Bainite Transformation-Kinetics-Microstructure Characterization of Austempered 4140 Steel

Jian G. Zhu 1,*, Xichen Sun 1, Gary C. Barber 2, Xue Han 2 and Hao Qin 1

1 Technology Center, Fiat Chrysler USA LLC, 800 Chrysler Dr., Auburn Hills, MI 48326, USA; xichen.sun@fcagroup.com (X.S.); hao.qin@fcagroup.com (H.Q.)
2 Department of Mechanical Engineering, Oakland University, Rochester, MI 48306, USA; barber@oakland.edu (G.C.B.); xhan@oakland.edu (X.H.)

* Correspondence: jian.zhu@fcagroup.com; Tel.: +1-2483791132

Received: 15 December 2019; Accepted: 3 February 2020; Published: 10 February 2020

Abstract: Bainite transformation is a kinetic process that involves complex solid diffusion and phase structure evolution. This research systematically studies the bainite transformation of austempered 4140 steel in a wide range of isothermal temperatures, in which four bainite phases structures were generated: upper bainite; mixed upper bainite and lower bainite; lower bainite and mixed lower bainite and martensite. The kinetics of bainite transformation has been described with a linear trend using an Avrami n-value. It was found that the bainitic ferrite sheaves grow with widthwise preference. The sheaves are stable when half-grown and are variable in length, due to austenite size limit or soft/hard impingement, or autocatalytic nucleation, or these conditions combined. The full-grown upper/lower bainite sheaves were found to be 1.9 µm/1.2 µm in width under the conditions of this study. Each individual bainite sheave is lath-like instead of wedge-like. The upper bainite sheaves mostly appear as broad-short-coarse lath, while the lower bainite sheaves appear as narrow-long-fine lath. The overall bainite transformation activation energy ranges from 50–167 kJ/mol.

Keywords: upper/lower bainite; lower bainite and martensite mixture; kinetics; morphology; bainite sheaves; activation energy

1. Introduction

Usually, in certain temperature ranges, isothermal heat-treated steels contain bainite [1,2]. Bainite is not like martensite, which is very hard and strong, nor like normal pearlite. Rather, the bainite microstructures have mechanical properties between the two. Bainite is called the “between structure phase” in German and was described by Dr. Bain as “acicular dark etching aggregate” that can be seen under a light optical microscope (LM) after polishing and etching [2].

Bainite is transformed from austenite through a heat-treating process. By heating steels or cast irons above their eutectoid reaction temperature, austenite can be obtained through the austenitizing process. When austenite cools down to a temperature below the eutectoid point, and then is held at a temperature below the pearlite transformation point, usually between 600 °C and 200 °C, austenite will start to decompose into bainite.
The mechanism of austenite to bainite transformation has been described by three theories: displacive theory, reconstructive or diffusional theory [3,4], and a combination of the theories [5]. The bainite transformation volume fraction increases with isothermal holding time. This is the kinetic aspect of the microstructure phase changes. Numerous efforts have been carried out to establish kinetic models that will agree with actual experimental data, but so far, there is not one model that all researchers accept and apply. However, the Johnson-Mehl-Kolmogorov-Avrami equation (JMKA) [6] is still popular 70 years after it was first reported. This kinetics model, or variations of this model, is the most commonly used model for transformation kinetics calculations.

The bainite transformation mechanisms, nucleation, and growth kinetics are often linked to the Gibbs free energy concept [3], which describes the thermodynamics of the bainite reaction. The thermodynamically induced physical-chemical driving force behind the reaction is expressed well by the Arrhenius equation [7], which can be applied to evaluate the phase transformation, and to assess newly proposed kinetic models. The Arrhenius equation also has been applied for more than 70 years since it was published. It remains popular and important in phase transformation evaluations.

4140 steel is widely used in industry for structures, tooling, and some key automotive components. This research addresses the kinetics, morphology, and activation energy characterization of austempered 4140 steel. The knowledge acquired in this work can help develop improved mechanical properties in terms of strength, ductility, hardness and toughness due to the microstructures achieved.

2. Background

Bainite transformation is a first order thermodynamic reaction, so the parent and product phase can coexist. The general term bainite does not refer to a single phase; rather bainite is an aggregate of phases [8] or a phase matrix. This phase matrix consists predominantly of bainitic ferrite with some carbides or cementite, or retained austenite or pre-existing martensite.

2.1. Bainite Morphology

Bainitic ferrite platelets are lath like or lenticular plate like structures. With increasing carbon content, bainite morphology changes from lath-like to plate-like [9,10]. It is believed that the bainitic ferrite platelets grow to a limited size, which is usually smaller than the austenite grain size. Further bainite transformation occurs by the formation of new parallel platelets in clusters known as sheaves [11]. The sheaves are sometimes in the form of a wedge shaped plate on a macroscopic scale [12].

Takahashi and Bhadeshia addressed the two classic morphologies for bainitic classification: upper bainite and lower bainite. In upper bainite, the bainitic ferrite plates are free of carbide precipitation, the carbides are trapped between the subunits of ferrite plates. In lower bainite, the bainitic ferrite contains a fine dispersion of plate like carbides [1,13,14]. In any case, the mixture of ferrite laths with retained austenite without carbides is regarded as a special type of carbide free bainite [15,16].

A typical bainitic ferrite plate has a slender elliptical shape with length of about 10 µm and width about 0.2 µm. The typical length to width or thickness ratio of a bainite plate is 50:1 according to Bhadeshia’s work [1]. This is consistent with the observation of bainitic steel, in which the formation of bainite causes a deformation in the bainitic ferrite plate with a shear component of about 0.26 and a dilatational strain normal to the plate of about 0.03. This strain condition is the so-called invariant plane strain (IPS), which is the key feature of the displacive bainite transformation theory.

Studies on bainite generated around or below Ms (martensite start temperature), through an austempering process show that a bainite and martensite phase mixture will be generated. In this bainite-martensite mixture structure, the lower bainite is present in not only acicular units but also in irregularly shaped laths. Chakraborty revealed that spear-like bainitic sheaves and narrow needle- like martensite plates, both dark etching, are uniformly distributed in the microstructure along with light etching retained austenite [17].
2.2. Bainite Transformation Kinetics

Bainite transformation kinetics usually involves bainitic ferrite nucleation and growth. There are many ways that ferrite plates can nucleate because there are many factors that affect the ferrite plate growth. The JMAK (also called Avrami) equation has been the most enduring, popular, and comprehensive kinetics model that can accurately characterize the bainite reaction. In this equation, an overall rate of reaction \( K \) is used to describe the nucleation and crystal growth processes \([18]\), benefited from diffusion controlled growth theory \([19]\).

Bhadeshia states that the Avrami equation can be used to “characterize the reaction as the function of time” \([1]\). The parameter ‘\( n \)’ in the Avrami equation can be related to the shape of the bainitic ferrite phase and can only be greater than zero. Below are the \( n \) values or value ranges calculated and summarized according to various experiments conducted by many researchers.

\[
\begin{align*}
 n &= 1, \text{rod-like shape} \ [20]; \\
 n &< 2, \text{nucleation controlled (e.g., } n = 1.7 \ [20]; \\
 n &= 2, \text{disk-like shape, linear growth} \ [21]; \\
 n &= 1-2.3, \text{interface controlled} \ [22]; \\
 n &= 3.5, \text{parabolic cylinder shape at constant rate} \ [23]; \\
 n &= 4, \text{with constant nucleation rate, equates to tri-dimensional linear growth} \ [21].
\end{align*}
\]

Many researchers tried to improve the Avrami equation by modifying its parameters for homogeneous or heterogeneous reactions \([24]\). Bhadeshia tried using an improved Avrami equation, which is consistent with the displacive mechanism of bainite transformation to calculate “overall transformation kinetics” with promising results and believed that it might be useful in the quantitative description of known experimental data \([24,25]\).

In the 1990s, many researchers tried to develop transformation kinetics for the specific aspects of bainite transformation using the Avrami equation. Takahashi and Bhadeshia used this equation to study the kinetics of cementite in the transition from upper bainite to lower bainite. Rees and Bhadeshia also developed a bainite transformation kinetics model considering the effects of alloy chemistry and temperatures \([26]\). They also improved the model to account for the effect of trapping of carbon atoms in films of retained austenite that accelerates the bainite transformation.

In the 2000s, many researchers worked on physical-based detailed overall bainite transformation mechanisms to improve the kinetics models. Nucleation and growth equations were included in the JMAK/Avrami equation to provide better agreement with experimental data. Furthermore, cooling history, stress state, dislocation density, and austenite grain size were all considered in Zarudi and Zhang’s kinetics model \([27]\). Liu and Di developed a method to add an autocatalysis factor into the JMAK/Avrami to cover the nucleation on the austenite grain boundary to better reveal the bainite transformation kinetics \([28]\). In recent research, sophisticated nanometer level measuring methods and equipment such as in-situ neutron diffraction and atom probe tomography (APT) were used to provide very precise data for fitting into the JMAK for kinetics characterization.

2.3. Chemical Composition Effect on Kinetics

The chemical composition of a steel affects the bainite transformation kinetics. For example, silicon in alloyed steel suppresses the formation of cementite in bainite and favors the formation of long and thin bainitic ferrite plates \([29]\). Table 1 is a summary of chemical element’s effects on bainite transformation kinetics.
Table 1. Effects of alloying elements on bainite transformation kinetics.

| Elements   | Effects on Bs                                                                 | Kinetics Function                                                                                                                                 |
|------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|
| C (Carbon) | As C content increases, Bs will decrease. When C content is high enough, Bs will not be affected. | Low Carbon, C diffusion easy, will generate carbide free bainite. High carbon content will decelerate transformation; Critical carbon content will determine when bainite transformation stops [30]. |
| B (Boron)  | Lower Bs                                                                      | Suppresses Transformation [31].                                                                                                                                                                           |
| Cr (Chromium) | Lower Bs                                                                    | Hinders transformation, decreases driving force and the rate as content increases [32,33].                                                                                                         |
| Mo (Molybdenum) | Lower Bs                                                                     | Retards/stabilities rate [33].                                                                                                                                                                          |
| Mn (Manganese) | Lower Bs                                                                    | Lowers rate, may result in incomplete bainite reaction phenomenon [34,35].                                                                                                                            |
| Co (Cobalt) | -                                                                            | Accelerates the transformation [29] at low temperature [34].                                                                                                                                            |
| Al (Aluminum) | -                                                                           | Accelerates the transformation due to its influence at low temperature [32].                                                                                                                              |
| Si (Silicon) | -                                                                            | Suppresses the formation of cementite, may result in incomplete bainite reaction [34].                                                                                                                  |
| Ni (Nickel) | Lower Bs                                                                     | Delays bainite reaction [33].                                                                                                                                                                           |
| Cu (Copper) | -                                                                            | Copper precipitation with displacive mechanism in bainite reaction.                                                                                                                                    |
| N (Nitrogen) | -                                                                            | Enrichment in nitrogen tends to slow down bainite transformation [35].                                                                                                                                  |

2.4. Bainite Transformation Activation Energy

A thermodynamic driving force is needed for the bainite reaction. The bainite activation energy required is directly proportional to the driving force. Bainite transformation kinetics will encompass all aspects of the of the bainite reaction; including the start of the reaction (which requires the activation energy in terms of Gibbs free energy), bainite sheave growth, hard or soft impingements, and the ending of the reaction. The Arrhenius equation [7] has been widely used for determining the rate of chemical reactions for the calculation of activation energy. Arrhenius argued that at an absolute temperature \( T \), the fraction of molecules that have a kinetic energy greater than activation energy \( Q \) could be calculated from statistical mechanics. Since the equation was published, it has been utilized in many kinetic theories.

Activation energy calculations are often used to help describe the bainite transformation kinetic characteristics [36–38] since overall activation energy is needed for the full bainite transformation processes. The activation energy predicted by the Arrhenius equation can be the energy at any percentage of the reaction. Below 20% reaction, it is believed the activation energy calculated is for single-phase microstructure; beyond 20% it would be the energy for mixed microstructure. Usually the 50% reaction point activation energy calculated can be representative of the overall activation energy required for that reaction [38,39]. This overall activation energy includes the energy needed for bainitic ferrite grain boundary nucleation and autocatalytic nucleation, subsequent carbon partitioning and dislocation effects, and bainitic ferrite plate growth until impingement occurs at the austenite grain boundary. However, the equation does not have enough parameters to link all the aspects together [37].

2.5. Literature Review Summary

The bainite transformation is very complicated and involves all of the following aspects:

- Nucleation and nucleation rate of bainitic ferrite plates;
- Nucleation sites, at austenite/martensite grain boundaries or at ferrite plate sub units;
- Nucleation sites, at the bainite/austenite interface/internal defect or dislocation;
• Nucleation surface availability;
• Austenite grain size and lattice parameters;
• Austenite strain/ausforming condition [40,41];
• Austenite stored energy, flow stress and transformation plasticity [42];
• Austenite film entrapment;
• Dislocation density in austenite [40];
• Chemical free energy exchange in austenite/bainite ferrite plate [40];
• Isothermal temperatures;
• Chemical/alloying elements, chemical compositions;
• Carbon content, average or local conditions;
• Carbon diffusion or redistribution rate in bainitic ferrite plate;
• Carbon diffusion or redistribution rate in parent austenite;
• Bainite and austenite boundary local conditions;
• Chemical segregation in austenite [35];
• Bainitic ferrite plates growth rate;
• Cementite/carbide precipitation conditions;
• Pre-existing martensite;
• Soft and hard impingement in the austenite;
• Incomplete bainite reaction phenomenon [43].

Numerous kinetics models have been developed to describe or address the bainite nucleation and growth or many of the aspects listed above, but so far there is not a single model that can be applied in a universal situation except for the JMKA equation. This equation does not specifically account for nucleation rate of growth acceleration nor aspects listed above, but it is the one which expresses the overall kinetics most successfully. In the present research, the specific kinetics behavior of austempered 4140 steel was is characterized with the JMKA equation.

3. Experimental Design and Procedures

The 4140 steel with chemical composition shown in Table 2 has as received a hardness of 26 HRC with the original microstructure of proeutectoid phases embedded in a pearlite matrix.

| Element | Cr | Mn | C | Si | Mo | S | P | Fe |
|---------|----|----|---|----|----|---|---|---|
| wt (%)  | 0.80–1.10 | 0.75–1.0 | 0.38–0.43 | 0.15–0.30 | 0.15–0.25 | 0.040 | 0.035 | Balance |

Heat treating was conducted according to Figure 1. All specimen were cut from stock into quarter disks with a diameter of 3 cm and a thickness of 1 cm. Seven isothermal temperatures were applied and four bainite phase matrices were generated. For each isothermal temperature, nine isothermal holding times were used.

The specimens, after austenitizing in a salt bath furnace, were dropped into an isothermal holding furnace within 1 s. They were then held at a constant temperature for 10, 30, 60, 90, 120, 180, 300, and 600 s respectively. Once the isothermal holding time was complete, the specimens were immediately dipped into water at room temperature to stop the bainite transformation so the exact amount of bainite transformed could be determined through hardness measurement via kinetics calculation. Four isothermal temperatures were selected above 343 °C, one of which is around 371 °C. Around this temperature, the transition between upper and lower bainite would occur. The other three of the seven temperatures were selected around and below Ms (which could generate lower bainite and martensite mixed microstructure) so the kinetics of each phase matrix could be studied.
All samples were measured for HRC hardness, and polished and etched with 2% nital. Images of microstructures were taken using a light optical microscope (LM) at 500× magnification.

4. Results and Analysis

The results of hardness measurement are shown in Table 3. As the bainite transformation proceeded, the hardness of the samples decreased. These values correlate to the fraction of bainite transformation, as the hardness measured is directly related to the volume fraction of bainitic microstructure transformed. The data was used to perform kinetics calculations.

Table 3. 4140 steel hardness HRC achieved with measured and estimated bainite transformation start and finish time.

| T (°C)/t(s) | *10 | 30 | 60 | 90 | 120 | 180 | 220 | 300 | 600 |
|------------|-----|----|----|----|-----|-----|-----|-----|-----|
| 454        | 59.8@3s | 57.3 | 49.2 | 35.5 | 35.5 | 33.8 | 32.2 | -   | 30.8 | 30.3**|
| 427        | 60.1@4s | 58.0 | 52.7 | 39.4 | 39.4 | 36.0 | 33.4 | -   | 32.9** | 32.3 |
| 399        | 60.3@5s | 59.2 | 55.2 | 42.5 | 42.5 | 38.9 | 35.7 | 34.8 | 34.6 | 33.8 |
| 371        | 60.4@6s | 59.9 | 57.3 | 47.8 | 47.8 | 43.7 | 38.8 | 36.2 | 35.9 | 35.1 |
| 343        | 60.5@6s | 60.2 | 58.1 | 52.4 | 52.4 | 48.7 | 42.8 | 41.9 | 41.8 | 41.3 |
| 316        | 60.6@8s | 60.5 | 59.4 | 55.0 | 55.0 | 51.7 | 45.6 | -   | 45.0** | 44.6 |
| 288        | -    | 60.7* | -   | 57.2 | 57.2 | 54.6 | 49.9 | -   | 49.2 | 48.9** |

*: Estimated start/finish time; **: Measured start/finish time.

4.1. Kinetics Calculation Based on Hardness Measurements

Sample hardness is a function of bainite transformation, since it is determined by the bainitic microstructures achieved during the isothermal process. By determining the change in hardness as the bainite volume fraction varies along the isothermal holding time, the bainite transformation rate can be calculated.

Using Equation (1) and the hardness data in Table 3 the bainite volume fraction \(x(t)\) can be calculated:

\[
x(t) = \frac{(H(0) - H(t))}{(H(0) - H(f))}
\]  
(1)

\(x(t)\): Bainite volume fraction at time \(t\);
\(H(0)\): Initial hardness achieved of an isothermal experiment;
\(H(f)\): Final hardness achieved of an isothermal experiment;
\(H(t)\): Hardness at bainite reaction time \(t\).
In Figure 2, it can be seen that isothermal temperatures from 399 °C to 454 °C are the temperatures at which typical upper bainite is formed. The kinetics curves have a common pattern. The curve is not a typical Sigmund shape; instead it is an asymptote to a limit when the transformation is finished.

\[ X(t) = 1 - \exp(-Kt^n) \]  \hspace{1cm} (2)

By applying a logarithm operation, this becomes a linear equation between \( \log(-\ln(1 - X)) \) and \( \log(t) \).

\[ \log(-\ln (1 - X)) = n \times \log(t) + \log(K) \]  \hspace{1cm} (3)
The $n$ and $\log(K)$ can be calculated using linear regression; results are shown in Table 4. $n$ ranges between 1 and 2.3, which indicates that all bainite reactions in the range of 288 °C to 454 °C were austenite and bainite interface controlled [13], and $n$ has a linear relationship with the isothermal temperature $T$.

$$n = 4.3294 - 0.0071T$$

Table 4. Summary of $n$ and $K$ of 4140 steel bainite transformation Avrami constants.

| Isothermal Temperature (°C) | $n$ | $\log(K)$ | $K$ | $R^2$ |
|-----------------------------|-----|-----------|-----|-------|
| 454                         | 1.0655 | $-1.9654$ | 0.01082929 | 0.9706 |
| 427                         | 1.3339 | $-2.4428$ | 0.003607447 | 0.9989 |
| 399                         | 1.5687 | $-2.9536$ | 0.001112756 | 0.9933 |
| 371                         | 1.7370 | $-3.4599$ | 0.000346817 | 0.9804 |
| 343                         | 1.8018 | $-3.6445$ | 3.12176 × 10$^{-5}$ | 0.9826 |
| 316                         | 2.2056 | $-4.5056$ | 1.31765 × 10$^{-5}$ | 0.9649 |
| 288                         | 2.2357 | $-4.8802$ | 1.31765 × 10$^{-5}$ | 0.9649 |

4.2. 4140 Bainitic Microstructures and Morphology

Between isothermal temperatures of 454 °C and 399 °C, typical upper bainite is transformed. Figure 4a,c show the early stage of the upper bainite transformation, when bainitic ferrite plates have formed. Figure 4a shows the typical needle-like acicular bainite sheaves that are formed after 10 seconds held at an isothermal temperature of 427 °C. The bainite half-grown sheaves grew quickly, and the broad, relatively short full-grown sheaves filled the entire observed section. At 427 °C, after isothermal holding for 30 s, many typical lath-like upper bainitic ferrite plates formed as shown in Figure 4c. Measured with a LM at 500×, the needle-like upper bainite sheaves show an average width of 0.63 µm at 10 s and 1.92 µm at 30 s, and the length of the lathes varies.

Figure 4. 4140 steel upper bainite microstructure and sheave length measurements during growth.
Figure 4b,d show the length distribution of the bainite sheaves. When comparing the two sheave length distributions, it can be seen that the upper bainite sheave length increased from 5.12 µm to 6.4 µm in 20 s. Considering the measurement error, such as low resolution and noise of the image, the difference can be considered negligible. The bainite sheave width increased by a factor of 3 on average, from 0.64 µm to 1.92 µm. This indicates that the sheaves grow preferably in width and are almost stable in length, possibly due to soft impingement in the parent austenite. The upper bainite and the carbide precipitates between the bainitic ferrite plates are both very coarse as shown in the photo. The coarse carbides contribute to the width increase of the upper bainite sheaves.

Figure 5a,b show the microstructure of the upper bainite at 399 °C. In Figure 5c,d, at 371 °C, it can be seen that upper bainite and lower bainite mixed structures formed. The upper bainite appears as broad, lath-like sheaves and the lower bainite appears as the narrow, needle-like sheaves. Segregations seem to be shown in Figure 5c, but it can be explained by imperfect sample preparation, or imperfect microstructures etching, or polishing was not evenly applied, or other deficiency of lab works.

Figure 5. (a-d) Microstructure of 4140 steel as a result of isothermal temperature at 399 °C and 371 °C. At 343 °C, after isothermal treatment for 10 s, many typical needle-like lower bainitic ferrite plates formed as shown in Figure 6a. Measured with a LM at 500×, the needle-like lower bainite sheaves have an average width of 0.63 µm, see Figure 6b, and the length of the lathes varies from 3.83 µm to 16.64 µm. After isothermal treatment for 30 s, many typical needle-like lower bainitic ferrite plates formed sheaves as shown in Figure 6c. The needle-like lower bainite sheaves have an average width of 1.26 µm. The lower bainite sheaves are full-grown and the length of the lathes varies from 5.76 µm to 24.32 µm. Figure 6d shows the length distribution of the visible individual needles. When comparing the two sheave length distributions it can be seen that the lower bainite sheave length changed from 6.4 µm to 8.9 µm in 20 s. It seems that most sheaves increase in length about 50%, while the bainite sheave width doubles, from 0.64 µm to 1.23 µm. This indicates that the sheaves still prefer widthwise
growth, but do not grow as quickly as the upper bainite, possibly due to the lack of coarse carbides precipitation between the bainitic ferrite plates (which makes the sheaves much slimmer compared to the upper bainite sheaves).

![Figure 6](image)

**Figure 6.** 4140 steel, 343 °C, 10–30 s, half to full grown lower bainite sheaves, LM 500×.

The lower bainite sheaves are much narrower compared to the upper bainite sheaves as shown in the photos. Figure 7a,b show the lower bainite and martensite mixed microstructure features. The preexisting martensite impacted the growth of bainite sheaves as well as the rate of volume fraction increase. The lower bainite volume evolved quickly to a peak rate due to the acceleration effect of the preexisting martensite.

![Figure 7](image)

**Figure 7.** Microstructure of the 4140 steel consisted of lower bainite and martensite. Isothermal heat treatment at 315 °C for 60 s (a) and for 300 s (b).
The LM observation reveals that full-grown bainite sheave-length varies, but the sheave width is very consistent; this suggests that for 4140 steel, the length will not increase once the bainite ferrite plate forms, likely due to the small austenite grain size limit (22 µm to 32 µm in diameter [44]) which provides hard impingement as well as soft impingement. However, the bainitic ferrite plate prefers to grow in the width direction, most probably due to the fact that carbide or cementite precipitations along the long width boundaries consumes many carbon atoms. Therefore, relatively low carbon density areas form on the ferrite plate in the widthwise direction, which promotes the nucleation of the new ferrite plates [23]. The nature of autocatalytic nucleation may play a large role as well. Bainite sheaves sidewise growth results in lath-like morphology. 4140 steel bainite grows in a process similar to low carbon steels [45] due to the coalescence of the bainite subunits.

4.3. Activation Energy of Bainite Transformation

4.3.1. Activation Energy Calculation

The isothermal temperatures selected for this work cover a wide range of temperatures in which upper bainite and lower bainite is transformed. Particularly, some lower bainite is transformed below Ms, the martensite start temperature. The bainite transformation activation energy of 4140 steel is determined as follows.

The activation energy $Q_x$ at reaction percentage $x$ is defined as:

$$Q_x = R \left[ \frac{\partial(\ln(K))}{\partial(\frac{1}{T})} \right]_x$$

where $K$ is the bainite reaction or phase transformation rate. $K$ can be in one of the forms shown in Equation (6) or (7) when the reaction rate $K$ corresponding to $x$ percentage of bainite volume growth.

If $K = \left( \frac{\partial(X)}{\partial(t)} \right)$, then $Q_x = R \left[ \frac{\partial(\ln(\frac{\partial(X)}{\partial(t)}))}{\partial(\frac{1}{T})} \right]_x$ (6)

If $K = 1/t_x$, then $Q_x = -R \left[ \frac{\partial(\ln t_x)}{\partial((1/T))} \right]_x$ (7)

Equation (7) is used when the reaction rate defined as the reciprocal of reaction corresponding to $x$ percentage. Usually researchers use the time at 50% reaction point to be the standard, symbolized as $t_{50}$. For simplicity, Equation (7) is commonly used, but Equation (6) is believed to be more accurate for activation energy calculation [39].

The activation energy $Q$ can be associated to transformation reaction rate $K$ in the Arrhenius equation.

$$K = A \cdot \exp(-QR/T)$$ (8)

where,

- $Q$: Bainite transformation activation energy [J/mol];
- $A$: Bainite transformation reaction frequency factor [1/s];
- $R$: General gas constant 8.31 [J/mol·K];
- $T$: Isothermal temperature at which bainite is transformed [K].

By applying the natural logarithm on both sides of this equation, a linear equation in the form shown in Equation (5) can be derived, in which $\ln(K)$ and $1/T$ have a linear relationship.

$$\ln(K) = \ln(A) - (Q/R) \cdot (1/T)$$ (9)
Once \(T\) and \(\ln(K)\) are known, \(-(Q/R)\) and \(\ln(A)\) can be obtained through linear regression. Thus, \(Q\), the activation energy, is found through calculation.

Some researchers use the reciprocal of 50% reaction time as the reaction rate \(K\), which is \(K = 1/t_{50}\), for example in [38,39], others choose to use the reaction constant \(K\) in the Avrami equation as the reaction rate, for example in [22]. For comparison purposes, \(Q\) is calculated in this research using both assumptions.

When using \(K = 1/t_{50}\) the relationship is:

\[
K = 1/t_{50} = A \exp \left(-\frac{Q}{RT}\right) \quad (10)
\]

Taking the logarithm of both sides of the equation:

\[
\ln(t_{50}) = -Q/RT \quad (11)
\]

4.3.2. Bainite Reaction Activation Energy Calculation Based on Reaction Rate \(1/t_{50}\)

With the derived Arvami equation, \(t_{50}\) can be obtained. Reaction rate can be defined as the reciprocal of the reaction time, at which 50% of the reaction has occurred; this can be written as \(K = 1/t_{50}\). The data used for performing linear regression are shown in Table 5. With the same method, the activation energy for all four phases or mixed phases of bainite were calculated.

Table 5. Data used for calculating activation energy of bainite transformation.

| Temp (°C) | \(T\) (K) | \(\ln(1-0.5)\) | \(K\) | \(n\) | \(t_{50}\) | \(1/t_{50}\) | \(1/T\) | \(\ln(t_{50})\) | \(\ln(K)\) |
|----------|-----------|----------------|------|------|----------|------------|--------|----------------|----------|
| 288      | 560.9     | 0.693147       | 0.000013 | 2.24 | 129      | 0.0078     | 0.001783 | 4.8589         | -11.2506 |
| 316      | 588.7     | 0.693147       | 0.000031 | 2.21 | 93       | 0.0108     | 0.001699 | 4.5317         | -10.3815 |
| 343      | 616.5     | 0.693147       | 0.000227 | 1.8  | 86       | 0.0116     | 0.001622 | 4.4578         | -8.39056 |
| 371      | 644.3     | 0.693147       | 0.000347 | 1.74 | 79       | 0.0127     | 0.001552 | 4.3676         | -7.96619 |
| 399      | 672.0     | 0.693147       | 0.001112 | 1.56 | 62       | 0.0162     | 0.001488 | 4.1250         | -6.8016  |
| 427      | 699.8     | 0.693147       | 0.003607 | 1.33 | 52       | 0.0192     | 0.001429 | 3.9537         | -5.62488 |
| 454      | 727.6     | 0.693147       | 0.010829 | 1.07 | 49       | 0.0205     | 0.001374 | 3.8869         | -4.52551 |

Table 6 below shows that the overall activation energy calculated is 19.3 kJ/mol. It is approximately the average of the activation energies of the phases or mixed phases. The mixed phases require more activation energy to transform. Both upper and lower bainite mixed phase, and lower bainite and martensite mixed phase, are approximately 32 kJ/mol, which is 150% of the average activation energy. Being both single phases, the upper bainite and lower bainite require less activation energy. They are approximately 50% of the average activation energy. QB and QLB are quite close, but they do not fall into the QUB > QLB pattern [39]. The calculated 19.3 kJ/mol overall activation energy is much lower than the activation energy for diffusion of carbon in ferrite, which is 70 kJ/mol [46]. Explained with displacive theory, once the bainitic ferrite plate forms, the carbon needs to diffuse within the plate to the boundary into the parent austenite to further the bainite transformation process. 70 kJ/mol is needed to start the carbon diffusion within the bainitic ferrite plate. This simple comparison may not be adequate, since the overall transformation involves a mix of phases. The upper bainite or lower bainite single phase activation energy (10.2 kJ/mol and 10.7 kJ/mol) are quite close to the ones reported in Umemoto’s paper for a 0.99C wt% steel, which is 11.7 kJ/mol [47]. They are also close to the 17 kJ/mol and 16 kJ/mol values calculated by Gaballero. Both Umemoto [47] and Gaballero [9] also used \(1/t_{50}\) as the reaction rate for calculation.
Table 6. Bainite reaction activation energy calculation based on $1/t_{50}$ and $K$ as reaction rate.

| Bainite Phase Matrix                        | $Q (1/t_{50})$ (kJ/mol) | $Q (K)$ (kJ/mol) |
|---------------------------------------------|--------------------------|------------------|
| Overall Bainite (QB)                        | 19.3                     | 136              |
| Upper Bainite (QUB)                        | 10.2                     | 167              |
| Upper Bainite + Lower Bainite Q (UB + LB)   | 31.5                     | 151              |
| Lower Bainite (QLB)                         | 10.7                     | 50               |
| Lower Bainite + Martensite Q (LB + M)       | 32.3                     | 86               |

4.3.3. Bainite Reaction Activation Energy Calculation Based on $K$

With the derived Avrami equation, $K$ can be obtained. $K$ is explained as the reaction rate constant, so the reaction rate $K$ used in the Arrhenius equation can be used for activation energy calculation [22]. Based on $K$, the overall bainite transformation activation energy is calculated as 136 kJ/mol, see Table 6, which is 20% higher than the average activation energy of the four phases or mixed phases. This value is close to the diffusion activation energy of carbon in austenite, which is 131 or 148 kJ/mol, [38,48,49], explained by displacive theory which states that carbon atoms from the bainitic ferrite plate partition into the parent austenite once the bainitic ferrite plate has formed. Carbon atoms need to diffuse within the austenite a further distance; the 136 kJ/mol activation energy is the amount of energy carbon atoms need to diffuse in the parent austenite. The results in Table 6 also show QUB (167 kJ/mol) > QLB (50 kJ/mol), the upper bainite activation energy is higher than the lower bainite activation energy. This agrees with many published papers. QLB <100kJ/mol also agrees with published results [38,39].

QUB, the upper bainite activation energy is 167 kJ/mol, which is higher than the 130–148 kJ/mol carbon diffusion activation energy in austenite. QUB(167 kJ/mol) > Q(UB + LB)(151 kJ/mol) > QLB(50 kJ/mol). As under-cooling increases, the driving forces required decrease, with upper bainite alone requiring the highest, then a mixture of upper and lower, and lower alone requiring the least; This trend agrees with Gibbs energy balance models for predicting the transition temperature between upper and lower bainite, which describe the kinetic competition between the bainitic ferrite and cementite nucleation in the bainite reaction. Yet Q(LB + M) > QBL, most probably due to prior athermal martensite accelerating the transformation, hence requiring more energy for this transformation. Results in Table 6 also agree with the reference values listed in Kang’s paper [38,39], which includes a summary of activation energies published for more than 30 steel grades.

4.3.4. Comparison of $1/t_{50}$ and $K$ Based Activation Energy Calculation Results

Based on the Avrami equation fitted with experimental data, both $1/t_{50}$ and $K$ are available as reaction rates for bainite activation energy calculation, see Table 6. With $K$ based reaction rate, overall bainite activation energy QB calculated is about 7 times higher than results using the $1/t_{50}$ based reaction rate. The calculation results based on $K$ agree with the data in some published papers [38,39]. $1/t_{50}$ reaction rate or 50% reaction time based calculation results fall outside the range of some published results [47,50]. Therefore, the $K$ based reaction rates are preferred to calculate activation energy with the Arrhenius concept.

5. Discussion and Conclusions

1. Bainite transformation kinetics fits the conventional JMKA model. Kinetically there is a clear separation between the four bainite phases matrices. The Avrami constant "n" is around $n = 1$ for upper bainite, $n = 1.7$ for mixed upper and lower bainite, $n = 1.8$ for lower bainite, and $n = 2.2$ for mixed lower bainite and martensite. The $n$ values have a linear relation with the isothermal holding temperature. The $n$ value is between 1 and 2.3, which indicates the reaction is austenite and bainite interface controlled [14]. The kinetic curve shapes changed from reverse exponential to typical sigmoid as undercooling increases in the experiments.
2. Bainitic ferrite morphology in experiments was revealed; both upper bainite and lower bainite ferrite plates grew to variable lengths, yet both half-grown bainite sheaves had the same width of 0.64 µm. The full-grown upper bainite was coarse and the sheaves were 1.9 µm in width, and full-grown lower bainite sheaves were slim and are 1.2 µm in width. Both have the typical lath-like appearance under LM. The bainite sheaves in 4140 steel have a width direction growth preference, possibly because its austenite grains are relative small in size or the soft impingement effect. The physical model of this widthwise growth needs further study. Other than the carbide precipitations difference, upper and lower bainite had the same transformation characteristics. Upper bainite and lower bainite mixtures, as well as lower bainite and martensite mixtures, were also observed; their mechanical properties need further exploration.

3. Bainite reaction rate can be defined either with the reciprocal of the percentage reaction time (usually the time at 50% reaction) or the rate constant $K$ fitted in the JMKA model. Once the rate was determined, the transformation activation energy can be calculated with the Arrhenius concept using linear regression. For 4140 steel, bainite activation energy was calculated using both methods. Results show that the $K$ based method is more accurate and thus is preferred. The overall activation energy for the entirety of bainite formed, which is the average of the four bainite or mixed bainite phases, is 136 kJ/mol. This matches the carbon diffusion activation energy in austenite. The lower bainite activation energy is 50 kJ/mol, which is lower than the iron diffusion activation energy in both austenite (285 kJ/mol) and in ferrite (259 kJ/mol); this is consistent with the displacive mechanism of bainite transformation, since the activation energy of bainite is much lower than required by a diffusional mechanism. Bainite transformation cannot be carried out by diffusion alone.

Author Contributions: Conceptualization, J.G.Z. and G.C.B.; methodology, X.S.; investigation, J.G.Z., X.S., G.C.B., H.H., H.Q.; data curation, J.G.Z., X.H., H.Q.; writing—original draft preparation, J.G.Z.; writing—review and editing, J.G.Z., G.C.B. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors gratefully acknowledge the material and lab support of Fiat Chrysler and Oakland University.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Bhadeshia, H.K.D.H. Bainite in Steel, 2nd ed.; Institute of Materials: London, UK, 1992.
2. Davenport, E.S.; Bain, E.S. Transformation of austenite at constant subcritical temperature. Trans. Am. Inst. Min. Metall. Eng. 1930, 90, 117–154.
3. Gibbs, J.W. A method of geometrical representation of the thermodynamic properties of substances by means of surfaces. transactions of the connecticut academy of arts and sciences 2. Trans. Connecticut Acad. Arts Sci. 1873, 2, 382–404.
4. Bhadeshia, H.K.D.H.; Edmonds, D.V. The mechanism of bainite formation in steel. Acta Metall. 1980, 28, 1265–1273. [CrossRef]
5. Liu, Z.; Ågren, J. On the transition from local equilibrium to para equilibrium during the growth of ferrite in Fe-Mn-C austenite. Acta Metall. 1989, 37, 3157–3163.
6. Avrami, M. Kinetics of phase change. I. General theory. J. Chem. Phys. 1939, 7, 1103–1132. [CrossRef]
7. Arrhenius, S.A. Uber die Dissociationswarme und den Einfluss der temperatur auf den Dissociationsgrad der Elektrolyte. Z. Phys. Chem. 1889, 4, 96–116. [CrossRef]
8. Bhadeshia, H.K.D.H. Atomic mechanism of the bainite transformation. HTM J. Heat Treatm. Mat. 2017, 6, 340–345. [CrossRef]
9. Caballero, F.G.; Roelofs, H.; Hasler, S.; Capdevila, C.; Chao, J.; Cornide, J.; Garcia-Mateo, C. Influence of bainite morphology on impact toughness of continuously cooled cementite free bainitic steels. Mater. Sci. Technol. 2012, 28, 95–102. [CrossRef]
10. Matas, S.J.; Hehemann, R.H. The structure of bainite in hypoeutectoid steel. *Trans. Metall. Soc. AIME* 1961, 221, 179–185.
11. Hehemann, R.F. *Phase Transformation*; ASM: Metals Park, OH, USA, 1970; pp. 397–432.
12. Jung, Y.C.; Ohmori, Y.; Nakai, K.; Ohtsubo, H. Bainite transformation in a silicon steel. *ISIJ Int.* 1997, 37, 789–806. [CrossRef]
13. Goldstein, H.; Aronson, H.I. Overall reaction kinetics and morphology of austenite decomposition between nose and Ms of a Hypereutectoid Fe-Cr alloy. *Metall. Mater. Trans. A* 1990, 22, 1465–1478. [CrossRef]
14. Bhadeshia, H.K.D.H. The lower bainite transformation and the significance of carbide precipitation. *Acta Metall.* 1980, 28, 1103–1114. [CrossRef]
15. Cui, G.; Zhang, Y.; Shi, C. Research on bainite-matrix TRIP steel produced by fully austenitized heat treatment. *Revista de la Facultad de Ingenieria U.C.V* 2017, 32, 535–541.
16. Lawrynowicz, Z. Rationalization of Austenite transformation to upper or lower bainite in steels. *Adv. Mater. Sci.* 2014, 14, 14–23. [CrossRef]
17. Navarro-Lopez, A.; Sietsma, J.; Santofimia, M.J. Effect of pre-existing martensite in a low-C high-Si steel. In Proceedings of the International Conference on Solid Phase Transformation in Inorganic Materials, Whistler, BC, Canada, 28 June–3 July 2015; pp. 1155–1156.
18. Khana, Y.P.; Tyalor, T.J. Comments and recommendations on the use of the Avrami equation for Physico-Chemical Kinetics. *Polyom. Eng. Sci.* 1988, 28, 1042–1045. [CrossRef]
19. Bosze, W.P.; Trivedi, R. On the kinetic expression for the growth of precipitate plates. *Metall. Trans.* 1974, 218, 511–512. [CrossRef]
20. Ko, T.; Cottrell, S.A. The formation of bainite. *J. Iron Steel Inst.* 1952, 172, 307–313.
21. Quidort, D.; Brechet, Y.J.M. A model of isothermal and non isothermal transformation kinetics of bainite in 0.5 C steel. *ISIJ Int.* 2002, 42, 1010–1017. [CrossRef]
22. Milosan, I. Aspects about the kinetics and thermodynamic transformation of a special S.G. cast iron. In Proceedings of the 6th International DAAAM Baltic Conference, Tallinn, Estonia, 24–26 April 2008.
23. Bhadeshia, H.K.D.H. Comments on “Bainite formation kinetics in high carbon alloyed steel”. *Scr. Mater.* 2008, 59, 1275–1276. [CrossRef]
24. Augis, J.A.; Bennett, J.E. Calculation of the Avrami parameters for heterogeneous solid state reaction using a modification of Kissinger method. *J. Therm. Anal.* 1978, 13, 283–292. [CrossRef]
25. Takahashi, M.; Bahadshhia, H.K.D.H. Model for transition from upper bainite to lower bainite. *Mater. Sci. Technol.* 1990, 6, 592–603. [CrossRef]
26. Rees, G.I.; Bhadeshia, H.K.D.H. Bainite transformation kinetics Part 1: Modified model. *Mater. Sci. Technol.* 1992, 8, 985–993. [CrossRef]
27. Zarudi, I.; Zhang, L.C. Modelling the structure changes in quenchable steel subjected to grinding. *J. Mater. Sci.* 2002, 37, 4333–4341. [CrossRef]
28. Liu, C.; Di, X.; Chen, C.; Guo, X.; Xue, Z. A bainite transformation kinetics model and its application to X70 pipeline steel. *J. Mater. Sci.* 2015, 50, 5079–5090. [CrossRef]
29. Hesse, O.; Kapusyna, A.; Brykov, M. Kinetics of isothermal transformation of high-carbon low alloyed austenite and its microstructure after such treatment. In Proceedings of the 8th International Conference on Material Technologies and Modeling MMT-2014, Ariel, Israel, 28 July–1 August 2014; pp. 186–194.
30. Hillert, M.; Hoglund, L.; Agren, J. Role of carbon and alloying elements in the formation of bainite ferrite. *Metall. Mater. Trans.* 2004, 35A, 3693–3700. [CrossRef]
31. Kaptio, A.; Stumpf, W.; Papo, M.J. The role of alloying elements in bainitic rail steels. *J. S. Afr. Inst. Min. Metall.* 2013, 113, 67–72.
32. Qin, X.; Cui, S.; An, W. Low temperature bainitic transformation behavior and microstructure & mechanical properties of a medium carbon high strength steel for railway forged center plate. In Proceedings of the 8th International Conference on Physical and Numerical Simulation of Materials Processing, ICPNS’16 Seattle Marriott Waterfront, Seattle, WA, USA, 14–17 October 2016.
33. Dischino, A. Analysis of phase transformation in high strength low-alloyed steels. *Metalurgija* 2017, 56, 349–352.
34. Jacques, P.; Girault, E.; Van Humbeeck, J.; Aernoudt, E.; Delannay, F. Experimental characterization of the bainitic transformation kinetics of residual austenite in Mn-Si TRIP assisted multiphase steels. *J. Phys. IV France* 1997, 7, 459–462. [CrossRef]
35. Goulas, C.; Mecozzi, M.G.; Sietsma, J. Bainite formation in medium-carbon low-silicon spring steels accounting for chemical segregation. *Metall. Mater. Trans. A* 2016, 47, 3077–3087. [CrossRef]

36. Kang, S.; Yoon, S.; Lee, S. Prediction of bainite start temperature in alloy steels with different grain size. *ISIJ Int.* 2014, 54, 997–999. [CrossRef]

37. Ravi, A.M.; Sietsma, J.; Santofimia, M.J. Exploring bainite formation kinetics distinguishing grain-boundary and autocatalytic nucleation in high and low-Si steels. *Acta Mater.* 2016, 105, 155–164. [CrossRef]

38. Kang, M.; Zhang, M.; Liu, F.; Zhu, M. Overall transformation energy of isothermal transformation in metal alloy and its mechanism. *Acta Metall. Sinica* 2009, 45, 25–31. (In Chinese)

39. Kang, M.; Zhang, M.; Liu, F.; Zhu, M. Kinetics and morphology of isothermal transformations at intermediate temperature in 15CrMnMoV steel. *Mater. Trans.* 2009, 50, 123–129. [CrossRef]

40. Garcia-Mateo, C.; Paul, G.; Somani, M.C.; Porter, D.A.; Bracke, L.; Latz, A.; Garcia De Andres, C.; Caballero, F.G. Transferring nanoscale bainite concept to lower C contents: A perspective. *Metals* 2017, 7, 159. [CrossRef]

41. Claesson, E. Development of a Heat Treatment Method to Form a Duplex Microstructure of Lower Bainite and Martensite in AISI 4140 Steel. Master’s Thesis, Royal Institute of Technology, Stockholm, Sweden, 2014.

42. Denis, S.; Sjostrom, S.; Simon, A. Coupled temperature, stress, phase transformation calculation model numerical illustration of the internal stresses evolution during cooling of a eutectoid carbon steel cylinder. *Metall. Mater. Trans. A* 1987, 18A, 1203–1212. [CrossRef]

43. Bhadeshia, H.K.D.H.; Waugh, A.R. Bainite: An atom-probe study of the incomplete reaction phenomenon. *Acta Metall.* 1982, 30, 775–784. [CrossRef]

44. Trzaska, J. Calculation of critical temperature by empirical formulas. *Arch. Metall. Mater.* 2016, 61, 981–986. [CrossRef]

45. Ohtani, H.; Okaguchi, S.; Fujishiro, Y.; Ohmori, Y. Morphology and properties of low-carbon steel. *Metall. Trans.* 1990, 21, 877–888. [CrossRef]

46. Vasudevan, P.; Graham, L.W.; Axon, H.J. The kinetics of bainite formation in a plain carbon steel. *J. Iron Steel Inst.* 1958, 190, 386–391.

47. Umemoto, M.; Horiuchi, K.; Tamura, I. Transformation Kinetics of bainite during isothermal holding and continuous cooling. *Trans. ISIJ* 1982, 22, 854–861. [CrossRef]

48. Gegner, J.; Vasilyev, A.A.; Wilbrandt, P.J.; Kaffenberger, M. Alloy dependence of the diffusion coefficient of carbon in austenite and analysis of carburization profiles in case hardening of steels. In Proceedings of the 7th International Conference on Mathematical Modeling and Computer Simulation of Material Technologies (MMT-2012), Ariel, Israel, 22–25 October 2013; pp. 261–287.

49. Agren, J. Revised expression for the diffusivity of carbon in binary Fe-C austenite. *Scr. Mater.* 1986, 20, 1507–1510.

50. Caballero, F.G.; Santofimia, M.J.; Garcia-Mateo, C.; De Andres, C.G. Time-temperature-transformation diagram within the bainite temperature range in a medium carbon steel. *Mater. Trans.* 2004, 45, 3272–3281. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).