EFFECT OF TUNGSTEN ON THE PEARLITE REACTION IN A EUTECTOID STEEL

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Abstract  The effect of an addition of 0.37 Wt % W on the overall transformation rate of the austenite-pearlite reaction in a eutectoid steel is examined. Pearlite growth rates and interlamellar spacing are measured as a function of transformation temperatures. Tungsten raises the Ael temperature, for most transformation temperatures, decreases the overall reaction rate, the growth rate and the interlamellar spacing. Partitioning studies carried out using analytical electron microscope showed that, tungsten partitioned preferentially to cementite at temperatures down to 668°C.

Key Words  Pearlite Growth Rate, Pearlite Interlamellar Spacing, Tungsten Eutectoid Steel, Partitioning Temperature

INTRODUCTION

For many years the effect of alloy additions on the hardenability of steel has been one of metallurgical interests. This has led to investigations on the effect of alloy additions on the kinetics of the austenite-pearlite reaction. Although there have been a number of studies, very few measurements have been made on well defined alloys of high purity. There is virtually no information on the partitioning of alloying elements between the ferrite and cementite components of the pearlite at the austenite-pearlite interface.

Cahn and Hagel [1] have stated that the partitioning of substitutional elements is a thermodynamic necessity at higher reaction temperatures if the transformation is to proceed. At lower temperatures, there is sufficient free energy to drive the reaction without the necessity for partitioning. The rate controlling process for pearlite growth will be different at the temperatures where partitioning involves the diffusion of substitutional elements, to that at lower temperatures were only carbon partitions.

PEARLITE GROWTH KINETICS IN Fe-C

The growth rate of pearlite in plain-carbon eutectoid steel has been the subject of many theoretical studies. Most of these theories assume that carbon diffusion is the rate controlling process. Diffusion paths which have been considered were mainly through the parent austenite (Volume diffusion) and in the advancing austenite-pearlite interface (boundary diffusion).

Considering pearlite growth, Zener [2] has assumed that the carbon diffusion in austenite from the tip of the ferrite lamella to the tip of the cementite lamella is the rate controlling process. The
concentration difference $\Delta C$, which will cause a diffusion current of carbon, is equal to the difference in carbon concentration at the $\gamma/\alpha$ interface, $C_{\gamma/\alpha}$, and at the $\gamma$/cementite interface, $C_{\gamma/C}$. Zener has also assumed that the effective diffusion distance, $L$, is related to the interlamellar spacing and is comparable to the thickness of cementite plate.

$$L = S = S_{\text{com}}$$  \hfill (1)

From the above arguments, the pearlite growth rate will be a maximum when the interlamellar spacing is equal to twice the critical spacing $S_C$. This critical spacing was calculated by Zener by equating the available free energy necessary for an increment of pearlite volume to the corresponding increase in interfacial energy:

$$S_c = \frac{2T_E \sigma_{\alpha/C}}{\rho \Delta H \Delta T}$$  \hfill (2)

where:

- $T_E$ = Eutectoid temperature.
- $\sigma_{\alpha/C}$ = Surface energy per unit area between ferrite and cementite.
- $\rho$ = Density of pearlite.
- $\Delta H$ = Heat of transformation per unit mass.
- $\Delta T = T_E - T$ = Under cooling.

Accordingly, the interlamellar spacing is inversely proportional to the amount of undercooling so that a logarithmic plot of the interlamellar spacing Vs. the amount of undercooling, should give a straight line with a slope of 1.

Hillert [3] showed that the pearlite growth rate may be presented as follows:

$$V = \frac{D_v S^2}{a} \frac{C_{\alpha} - C_{\gamma/C}}{C_{e} - C_{\alpha}} \frac{1}{S} \frac{(1 - S_s)}{S_S}$$  \hfill (3)

Where $D_v$ is volume diffusion coefficient of carbon in austenite at the interface, $C_{\alpha}$, $C_{e}$ are the concentration of carbon in ferrite and cementite, respectively; "a" is a geometric parameter which has a Value of 0.72 for Fe-C pearlite of eutectoid Composition; and $S$ & $S_s$ are the thickness of ferrite and cementite lamella, respectively. For Volume Diffusion Control, $S/S_s$ is equal to two or three according to the maximum growth rate and maximum entropy rate criteria respectively.

**PEARLITE GROWTH KINETICS IN Fe-C-X**

Generally, addition of alloying elements (X) has been found to decrease the growth rate of pearlite during the austenite decomposition. Referring to Parcel and Mehl [4] the growth rate of pearlite is decreased by molybdenum and by nickel at all transformation temperatures for a number of Fe-C-Mo and Fe-C-Ni alloys. Brooks and Stansbury [5] showed that the growth rate of pearlite in a high purity 0.3 Wt% Mo eutectoid steel was reduced by a factor of ten at all transformation temperatures, as compared to that of a high-purity plain carbon eutectoid steel.

Brown and Ridley [6] have investigated the effect of nickel on growth rate and interlamellar spacing. The reduction of growth rate was proportional to the concentration of nickel and it was seen that interlamellar spacing was increased. Similarly, manganese and chromium decrease the growth rate of pearlite [8,7]. Cobalt tends to be anomalous as it accelerates the rate of growth and decreases the interlamellar spacing [9].

Theoretical investigation of the effect of alloying elements on the growth kinetics where mostly limited to low temperature cases where carbon was the only diffusing species and the alloying element was considered to influence the boundary conditions for the diffusion process. At higher temperatures, the alloying element was considered to be the rate controlling mechanism. For the case in which the alloying element partitions only partially at the interface, theoretical treatment seems to be more
difficult. Ridley et.al. [10, 11] investigated the effect of alloy addition on pearlite growth rate for addition of Mn, Cr, Mo, Ni and have pointed out that when eutectoid steels containing alloy additions are transformed at temperatures above $T_p$, partitioning of the alloying elements between the ferrite and cementite phase occurs at the austenite-pearlite transformation front. The rate of pearlite growth at these temperatures will depend on the low mobility of the alloying element.

Carbon is the only species being redistributed so that alloy additions influence the growth rate through their effect on the carbon concentration gradient at the interface, which is proportional to the driving force for growth, and carbon diffusivity.

The redistribution of carbon can occur by Volume diffusion through the austenite-pearlite boundary. For Fe-C, manganese, and chromium eutectoid steels the kinetic data are not inconsistent with volume diffusion & carbon being the rate controlling process for growth. It was proposed by kirkaldy [12], Hillert [13], Cahn, Hagel [1] and Sundquist [14] that interface diffusion of carbon is rate controlling. However, since the measured growth rates are consistently greater than those calculated for Volume diffusion control, it is reasonable to assume that the interfacial diffusion of carbon may be simultaneously involved.

Zhou, et.al. [15], showed the role of interfacial steps in the growth mechanism of pearlite. Hackney [16] studied the morphological instabilities and branching process at the initiation of eutectoid temperature. Enomoto et.al. [17] studing partitioning and growth Kinetics of proeutectoid ferrite, showed that only partitioned ferrite formed if local equilibrium with respect to both carbon and alloying elements was achieved at the interface. Mg or Ni partitioning did not take place at medium and low temperatures, indicating the limited role of interface/grain boundary diffusion in sustaining local equilibrium during the growth of ferrite allotriomorphs.

**EXPERIMENT AND RESULTS**

**Material**

A eutectoid steel with the following composition in wt% was produced in a vacuum melting furnace from high purity materials;

$$C = 0.81; \ W = 0.37; \ P, S < 0.008$$

The alloy was supplied for investigation in the form of hot rolled 12 mm dia. bars. Short lengths (75mm) of the bars were homogenized for 3 days at 1200°C under vacuum, and then furnace cooled.

**Isothermal Transformation**

Slices about 2mm thick, were cut from the homogenized bar and then austenitized in a Nitrogen atmosphere at 1000°C for 30 minutes. The specimens were rapidly transferred to a lead bath held on temperatures in the range of 600-700°C for exact times and then quenched in the cold water.

The temperature of the lead bath was controlled by an alumel-chromel thermocouple, which was placed at the same depth as the specimen. In this way it was found that the temperature variation was about ±2°C. The lead bath was kept covered with granulated charcoal to reduce oxidation.

The transformed specimens were mounted into plastic blocks, surface ground to remove any decarburization, then ground on emery papers of increasing fineness and polished on 6µm and 1µm diamond impregnated cloths.

The etchant used was a 2% nital solution. The T.T.T diagram for that start and the end of the pearlite transformation is presented in Figure 1. The corresponding diagram for a plain carbon eutectoid steel is also included.

It can be seen that the tungsten addition displaces the T. T. T. curve towards the right, i.e., the transformation ratio will be retarded.
Growth Rate Measurements

Growth rates were obtained for the early stages of transformation from measurements of the radius of the largest non-impinging pearlite spheres or hemispheres using an optical microscope with a micrometer eyepiece. Plotting the maximum radius as a function of time gives an approximately straight line, the slope of which gives the growth rate at each temperature.

To obtain accurate results, many specimens were investigated. It is difficult to apply the above-mentioned method for the systems where the product phases grow in a form other than nodular, e.g., slabs at a grain boundary. In the previous work, it was pointed out [6, 14, 18] that, the growth rate in the early stages of the reaction was constant with time at the same temperature, and it was insensitive to variation in austenite grain size. The plot of the maximum nodule radius vs. transformation time tends to give reasonably straight lines (Figures 2, 3, 4, 5, 6). The relationship between the pearlite growth rate, \( V \), and the transformation temperature for 0.37% W alloy is presented in Figure 7, with the corresponding relationship for a 0% W eutectoid steel. It is seen that tungsten addition retards the pearlite growth rate for all transformation temperatures.

Interlamellar - Spacing Measurement

Several methods have been proposed for measuring
replicas from partially transformed specimens were prepared and scanned in the microscope and the number of lamellars which was intersected at right angles by the diameter of the reference circle was counted.
Quantitative Analysis

According to the so-called "Simple Ratio" technique, which was developed by Lorimer et al. [23], if a specimen is sufficiently thin for conventional transmission electron microscopy to be carried out at 100 KV, then the primary X-rays produced by the incident electron beam have a low probability of either being absorbed or exciting fluorescent radiation [24]. If the characteristic X-ray intensities from the specimen are measured simultaneously, their ratio is independent of the specimen thickness, and a change in this ratio represents changes in the weight fraction ratio of the two analysed elements.

When the average composition of the specimen, which is thin and yet large enough to be representative of the bulk, the composition can be related to the measured composition by the simple expression:

\[ \frac{I_1}{I_2} = K \frac{C_1}{C_2} \]  

(4)

where:

- \( I_1, I_2 \) = observed X-ray intensities; \( C_1, C_2 \) are the unknown weight fractions, and \( K \) is a constant.

Once the constant measurement is observed, it can be used to convert X-ray intensities into weight fraction ratios. It has been assumed that the thickness of the specimen does not affect the intensity ratio \( I_1 / I_2 \) up to a certain limit.

The partitioning coefficient of the alloying element (X) between cementite and ferrite can be defined as [25]:

\[ K_{\text{com}}(X) = \frac{(C_X/C_{Fe})_{\text{com}}}{(C_X/C_{Fe})_\alpha} \]  

(5)

Where \( C_X \) and \( C_{Fe} \) are the weight fractions of the alloying element and iron, respectively, in the identified phases.

A combination of Equations 4 and 5 will yield:

\[ K_{\text{com}}(X) = \frac{(I_X/I_{Fe})_{\text{com}}}{(I_X/I_{Fe})_\alpha} \]  

(6)

Therefore, the partitioning coefficient can be simply calculated from the recorded X-ray intensities. If the atoms of the alloying element remain in situ during the austenite-pearlite transformation, this ratio will be about 1.1; this is because of the difference in iron content within two phases [26]. If the alloying element segregates to the cementite phase, the ratio will be > 1.1 depending on the extent of segregation.

The thin foils from partially transformed and completely transformed specimens were prepared, and the ferrite and cementite lamellae were analysed "in situ". Figures 11 and 12 show the trace of the electron probe beams on the adjacent ferrite and cementite lamellae from the investigated steel.

The diameter of the beam is usually smaller than
the diameter of the contamination spot [26] and may be half its value [27]. The reason for this contamination spot is not definitely known, but it is usually believed that it consists of carbon, sulphur and other organic materials from the vapours of the diffusion-pump oils, which are always present in any continuously-pumped system.

**DISCUSSION**

From Figure 1 it is apparent that tungsten additions tend to move the T.T.T curve toward the right, i.e., both the start and the end forward the transformation are retarded.

The relationship between the pearlite growth rate and transformation temperature is shown in Figure 7 for 0.37% W and the corresponding curve for the plain carbon steel is also added. Tungsten additions cause a reduction in the growth rate of pearlite.

Ridley [10] has pointed out that the important growth parameters are the interface of growth velocity \( V \), and the interlamellar spacing, \( S \). Large number of measurements of one or more than one of these parameters have been made on steels of commercial purity, but only on a few occasions have unified measurements of both parameters been made on pure Fe-C alloy or well defined ternary alloys.

Tungsten additions raise the eutectoid temperature (Ae1) of the Fe-C System. A similar effect has been observed [19] on the addition of molybdenum, chromium, and silicon. Tungsten, molybdenum, chromium and, to a lesser extent, manganese, are carbide formers while silicon and nickel tend to segregate preferentially to the ferrite.

The rate-controlling process of pearlite growth will clearly be different at temperatures where substitutional alloy elements have to diffuse from that at lower temperatures where only carbon partitions. The overall reaction rate determines hardenability and it is controlled primarily by growth rate. Hence, it is apparent that alloy additions may affect hardenability at lower temperatures through their influence on the growth rate of unpartitioned pearlite.

To examine the rate-controlling process for pearlite growth at these lower temperature, it is necessary to have, (a) growth rates and interlamellar spacing, (b) data from which no-partition phase boundaries can be calculated, and (c) information on the effect of alloy additions on both volume and boundary diffusivity of carbon. There is no ternary system for which all of the required measurements have been made (particularly in the case of tungsten additions).

Figures 2, 3, 4, 5 and 6 show the growth rates at temperatures 600, 620, 640, 660, 680°C, respectively.

Figure 10 shows the relation between \( l/s \) and \( T \) for the 0.37%W and plain-carbon steels. The tungsten addition tends to decrease the interlamellar spacing at high temperatures. Reasonably linear relationships were obtained. The slope of the line for the W steel, was only slightly different from that for the plain carbon steel.

Several methods have been suggested for measuring interlamellar spacings; considering the
different positions of the pearlite colonies in the space (due to growth in different direction), the surface of the specimen will be cut by the lamellae at different angles, varying from 0 to 90 degrees. The smallest observed spacing is presumably equal to the true spacing as this is the spacing lamellae oriented normal to the surface of the specimen (Figures 9, 8, 11).

However, Pellisier et al., [28] have demonstrated that the interlamellar spacing of pearlite formed isothermally is not exactly constant but rather consists of a statistical distribution of spacing about a "mean" value. By taking many optical micrographs of transformed specimens, they found that this "mean" value was approximately equal to 1.65 times that of the smallest observed apparent spacing. They suggested that this mean value could be used to specify interlamellar spacing.

To include measurements of spacing for the unresolved pearlite by the optical microscope, a method called the "limit method" was employed. The method consists essentially of using a microscope objective which resolves only a fraction of the pearlite. The fraction of the area not resolvable by the objective lens, is measured and the mean interlamellar spacing is calculated from a knowledge for the numerical aperture of the objective lens and the wave length of the light used.

Cahn and Hagel [18] have found that the growth rate of pearlite can vary with transformation time and they expected, therefore, that the interlamellar spacing would also vary with time.

However, Brown and Ridlay [6] have pointed out that the methods used previously to determine the interlamellar spacing are both tedious and questionable. Recent developments in measuring true interlamellar spacing [19, 20, 21] may be considered for accurate measuring of spacing, but the present method seem reasonably accurate.

The Zener Equation 2 for the relationship between S and T can be written as follows:

Assuming \( S = b \Delta c \), where \( b \) is a constant;

\[
\frac{1}{S} = -AT + AT_F \tag{7}
\]

Where

\[
A = \frac{\rho \Delta H \gamma}{2bT_F \sigma}
\]

Thus, the change of the slope of the straight line for the alloy steels in comparison to that for plain carbon steel can be explained by the complex effect of the alloying element on the parameter \( A \).

Equation 7 suggests that the intercept on the temperature axis for the relation between \( 1/S \) and \( T \) will yield the eutectoid temperature \( T_F \) of the steel.

Figure 10 gives \( 729^\circ \text{C} \) as the temperature of intercept for 0.37% W steel. There is a good agreement between the measured eutectoid temperature and the one predicted [29].

Cahn and Hagel [1] have calculated a minimum possible spacing below which partitioning does not occur, Sp. as:

\[
S_p = \frac{-2\sigma W_m}{(T_p - T)\Delta S_0} \tag{8}
\]

where \( \sigma \) is the interfacial energy between cementite and ferrite, \( W_m \) is the molar volume, \( T_p \) is the no-partition temperature and \( S_0 \) is the entropy change. They proposed that a slope of \( 1/S \) Vs T should show a distinct change of slope in the vicinity of \( T_p \).

Equation 8 suggests that the points below the no-partition temperature must extrapolate to \( T_p \) which was considered as the temperature above which equilibrium partitioning occurs.

In the present work, there was no evidence for the existence of no-partitioning temperature in the graph of reciprocal spacing versus reaction temperature. Likewise, in previous studies of the pearlite reaction in eutectoid steels containing nickel, manganese or chromium no change of slope was observed in the interlamellar spacing [6, 10].

Tashiro et al., [30] have devised the effect of
alloying elements on the lamellar spacing into three
groups; narrowing, widening not affecting.

Partitioning of Tungsten
During the present study, it was possible to carry out
an investigation of the partitioning of tungsten between
ferrite and cementite (Figure 11). It seems that
partitioning of tungsten occurs at temperatures well
below the eutectoid temperature; segregation of
tungsten to the Carbide was observed at temperatures
of 680°C, 690°C, and 704°C. Tungsten seems to act
like chromium, a strong carbide former element (31).

There is a small gap between the characteristic
X-ray lines of W and Si (Figures 14, 13). Therefore,
the results are best regarded as qualitative (i.e. It is
difficult to measure K_{ceq} (W), because any possible
segregation of silicon should be taken into account).
However, silicon will partition to the ferrite [10]
whereas tungsten goes to the carbide; therefore, the
result is likely to be satisfactory. Below 668°C,
partitioning was not measured because the
interlamellar spacing was too fine.

Kirkaldy [12] has distinguished between the effect
at the austenite stabilizers and the ferrite stabilizers.
He observed that the austenite stabilizers such as
manganese do not partition between cementite and
ferrite over a wide temperature range, while ferrite
stabilizers, like chromium and tungsten, do partition.
The present observation seems to support the views
of kirkaldy.

As was pointed out earlier, the rate controlling
process for pearlite growth will be different for a
temperature range in which the alloying addition
partitioned, compared with that in which only carbon
diffused. Therefore, it seems that the retarding effect
on both the pearlite transformation rate and growth
rate is primarily brought about the necessity for
tungsten to segregate at the transformation front.
Clearly, the rate at which the substitutional element
can partition will be less that at which carbon
partitions, and so the former process will be rate
controlling.

It has been suggested by Goates [32] that the
considerable hardenability induced by strong carbide
formers such as molybdenum and chromium can be
attributed in part to a solute drag effect on pearlite
growth similar to that observed for the pro-eutectoid
reaction by Kinsman and Aaronson [33]. The T. T. T.
curve for a plain carbon eutectoid steel shows a single
C curve having a maximum reaction rate at 500°C -
600°C.

Pearlite forms down to 550°C while bainite is the
transformation product at lower temperatures. In
steels containing strong carbide forms a bay of
austenite stability develops and separates two C
curves formation. As a consequence, the nose of the
pearlite reaction tends to be displaced to higher
temperatures and longer times compared with the
plain carbon steel, which suggests its position may
have been influenced by the alloy elements exerting
a solute drag effect (Figure 15).
CONCLUSION

1. Pearlite growth rate in a eutectoid steel is decreased by an addition of 0.37 Wt% of tungsten.
2. The effect of these additions on pearlite growth rate at temperatures around near the nose of the T. T. T. curves is quantitatively consistent with its effects on hardenability.
3. The tungsten addition increases the A1 temperatures. This confirms the α-stabilizing effect of tungsten.
4. Tungsten tends to decrease the interlamellar spacing at high temperatures and a plot of reciprocal of pearlite interlamellar spacing VS temperature gave an approximately straight-line relationship. This line extrapolated to give an A1 temperature of 729°C for the 0.37 Wt% tungsten.
5. Partitioning of tungsten was seen in temperatures above 668°C.
6. Tungsten segregates to the carbide phase (i.e. W is the carbide former).

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