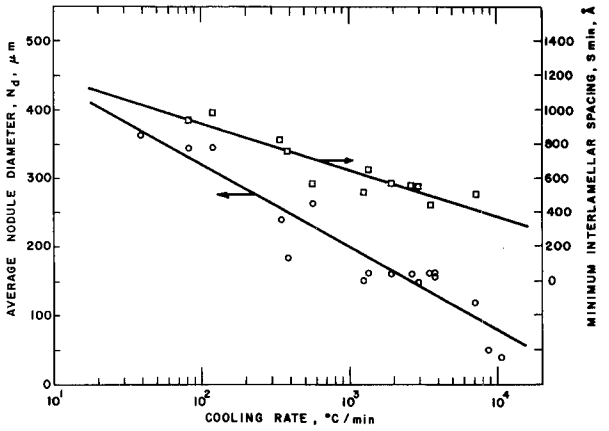


Fig. 3—Effect of cooling rate on average nodule diameter and minimum interlamellar spacing.

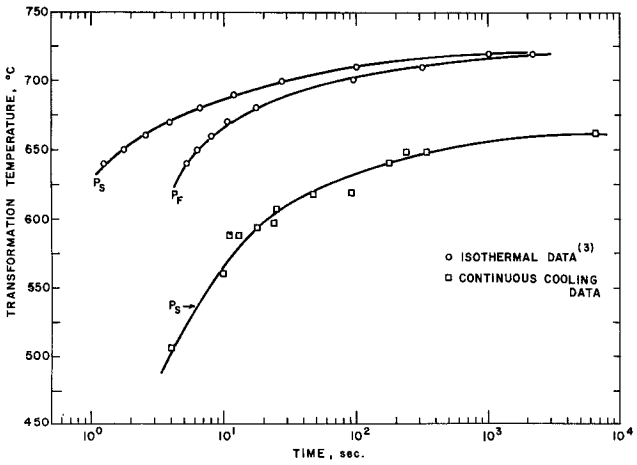


Fig. 1—Relationship between continuous cooling and isothermal transformation for pearlite in a 0.81C Alloy.

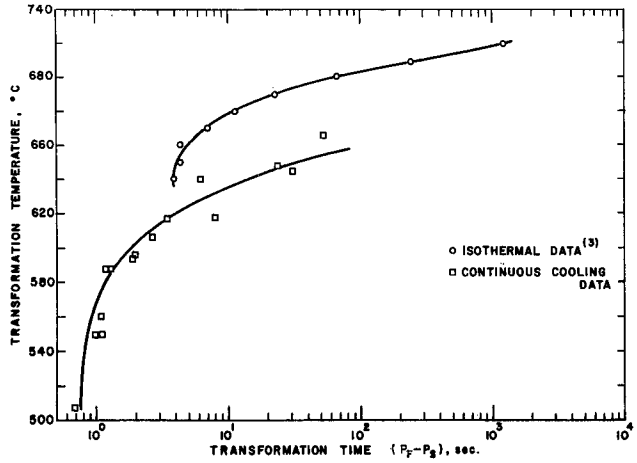
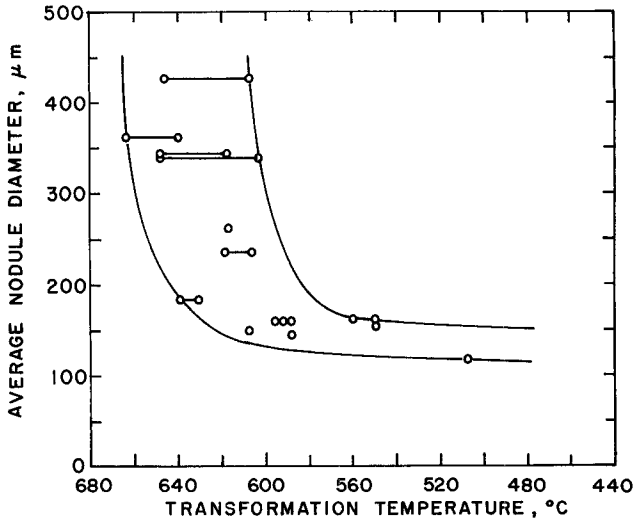


Fig. 2—Completion time for transformation (P_f − P_s) of pearlite during continuous cooling and isothermal transformation.



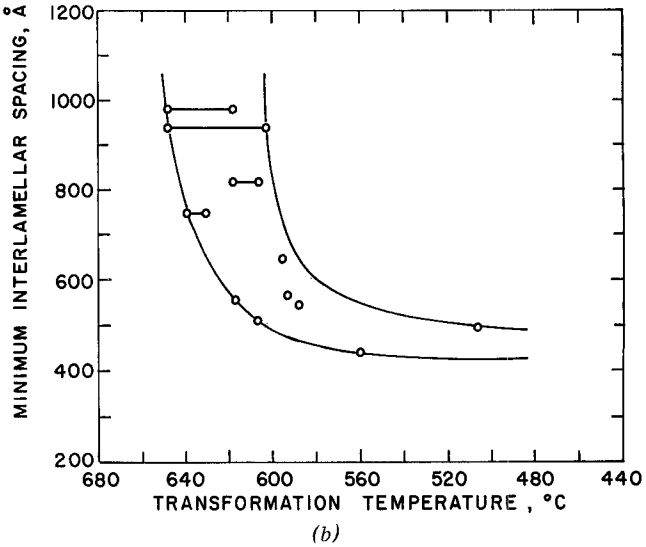


Fig. 4—Effect of transformation temperature on (*a*) average nodule diameter and (*b*) minimum interlamellar spacing.

function of transformation temperature is shown in Fig. 7 for the continuous cooling data. Also included in this figure are the isothermal data of Brown and Ridley,[4] Williams and Glover,[15] Bolling and Richman[7] and Cheetham and Ridley.[8] It is obvious from these results that interlamellar spacing is related to the reaction temperature no matter what the mode of transformation, *i.e.*, continuous cooling or isothermal modes of transformation produce virtually the same interlamellar spacing at a given reaction temperature. It is quite possible that this relationship also holds for the isovelocity mode if it were possible to accurately determine the transformation temperature. Growth-rate measurements are plotted in Fig. 8 for the continuous cooling data of this study along with the isothermal data of Brown and Ridley,[4] Cheetham and Ridley,[8] and calculations made by Puls and Kirkaldy.[9] The exceptionally good agreement between the isothermal and continuous cooling modes of transformation indicates that the reaction temperature is the controlling source of the microstructure.

DISCUSSION

Rate-Controlling Process for Growth

The volume diffusion model of Zener[16] that predicts the growth of pearlite leads to the equation:

$$v \propto (\Delta T)^2 \exp\left(-\frac{Q}{RT}\right) \quad [1]$$

where v is the pearlite growth rate, ΔT is the degree of undercooling relative to the equilibrium transformation temperature, and Q is the activation energy of the rate-controlling mechanism. According to Zener, $S \propto 1/\Delta T$; therefore Eq. [1] can be rewritten as:

$$vS^2 \propto \exp\left(-\frac{Q}{RT}\right) \quad [2]$$

and, assuming that Q is constant over the range of undercooling temperatures, then Eq. [2] reduces to:

$$vS^2 = \text{constant} \quad [3]$$

Sundquist[17] has proposed an interface diffusion model where the temperature dependence of the growth rate was found to be:

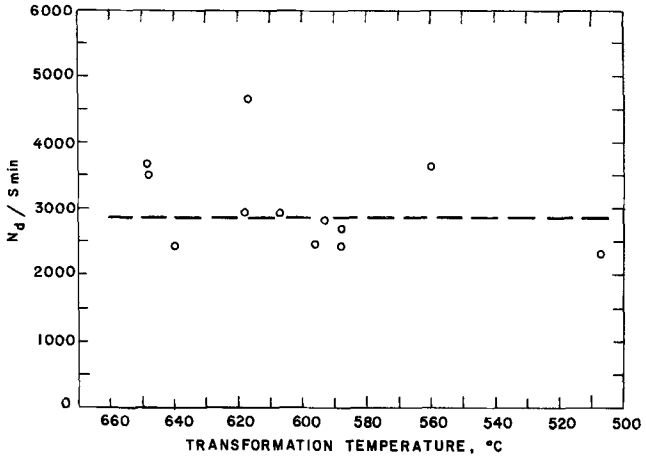


Fig. 5—Effect of transformation temperature on the average nodule diameter and minimum interlamellar spacing (N_d/S_{min}) ratio.

$$v \propto (\Delta T)^3 \exp\left(-\frac{Q}{RT}\right) \quad [4]$$

This relationship reduces to:

$$vS^3 = \text{constant} \quad [5]$$

Similar relationships have been proposed by Shapiro and Kirkaldy[18] and by Hillert.[19]

Fig. 7 shows that the Zener relationship,[16] $S \propto 1/\Delta T$, holds for the continuous cooling data as well as for the isothermal data found in the literature. Fig. 9 is a plot

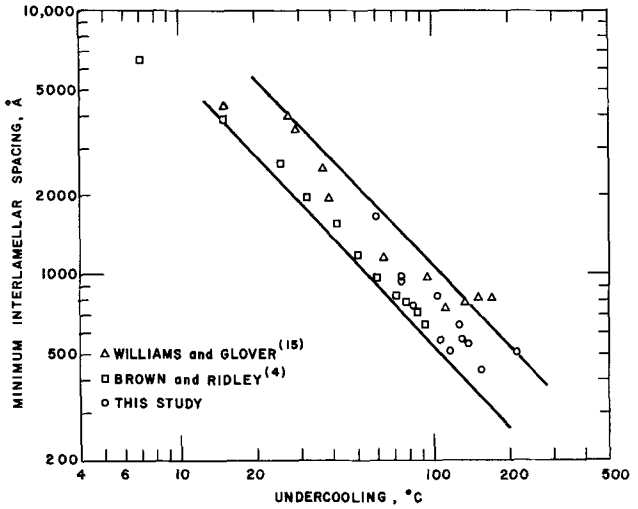


Fig. 6—Effect of degree of undercooling on the interlamellar spacing.

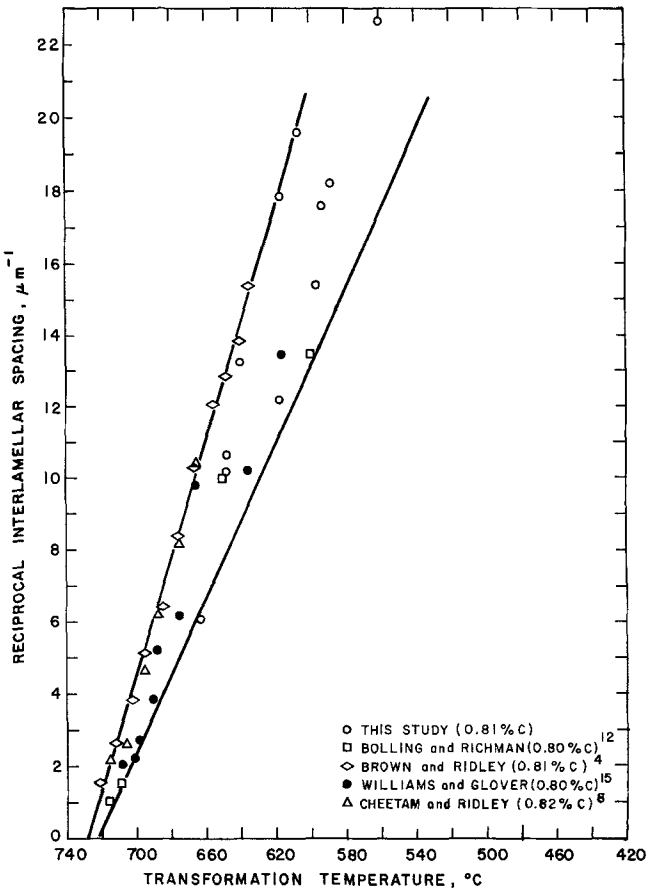


Fig. 7—Effect of transformation temperature on the reciprocal of interlamellar spacing.

of the continuous cooling velocity data *vs* spacing and shows an excellent agreement with vS^2 = constant. The data are also superimposed on the spacing-velocity plot of Puls and Kirkaldy,[9] Fig. 10, and show that the vS^2 = constant relationship continues to higher growth rates without any significant deviation except for the two high velocity data points of Bolling and Richman.[7] Again, the vS^3 = constant for interface diffusion is included and is clearly unrelated to the bulk of the data. Thus, continuous cooling allows the volume-diffusion mechanism for the pearlite transformation to be extended to lower temperatures without any apparent contribution from an interface-diffusion mechanism.

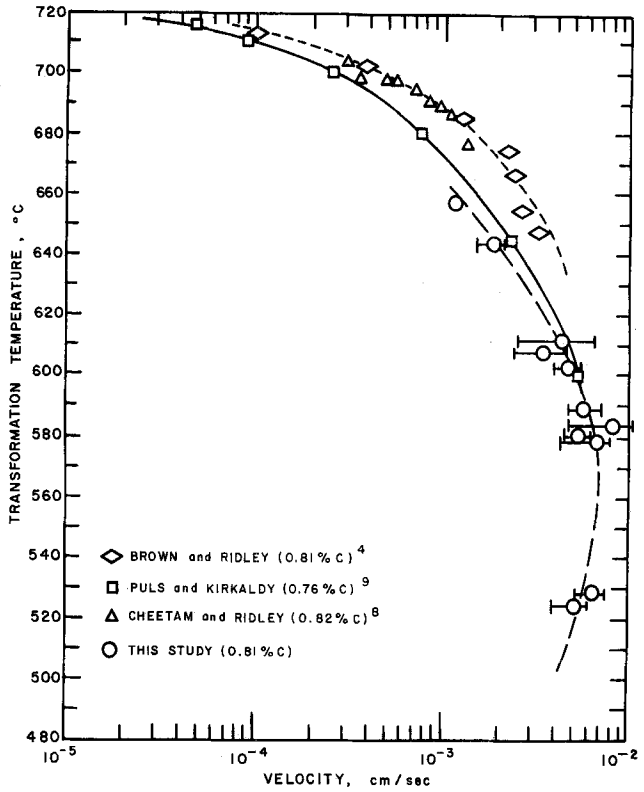


Fig. 8—Variation in growth rate with transformation temperature.

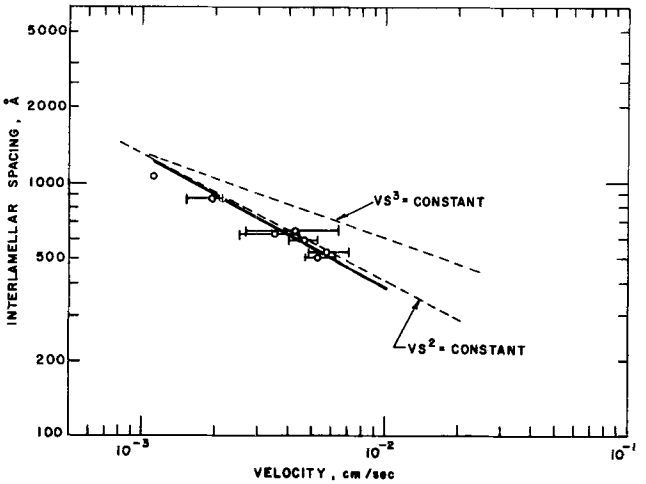


Fig. 9—Relationship between growth rate and interlamellar spacing.

Criteria for Volume Diffusion

A relationship between interlamellar spacing, S, and undercooling, ΔT, was first proposed by Zener,[16] who believed that the system stabilized at that spacing for which the velocity was a maximum. Later Hillert adopted this relationship in the form of:

$$S = 2S_c = \frac{4\sigma^{\alpha/Fe_3C} T_E}{\Delta H_v \Delta T} \quad [6]$$

where S_c is a theoretical critical spacing for which the velocity of reaction is zero, σ^{α/Fe_3C} is the surface energy of the α/Fe_3C phase boundary, T_E the equilibrium temperature, and ΔH_v is the change in enthalpy per unit volume between α and Fe_3C phases. Using the principle of maximum rate of entropy production, Puls and Kirkaldy[9] modified the above equation, as follows:

$$S = 3S_c = \frac{6\sigma^{\alpha/Fe_3C} T_E}{\Delta H_v \Delta T} \quad [7]$$

These equations can be rearranged to take the form:

$$S\Delta T = \text{constant} \quad [8]$$

with ΔH_v = 145 cal/cm^3 [Ref. 9], T_E = 1,000 K and σ^{α/Fe_3C} = 700 ± 300 ergs/cm^2 [Ref. 21], the constant for the Zener-Hillert (Z-H) relationship is 4.61×10^4 Å K and the Puls-Kirkaldy (P-K) relationship is 6.92×10^4 Å K.

Eq. [8] takes the form of an equilateral hyperbola and is plotted in Fig. 11 for the Z-H and P-K relationships. Using the data of undercooling and interlamellar spacing, the average constant was calculated for the isothermal data of Brown and Ridley[3] ($C = 6.00 \times 10^4$ Å K), Williams and Glover[15] ($C = 9.57 \times 10^4$ Å K), and Bolling and Richman[7] ($C = 9.22 \times 10^4$ Å K). Although the spread in the constant is great, the results are good, because the ±300 ergs/cm^2 error in the interfacial energy[21] would result in an actual variation in the P-K constant from 3.97×10^4 to 9.89×10^4 Å K, a spread that would bracket all of the data. A curve representing all the data using an average $C = 8.02 \times 10^4$ Å K is also included in Fig. 11. The data fit the P-K relationship better than the Z-H relationship, especially at the knee of the curve. The continuous cooling data of this investigation are also plotted in Fig. 11. In the continuous cooling results the average constant was found to be 7.94×10^4 Å K, which was in excellent

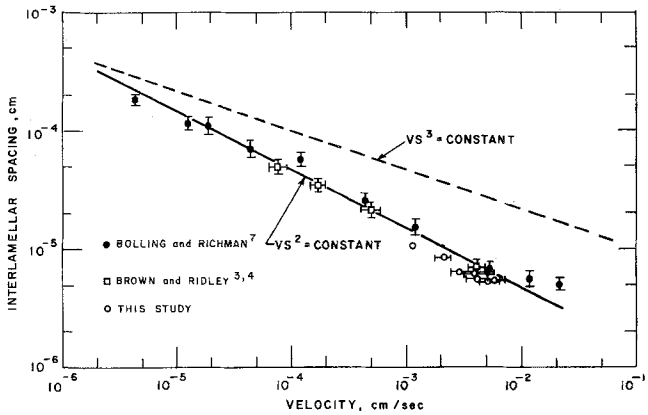


Fig. 10—Spacing *vs* velocity relationship for isothermal, isovelocity and continuously cooled pearlite.

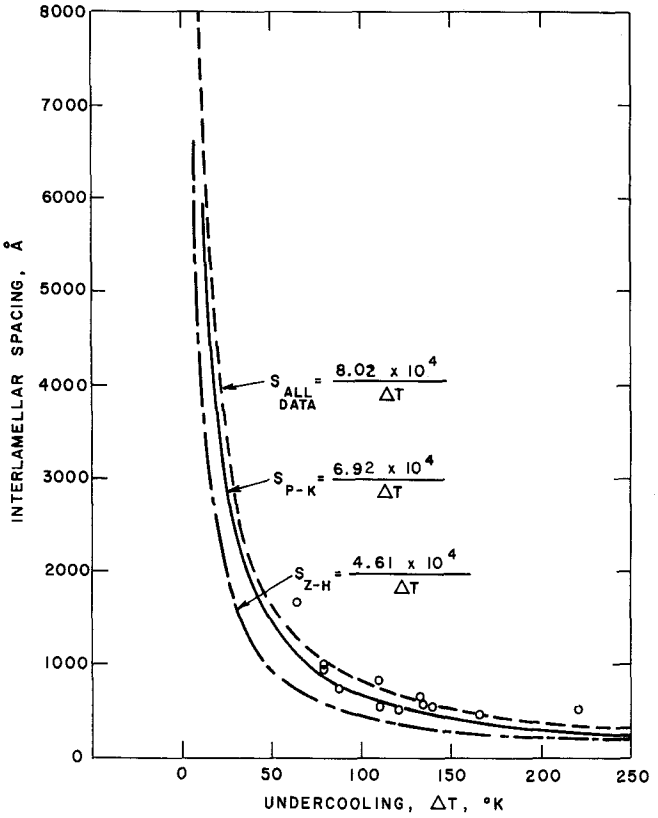


Fig. 11—Plot of undercooling *vs* interlamellar spacing (O - data from this investigation).

agreement with previous results. Thus, the maximum rate of entropy criterion, $S = 3S_c$, appears to hold for all the results better than the maximum velocity criterion. Also, a direct relationship exists between interlamellar spacing and undercooling no matter how the eutectoid alloy is transformed, *i.e.*, whether by isothermal transformation or continuous cooling transformation. Using the grand average of all data to determine the constant, the relationship of interlamellar spacing and undercooling can be represented as:

$$S\Delta T = 8.02 \times 10^4 \text{Å K} \qquad [9]$$

Therefore, for a given transformation temperature or degree of undercooling the interlamellar spacing can be determined for a eutectoid Fe-C alloy, the difficulty in determination becoming much greater at the lower undercooling values.

Puls and Kirkaldy used the maximum rate of entropy expression, Eq. [7], to calculate growth rate velocities as a function of undercooling. These calculations are seen in Fig. 8. The agreement between the theory and the continuous cooling results is excellent, especially within the temperature range of 580 to 640°C. At these temperatures a change from volume diffusion to interface diffusion is expected to occur.[9] However, because theory and experiment are so exceptionally close, it must be concluded that the volume-diffusion model describes the data at temperatures above 580°C.

Morphology of Pearlite

As our data showed, continuous cooling suppresses the reaction temperature of the pearlite transformation (Figs. 1 and 2), thus reducing the interlamellar spacing and nodule diameter (Figs. 3 and 4). As might be expected, a relationship between nodule diameter and interlamellar spacing was found to be constant. Although continuous cooling did indeed produce finer pearlite structures, these structures were in conformity with many of the relationships found for the isothermal mode of transformation. For example, the Zener relationship of $S \propto 1/\Delta T$, Fig. 7, held for continuous cooling as it did for isothermal pearlite. The data on continuous cooling growth rates (Fig. 8) were also in substantial agreement with those for the isothermal mode of transformation, and these results showed that the mechanism for the pearlite transformation was volume diffusion (Figs. 10 and 11).

That the mechanism is the same for the continuous cooling and isothermal modes of transformation is not surprising, considering the similar morphologies between pearlite formed isothermally and by continuous cooling, *i.e.*, by nodular growth, Fig. 12(*a*). In contrast to isothermal and continuously cooled pearlite, the bidirectional, or "herringbone" colonies of isovelocity pearlite appears to be morphologically different, Fig. 12(*b*). Cheetham and Ridley[8] believed that the structure of isovelocity pearlite was primarily a result of the cusped transformation front which is identical to the transformation front of nodular pearlite, except that the radius of the nodule could be so much greater than the individual isovelocity cusp, Fig. 12(*c*). In isovelocity pearlite, according to Cheetham and Ridley,[8] the ferrite and cementite lamellae grow perpendicular to the local curvature of the interface, thus giving rise to the bidirectional morphology and an expected similarity in growth rate and interlamellar spacing with isothermal and continuously cooled pearlite, Fig. 10.

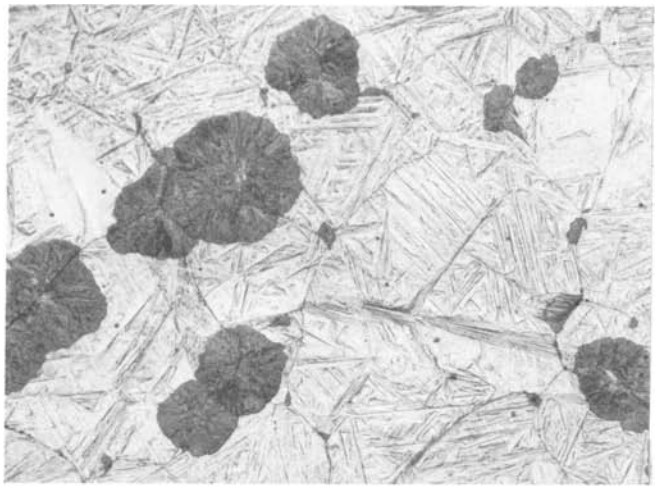
In the range of temperatures studied for all of these modes of transformation, the apparent mechanism is volume diffusion. The interlamellar spacing is obviously dependent on the growth velocity, which is in turn related to the temperature of growth and is independent of whether: 1) growth velocity is the imposed variable that determines the transformation temperature, as in the isovelocity transformation, 2) undercooling temperature is the selected variable, as in the isothermal transformation, or 3) the imposed cooling rate is used to determine the reaction temperature. Thus, the mode of transformation does not affect the validity of Zener's steady state analysis of a eutectoid configuration, which leads to a single relationship between spacing, velocity and undercooling, *i.e.*,

$$S = S(v, \Delta T) \qquad [10]$$

CONCLUSIONS

The following conclusions can be drawn from this study:

1) Continuous cooling suppresses the start of the pearlite transformation to lower reaction temperatures than those found in isothermal transformation studies. As in isothermal studies, the lower transformation temperatures produced by continuous cooling provide for a finer microstructure, *i.e.*, smaller average nodule diameter, N_d, and minimum interlamellar spacing, S_{min}; and a direct relationship exists between N_d and S_{min} over the range of transformation temperatures studied.



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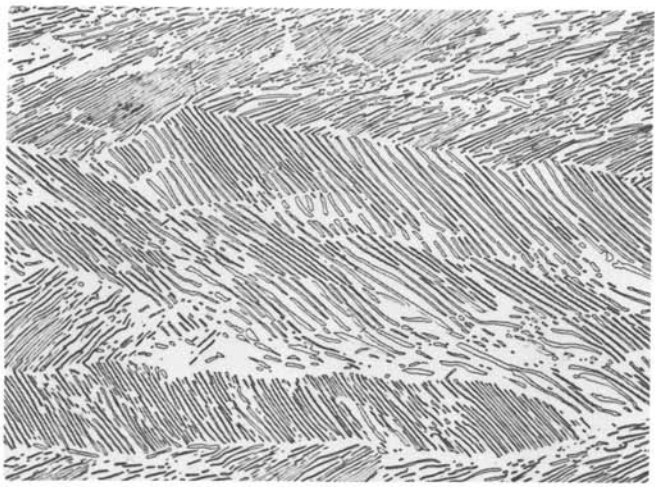

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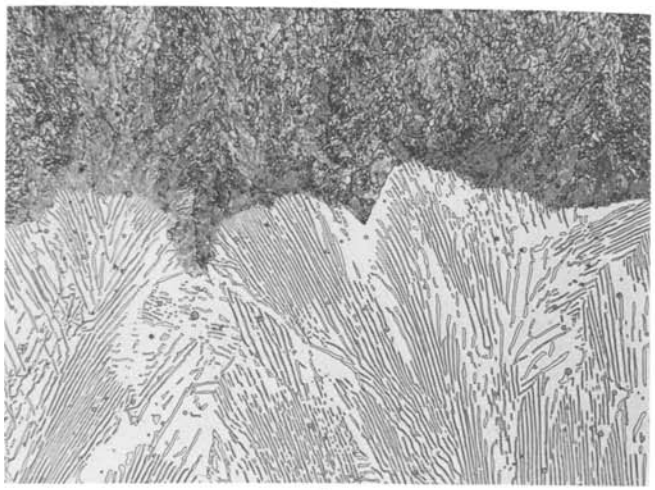

(c)

Fig. 12—Typical microstructure of: (*a*) continuously cooled pearlite at a magnification of 212.5 times, and (*b*) isovelocity pearlite at a magnification of 425 times, and (*c*) isovelocity pearlite interface at a magnification of 425 times. Picral etch.

2) For the temperature range studied, the rate-controlling process for growth in the continuous cooling transformation made was found to be the same as that of other modes of transformation, *i.e.*, volume diffusion. However, the possibility of interface diffusion cannot be totally ruled out in the lower transformation temperature region. Continuous cooling transformation produced growth rate results identical with those for the isovelocity and isothermal transformations while extending the pearlite transformation to lower temperatures.

3) Continuous cooling and isothermal data are better characterized by the Puls-Kirkaldy principle of maximum rate of entropy than by Zener's principle of maximum velocity. The relationship between interlamellar and undercooling for all data was found to be

$$S\Delta T = 8.02 \times 10^4 \text{Å K}$$

4) The interlamellar spacing of pearlite is determined by pearlite growth rate, which is determined by the transformation temperature, regardless of the particular mode of transformation—isothermal, isovelocity, or continuous cooling.

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