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Time-Temperature Equivalence in Martensite Tempering

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Abstract

The relationship between time and temperature is of great consequence in many materials-related processes including the tempering of martensite. In 1945, Hollomon and Jaffe quantified the "degree of tempering" as a function of both tempering time, t, and absolute tempering temperature, T, using the expression, T(log t +c) [1]. Here, c is thought to be a material constant and appears to decrease linearly with increasing carbon content. The Hollomon-Jaffe tempering parameter is frequently cited in the literature. This work reviews the original derivation of the tempering parameter concept, and presents the use of the characteristic diffusion distance as an alternative time-temperature relationship during martensite tempering. During tempering of martensite, interstitial carbon atoms diffuse to form carbides and austenite decomposes. In addition, dislocations and grain boundaries rearrange, associated with iron self diffusion. Since these are all diffusional processes, it is reasonable to expect the degree of tempering to relate to the extent of diffusion.

Introduction

Interest in time-temperature relationships originated in the authors' work in attempting to understand the expected partitioning response during coil cooling of a conceptual hot-rolled quenched and partitioned (Q&P) steel. Q&P is a process where partial transformation of austenite to martensite is assumed to be followed by partitioning of carbon between the phases, with the goal of stabilizing austenite [2]. Partitioning is similar to tempering in that they both involve diffusion of carbon in martensite and austenite. Two methods were considered for estimating the non-isothermal partitioning responses during coil cooling that may be *equivalent* to the isothermal partitioning responses from earlier Q&P research. The two methods considered were the Hollomon-Jaffe tempering parameter and the characteristic diffusion distance, both of which are a function of both time and temperature. In both methods, partitioning responses involving the integration over the non-isothermal coil-cooling curve were compared to isothermal partitioning conditions previously studied in Q&P literature. Further explanation on the application of these methods for calculating equivalent non-isothermal partitioning effects can be found elsewhere [3]. While using the Hollomon-Jaffe tempering parameter to calculate equivalent partitioning effects, questions arose regarding the basis upon which the parameter was derived. Thus, a further examination of the isothermal tempering parameter as it related to isothermal martensite tempering was conducted. This work presents some of those issues and compares different time-temperature relationships that may be applicable.

In 1945, Hollomon and Jaffe published work on the time-temperature relations in tempering of martensite and other microstructures [1]. The result of their work, the Hollomon-Jaffe tempering parameter, relates tempering conditions of different

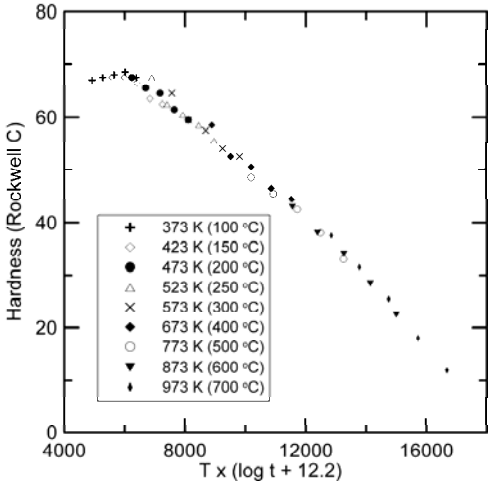

Figure 1. Plot of tempered hardness vs. the Hollomon-Jaffe tempering parameter for 0.89 % carbon steel. From tabulated data given by Hollomon and Jaffe (Steel W) [1].

time and temperature combinations to relative hardness. That is, for a given tempering parameter, the hardness should be the same. The tempering parameter takes the form T (log t/t_o), or the equivalent, more well known form, T (log t + c), where T is absolute temperature, t is the time, and t_o and c are constants for the steel. Use of the tempering parameter allows one to estimate time-temperature combinations that yield equivalent degrees of tempering. The tempering parameter has been employed over a wide range of conditions, spanning a temperature range at least from 95 °C to 750 °C [4,5], while times range at least from 0.6 seconds to 100 hours [6,4]. The Hollomon-Jaffe tempering parameter is used extensively in the literature, especially to plot tempered hardness vs. time and temperature on a unified axis, as shown in Figure 1 [1,4,5,7]. An equivalent approach is represented by the Larson-Miller relationship for creep data, which takes the same form as the tempering parameter [8].

The literature, however, also raises some questions about the tempering parameter, especially with regard to the constant, c. According to Hollomon and Jaffe, c varies only with carbon content. However, Roberts, Grobe and Moersh [4] reported an "inexplicable variation of c." Based on independent discussions with Jaffe and Cohen, Roberts et al. chose to average the values of c determined, and thus used a value of 20 for times in hours.[a] In that same work [4], Cohen offered a written discussion expressing that he had found that the c-value did not vary consistently with systematic changes in steel chemistry. Additionally, Grange and

[a] Unless otherwise noted, throughout this work the units of temperature are Kelvin and the units of time are seconds. In literature, the c-value of the tempering parameter is often based on times in hours. To convert the c-value for times in seconds to times in hours, one must add log 3600≈3.57 to the value of c.

Baughman [7] found c to vary with hardness in an alloy steel by a factor of four or more; to solve this problem they chose a single c-value that gave the least scatter for all of their steels. The practice of empirically choosing a single c-value such that tempering data can conveniently be compared between steels is not uncommon in the literature. The aim of the first part of this paper is to evaluate the c-value and understand its origins, to determine if the experimental data fit the model inherent to the tempering parameter.

Form of the Tempering Parameter

When deriving the tempering parameter, Hollomon and Jaffe first assumed that the relationship between tempering time and temperature "took the usual form of the diffusion equations [1]." That is, hardness, H, was expected to be a function of the extent of diffusion, H = f(t•exp(-Q/RT), where the activation energy, Q, is a constant, characteristic of the steel and R is the ideal gas constant. *However*, when Hollomon and Jaffe calculated the value of Q, they found that it was not constant, but rather varied with hardness, from about 209 kJ/mol (50 kcal/mol) at 20 HRC to 50 kJ/mol (12 kcal/mol) at 65 HRC. With this information *Hollomon and Jaffe diverged from the usual form of the diffusion equations* and employed a value of Q that varied with hardness. Hollomon and Jaffe further asserted that the value of the expression, t•exp(-Q/RT), was constant for all hardness, which they labeled t_o, as shown in Equation 1. Equation 1 is not consistent with the typical diffusion equations in which Q is constant and the value of t_o, or the extent of diffusion, would usually be expected to increase with increasing time or temperature.

$$t_o = t\exp\left(\frac{-Q}{RT}\right) = CONSTANT \tag{1}$$

Assuming that t_o in Equation 1 is a constant, it is simply a matter of mathematical rearrangement to arrive at the final expression for the tempering parameter, T(log t + c), where c = -log t_o. It is important to recognize that a constant c-value is a fundamental element of the tempering parameter derivation. The values of t_o and c must be constant if the tempering parameter is to take its customary form.

Re-evaluation of the Tempering Parameter

Based on the previously cited literature reports of inconsistencies in c-value [4,7] and the fact that the derivation is not consistent with the typical diffusion equations, it was desired to re-evaluate the tempering parameter and understand how experimental data fit the model that Hollomon and Jaffe proposed. By rearranging Equation 1 it is straightforward to arrive at Equation 2:

$$\ln t = \ln t_o + \frac{Q}{R}\frac{1}{T} \tag{2}$$

When plotted as ln time vs. reciprocal temperature, Equation 2 represents a straight line with slope Q/R and intercept ln t_o as shown in Figure 2. According to Hollomon and Jaffe's model, activation energy varies with hardness, and thus slope of the line is different for conditions representing each hardness series in Figure 2. Additionally, each series shares a common intercept, ln t_o, related to the c-value by c = -log t_o. This approach is another method for the determination of the c-value (and activation energy) using multiple data points from each hardness curve, rather than the two points used by Hollomon and Jaffe [1]. Figure 2 represents the behavior that is implied by the tempering parameter formulation. The same experimental data originally published by Hollomon and Jaffe were re-evaluated here. The analysis performed with one data set is presented here in detail. Five additional data sets published in the original Hollomon and Jaffe work were also analyzed. The results were similar to those shown here and thus are not presented in full detail.

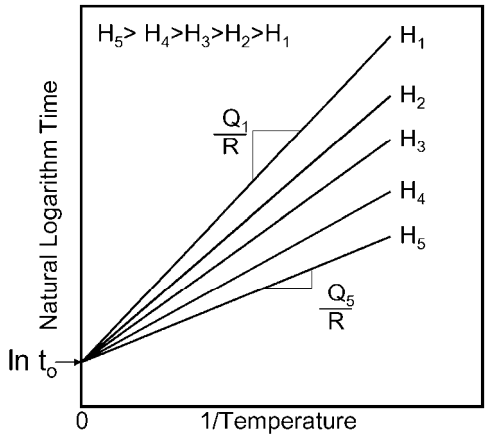

Figure 2. Schematic of Hollomon and Jaffe's tempering parameter model.

Hollomon and Jaffe's Experimental Data

The data analyzed here were experimental data generated by Hollomon and Jaffe that they designated as "Steel W." Steel W contained 0.89% carbon and was chosen for presentation here because of its wide range of hardness values and because it exhibited the smoothest variation of activation energy with hardness (shown below). Hollomon and Jaffe tabulated experimental tempered hardness as a function of tempering times and temperatures ranging from 10 to 86,400 seconds (24 hours) and 373 to 973 K, respectively. In order to obtain sufficient data for this investigation, the tabulated hardness data were interpolated as a function of tempering time using a logarithmic regression for each temperature. The results of the interpolations are shown in Figure 3.

The hardness data were plotted on axes of ln time vs. reciprocal temperature using the interpolated data, as shown in Figure 4. Linear regressions were developed for each hardness series in order to determine the activation energies and c-values from the slopes and intercepts, respectively. Linear regressions were performed at ½ point Rockwell C intervals over the range from 20 to 65 HRC to determine the corresponding activation energy and c-value; however, Figure 4 shows only select data for clarity.

The activation energy at each hardness level was determined from the slope of each linear regression from Figure 4 and multiplying by the ideal gas constant, R, since the slope is equal to Q/R. The activation energy is plotted in Figure 5 as a function of hardness. The c-value at each hardness level was determined from the intercept, ln t_o, of each regression line using c = -log t_o. The c-values vs. hardness are plotted in Figure 6. The dashed line on Figure 6 indicates the value that Hollomon and Jaffe reported for the c-value. They obtained this value by averaging all of the c-values found using their method [1]. The discontinuities observed in Figure 5 and 6 can be traced to changes in the temperature combinations in Figure 3 that were used to interpolate data for Figure 4. It is anticipated that the discontinuities would become less pronounced if data for more tempering temperatures were available, and ultimately the activation energy and c-value would vary smoothly with hardness in Figures 5 and 6.

The data plotted for Hollomon and Jaffe's Steel W in Figure 5 show that the values of the activation energy vary in the same general manner as reported by Hollomon and Jaffe. That is, lower values are found for activation energy at higher hardness and higher values at lower hardness. However, the c-values, which are equal to -log $t_{o,}$ vary substantially with hardness. As seen in Figure 6, the c-values for Steel W vary between about 6 and 15. Since the form of the tempering parameter requires that t_o, and hence c, be constant, this large variation in the c-value indicates that the data may not fit well with the tempering parameter model. A change in the c-value of just one integer corresponds to an order of magnitude change in t_o. Thus, given the variation in the c-value, it seems that simply averaging the c-values to force a single value for c, does not represent the data well.

The analysis shown for Steel W was also performed on the five other experimental data from the original tempering parameter paper (Steels R, S, T, U and V) [1]. As shown in Table I, all five steels exhibited a large range in c-value. Similarly to Steel W, the c-values tended to increase with decreasing hardness for all of the steels. Again, the variation in the c-value indicates that the value of t_o is not constant.

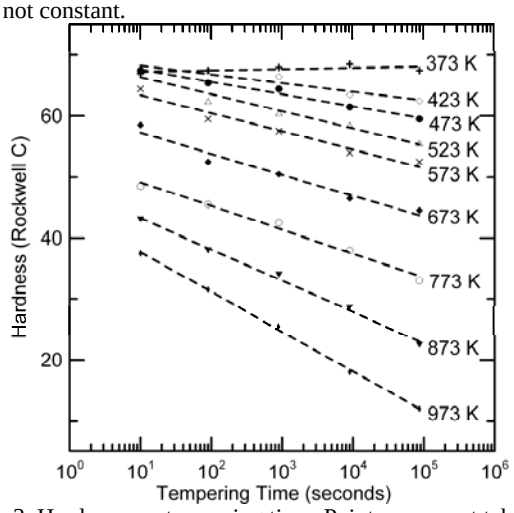

Figure 3. Hardness vs. tempering time. Points represent tabulated data from Hollomon and Jaffe Steel W (0.89% C) [1]. Dashed lines represent logarithmic regressions of the tabulated data for interpolation purposes.

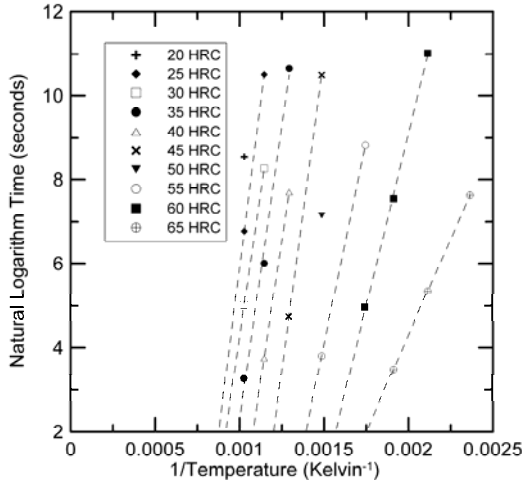

Figure 4. Plot of ln time vs. reciprocal temperature for Steel W. Data points represent data interpolated from Figure 3. Dashed lines represent linear regressions of the interpolated data.

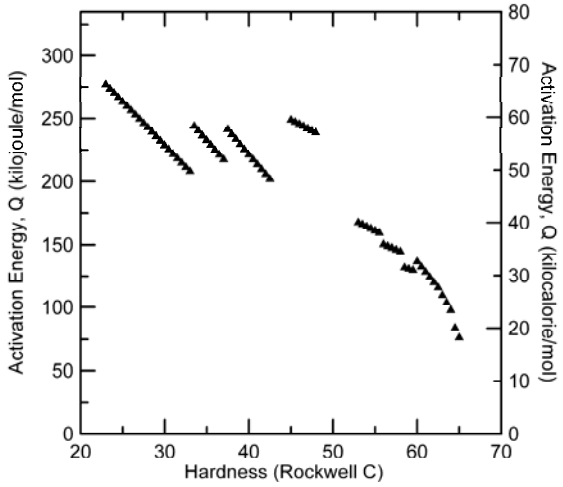

Figure 5. Activation energy, Q, versus hardness for Steel W. Each Q was calculated from the slope of the linear regressions fit to interpolated data shown in Figure 4.

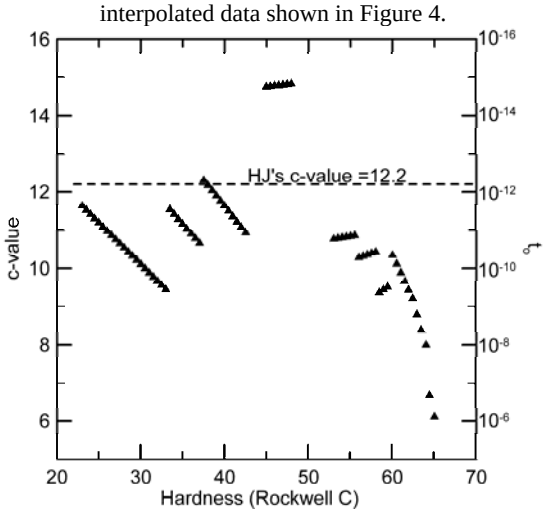

Figure 6. c-value as a function of hardness for Steel W. The value of t_o is also indicated. Each c-value and t_c were calculated from the intercepts of the linear regressions shown in Figure 4. The average c-value found by Hollomon and Jaffe was 12.2, as indicated by the dashed line.

Table I. Range of c-values found for six data sets provided in the original tempering parameter paper [1].

Steel	Minimum c-value	Maximum c-value
R	6	12.7
S	1.7	15.3
T	6.8	14.9
U	5.7	14.8
V	1.7	13.8
W	6.1	14.8

Discussion of the Tempering Parameter Formalism

A constant value for t_o (and thus c-value) is fundamental to the tempering parameter model. If the value of t_o is not constant, the tempering parameter could not take the form that it does since the parameter is derived from Equation 1, which requires that t_o be constant. As shown above, the data from the Hollomon and Jaffe

publication exhibit significant variation in the c-value. Hollomon and Jaffe addressed the problem of the non-constant c-value by averaging the values to obtain a single value. However, variation in the c-value with hardness should indicate a fundamental concern with the tempering parameter model. The non-constant c-value indicates that the value of t_o is not constant, contrary to a basic assumption used in the derivation of the tempering parameter. Grange and Baughman modified the tempering parameter such that the c-value was empirically assigned simply to reduce the scatter in the data when plotted as shown in Figure 1. However, the form of the tempering parameter remained unchanged, T(log t +c). They reported that the actual value chosen for c did not make a large difference in the results [7]. In this respect, the tempering parameter may remain useful as an *engineering tool* to empirically estimate equivalent tempering conditions.

The diffusion of carbon and iron atoms are two of the physical phenomena generally associated with martensite tempering. Hollomon and Jaffe alluded to this fact in their first attempt to derive a time-temperature relationship. Originally, Hollomon and Jaffe attempted to relate hardness, H, to the extent of diffusion, H = f(t•exp(-Q/RT). However, they diverged from the typical diffusion equation when they found that the tempering data could not be explained using a constant activation energy. Their response, assuming that t•exp(-Q/RT) is constant for all tempering conditions, seems hard to justify, and has been shown not to fit the data especially well. Thus it is appropriate to consider other methods for representing time-temperature equivalence during tempering.

Alternative Time-Temperature Relationship

As an alternative to the empirical tempering parameter approach, the characteristic diffusion distance, shown in Equation 3, may provide another means for addressing the time-temperature equivalence in martensite tempering. This method is mechanistically satisfying based on fundamental diffusion concepts. Since tempering is controlled by diffusional processes, it seems reasonable that the characteristic diffusion distance should be a viable method to represent time-temperature equivalence. That is, for a given diffusion distance the degree of tempering may be fixed. The characteristic diffusion distance is approximated as:

$$x_c \approx \sqrt{2Dt} \tag{3}$$

where t is time and D is the diffusivity, given by the Arrhenius type equation:

$$D = D_o e^{-\frac{Q}{RT}} \tag{4}$$

D_o is the pre-exponential frequency factor, Q is the appropriate activation energy for diffusion, R is the universal gas constant, and T is absolute temperature. Equation 1 from the Hollomon and Jaffe formalism resembles the form of the equation for diffusion distance (i.e. Equation 3 combined with Equation 4) with the exception that here the activation energy is assumed to be constant instead of the extent of diffusion. A similar concept was employed by Orr et al. for creep data, where the activation energy was independent of stress and exhibited values similar to those for self-diffusion [9].

In order to apply the characteristic diffusion distance to tempering data, it is necessary to obtain values for the activation energy, Q, and the pre-exponential factor, D_o, in Equation 4. Extensive work has been performed since Hollomon and Jaffe's paper was published, characterizing these values more accurately. The classic literature has divided martensite tempering into three stages [10,11,12,13,14]. Stage I, the formation of transition carbides, has been shown to be dependent on the diffusion of carbon through martensite with an activation energy of about 67 kJ/mol (16 kcal/mol) [10]. Stage II, the decomposition of retained austenite, has been shown to have an activation energy similar to that for the diffusion of carbon in austenite [12,15], with an activation energy of about 134 kJ/mol (32 kcal/mol) and a pre-exponential factor of about 0.15 cm^2/sec for a carbon concentration of 0.1 wt% [16,17]. Stage III, the formation of ferrite and cementite from martensite and transition carbides, requires iron atom displacements and carbon diffusion [14]. Therefore the activation energy for Stage III is similar to that of iron self-diffusion in ferrite, 252 kJ/mol (60.3 kcal/mol) with a pre-exponential factor of 5.4 cm^2/sec [18]. At temperatures above Stage III, recovery, recrystallization and grain growth processes take place [19], which also require the diffusion of iron and carbon atoms, and therefore may also be limited by the self-diffusion of iron in ferrite. As reported by Speich, the temperature ranges for the stages overlap and depend on the tempering times used, but the approximate ranges are 100 to 250 °C, 200 to 300 °C, and 250 to 700 °C (presumably for a one hour tempering time) for Stages I, II, and III respectively. Recovery, recrystallization, and grain growth may occur at temperatures above 400 °C [19]. It is worth noting, that the variation and magnitudes of the activation energies for each of the stages correspond reasonably well with those determined from analysis of the Hollomon and Jaffe tempering data as shown in Figure 5.

Application to Experimental Data (Steel W: 0.89 wt% C)

Using the diffusion constants (D_o and Q) appropriate to each stage of tempering as discussed above, the diffusion distances for each time temperature combination given by Hollomon and Jaffe were calculated.[b] Then the tempered hardness of Steel W was plotted as a function of the diffusion distance, as shown in Figure 7. The particular stage for each time-temperature combination was estimated based on the hardness value. Grange et al. [21] plotted tempered hardness as a function of carbon content, for tempering treatments of one hour at various temperatures. Thus, the hardness range for each stage could be associated with the temperature ranges given by Speich [19]. To eliminate the overlap of the temperature ranges, the temperature ranges used for assigning the three stages were 100-200 °C, 200-300°C, and 300-700 °C, for Stage I, II, and III, respectively. Using this method, hardness values greater than 63 HRC were considered to be in Stage I; hardness values less than or equal to 52 HRC were considered to be in Stage III, and intermediate hardness values were considered to be in Stage II. These hardness limits are specific to the carbon concentration in this particular steel.

The curves fit to the data in Figure 7 indicate that within a given stage, the hardness was about the same for a given diffusion distance, for the different time-temperature histories employed.

[b] The study reporting the activation energy for carbon diffusion in martensite did not report a pre-exponential factor [10]. Thus, the pre-exponential factor and activation energy for carbon in ferrite were used in this work to represent the carbon diffusion in martensite. Those values are 0.02 cm^2/sec and 84.1 kJ/mol (20.1 kcal/mol), respectively [20].

Thus, it appears that diffusional concepts are able to represent time-temperature equivalence, if knowledge of the appropriate mechanism is available. Such knowledge was less available when the tempering parameter concept was first introduced. The smallest diffusion distances occur in Stage III. The magnitude of the shortest diffusion distance in Stage III is on the order of one lattice spacing of ferrite, 0.287 nm [22]. This value is satisfying based on mechanistic considerations, indicating the onset of Stage III, where the iron atoms make a few atomic jumps. The longer diffusion distances at lower hardness values in Stage III may presumably involve recovery, recrystallization and grain growth, and may explain the diffusion distances on the order of a micron. The carbon diffusion distances observed in Stage I and II are in the range of nanometers to about 1 micron, and are perhaps reasonably consistent with transition carbide formation and austenite decomposition mechanisms. It should be noted that Stage II follows Stage I because carbon mobility is greater in martensite than in austenite.

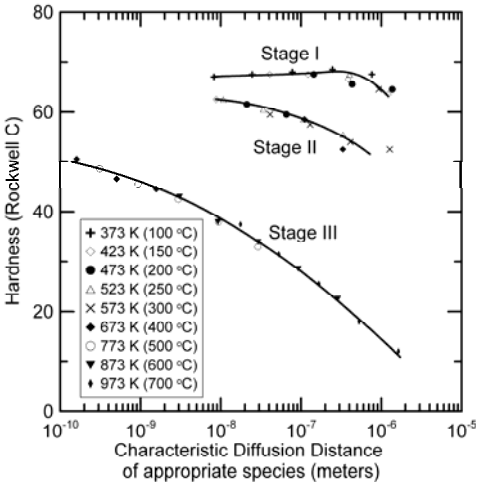

Figure 7. Hardness vs. characteristic diffusion distance for Hollomon and Jaffe's Steel W.

Iso-Tempering Conditions

Iso-tempering curves (or iso-diffusion distance curves) based on the equivalent diffusion distance for the appropriate mechanism during each stage are shown in Figure 8. The boundaries for any given stage were defined by the maximum and minimum diffusion distances of the appropriate species for tempering time of one hour at the maximum and minimum temperatures employed to create Figure 7. For simplicity, the stages were assumed not to overlap at one hour tempering time, although it is recognized that the literature reports overlap between the applicable temperature ranges for each stage [19]. When calculated in this manner, the iso-tempering curves for the three different stages overlap at times other than one hour. Thus, the mechanisms associated with each stage may occur simultaneously or even out of the normal sequence, especially for short tempering times at higher temperatures. For instance, based on the particular conditions involved, it may be possible for Stage II to be completely finished prior to the end of Stage I. These changes in the relative kinetics of the different tempering reactions with time/temperature may not be fully appreciated in the existing literature.

The iso-tempering curves for the time-temperature combinations that may yield purely one stage or another (see Figure 8) are compared to the iso-tempering curves predicted by the tempering parameter in Figure 9. The same curves plotted in Figure 8 also appear in Figure 9 along with additional iso-tempering curves, shown for increased resolution. As seen in the Figure, the tempering parameter predicts iso-tempering curves that have slopes similar to those predicted using the diffusion distances for Stage III. However, the tempering parameter varies significantly from the iso-tempering curves for Stage I as evidenced by the non-parallel curves. Consequently, the tempering parameter may be less effective in characterizing Stage I behavior, although further work would be helpful to better characterize the behavior in this regime.

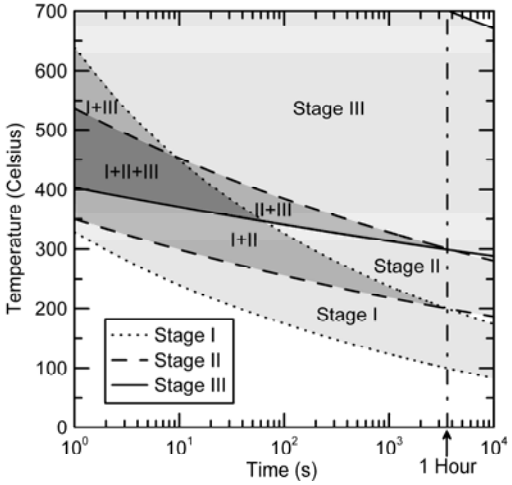

Figure 8. Iso-tempering curves for the three stages of tempering based on equivalent diffusion distances of appropriate species. Darker shading represents regions where combinations of mechanisms associated with Stages I, II, III may be active.

Summary

The derivation of Hollomon and Jaffe's tempering parameter requires a constant value of t_o and therefore c-value; although a constant value of t_o is not consistent with fundamental diffusion mechanisms where the extent of diffusion increases with increasing time for a given activation energy. The experimental data used by Hollomon and Jaffe in the original tempering parameter paper were found to show significant variations in the value of c and thus t_o. Thus, it appears that the tempering parameter concept may suffer fundamental limitations, although it has served as a viable method to estimate empirically the time-temperature equivalence in martensite tempering.

The characteristic diffusion distance was shown to offer an alternative time-temperature relationship, with a mechanistic basis, and a good fit to the data. Within a given stage, the hardness was approximately constant for a given diffusion distance. Finally, iso-tempering curves were presented for each of the three stages of tempering and were compared to the iso-tempering curves predicted by Hollomon and Jaffe.

Acknowledgements

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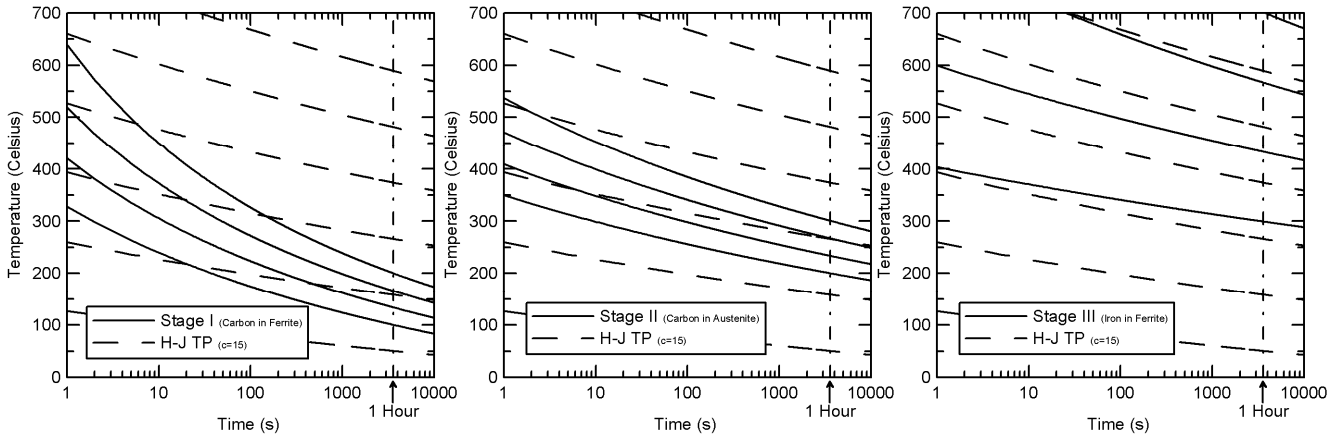

Figure 9. Iso-tempering curves for the three stages of tempering based on equivalent diffusion distances of appropriate species compared with the iso-tempering curves predicted by the Hollomon-Jaffe tempering parameter for c=15.

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