Determination of Martensite Start Temperature in Engineering Steels

Part I. Empirical Relations Describing the Effect of Steel Chemistry

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The dependency of the martensite start (M_s) temperature upon composition of engineering steels has been examined by analyzing the results predicted by an artificial neural network (ANN) model and thermodynamic data. Two new formulas, the simple linear and binary interaction ones, have been statistically derived and applied to predict the M_s temperature in an Fe–C–Si–Mn–Cr–Mo system. It is shown that the separation of the influence of interactions from that of individual alloying elements is successful since most of the statistical results are reasonable and thus have been physically interpreted. The thermodynamic calculations show that the alloying elements have similar influence upon the M_s and A_3 temperatures. The apparent effect of carbon depends largely on C–X interactions. C–Mn and C–Mo interactions weaken the effect of carbon while that of C–Si interaction intensifies the role of C. This is supported by phenomenological results and has been physically interpreted. The interactions between substitutional alloying elements have also significant influence upon the M_s temperature. The Si–Mn interaction strongly increases the M_s , while Si–Mo interaction significantly decreases the M_s . So far, there is no proper physical explanation for this though supportive evidence has been obtained from phenomenological results. Mn and Mo have the weakest apparent interaction, that is, their influence can be simply added up. Moreover, a semi-physical model has been built to predict the M_s temperature from a critical temperature, which can be calculated thermodynamically. It shows that the semi-physical method gives a satisfactory prediction of M_s with a standard error of 15.3°C. Evaluation of nine common empirical methods indicates that the Kung and Rayment (KR) formula gives the best predicting results amongst them.

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1. Introduction

The martensite start temperature, M_s , is of vital importance for engineering steels. Hence, great efforts have been made in predicting the M_s 's of steels. Obviously, chemical composition of a steel is a main factor in affecting its M_s ^{1–9} although the microstructure, (dislocation, vacancies, grain, twin, inter-phase boundaries, and precipitates), external stress and plastic deformation, may sometimes play an important role, too. The composition dependence of M_s has been intensively examined and statistically expressed in terms of regressive equations for both low^{1–9} and high alloy^{10,11} steels. However, most of the empirical regressions⁴ employ a set of linear dependencies,¹ ignoring interaction effects.^{3–6,8,9} It has been recognized that the effect of an element on the M_s is not necessarily linear^{12,13} over a very wide range of composition. In this article, the influence of single alloying elements as well as their interactions will be statistically examined. The relation between the M_s and the critical driving force in this alloy system will be discussed in the accompanied article.¹⁴

2. Test Alloys and Methods

It is well known that a large number of experimental data are required for any systematic analysis of M_s data. For the Fe–C–Si–Mn–Cr–Mo system considered in this article, which serves as a model system for a major set of engineering steels, if compositional variation steps of all alloying elements are set to 4, in total 1024 experimental alloys would be required to build a full mechanism of test data. In fact, preparing experimental alloys for this purpose is practically impossible.

Rather than creating a set of special alloys, an artificial neural network (ANN) model¹⁵ for predicting M_s over the composition range of interest was used. This ANN model was trained on a large data set of 157 alloys in the approximate domain of interest. The original ANN model offers the advantage of reproducing complete composition dependencies on higher order interactions without making a priori assumption during fitting of the model to the data.

Using this ANN model, the compositional dependency of M_s in a class of Fe–C–Si–Mn–Cr–Mo steels has been tested with the composition range of 0.2–0.5C, 0.5–2.0Si, 0.5–2.0Mn, 0.5–2.0Cr, and 0.1–0.7Mo (mass%). The systematic variation step in C concentration is 0.1 mass%, that of Si, Mn, and Cr is 0.5 mass%, and that of Mo is 0.2 mass%. The M_s 's of these test alloys were first predicted by an artificial neural network (ANN) model. The validity of the ANN model is important for this study. The method, the principal results, and accuracy of this ANN model have been described in detail in our previous publications.^{15,16} The standard deviation of the predicted M_s is around 12°C. Note that, in this research, we have confined the composition of the test alloys in the maximum composition frequency region of the original database. Thus, the standard error of the predictions given by ANN may be well less than 12°C.

The thermodynamic calculation was performed with a commercial thermodynamic software package, MTDATA.¹⁷

3. Statistical Analysis

3.1 Existing empirical relations

It is well known that M_s of an iron alloy can be estimated by statistical formulas in the general linear form of

$$Ms = k_0 + \sum k_i w_i \quad (1)$$

k_0 is the offset parameter, i s indicate the alloying elements, w_i s stand for the concentration (mass%) of elements i s, and k_i s are their corresponding linear coefficients. The offset parameters regressed by different researchers^{1,3-9} are different, but scatter around 500 to 560°C, as shown in Table 1. Note that Carapella²⁾ used a product formula and Andrews¹⁾ used both linear and non-linear regressive methods. By taking the values of coefficients in different equations, the offset parameters can be adapted by calculating the deviations of the offset parameters, which are defined as

$$\Delta \bar{k} = \frac{\sum_{i=1}^n (k_0^i - k_0)}{n},$$

indicating the overall systematic shift of the correspondent prediction. n is the number of alloys studied, k_0^i and k_0 are the offset parameter adapted for alloy i and that set by different researchers. The deviation has been calculated and given in Table 1. It is clear that Kung and Rayment's⁴⁾ formula gives the best prediction. Table 1 also lists the standard deviation of the Ms s predicted by different methods, $\sigma_1(Ms)$. With the consideration of the error introduced by the ANN model, 12°C, the total error is written in the form, $\sigma_2(Ms) = \sqrt{(\sigma_1(Ms))^2 + 12^2}$. From the standard deviations of Ms 's predicted by different formulas from those given by the ANN model, we see again that Kung and Rayment (KR)⁴⁾ equation, which was actually derived by Steven and Haynes,⁹⁾ and improved first by Andrews,¹⁾ still has the minimum error. In their later work, Kung and Rayment¹⁸⁾ made the similar comparison between the predictions by different empirical formulae, and concluded that Andrews and Steven-Haynes linear equations gave the best fit. However, the results shown in Table 1 suggest that Nehrenberg's equation gives better fit.

For comparison, the Ms temperatures calculated by both the KR method and ANN model are plotted in Fig. 1(a). If

they had the same accuracy, all data points would lie along the diagonal centerline $Ms^{KR} = Ms^{ANN}$. However, from Fig. 1(a), we see that it is better to represent the correlation of the two sets of predicted Ms temperatures in terms of the dark solid line, which has a regressive equation

$$Ms^{KR} = 0.849 \cdot Ms^{ANN} + 54, \quad ^\circ\text{C}. \quad (2)$$

The non-unity coefficient of 0.849 implies a deviation over the temperature range of interest. That the coefficient is less than unity indicates the KR method overestimates the Ms at low temperatures, but underestimates the Ms at high temperatures. By drawing two maximum error lines (the pair of gray dashed lines in Fig. 1(a)) of

$$[Ms^{KR}]_{\text{upper/lower}} = [Ms^{KR}] \pm 25, \quad ^\circ\text{C} \quad (3)$$

where $\pm 25^\circ\text{C}$ is the reported error range of KR equation,¹⁹⁾ we find 92.3% of the points are located within the pair of parallel lines. This means that two models give a consistent prediction of the Ms s. As a matter of fact, the standard error of this regression is around 16.5°C (indicated by a pair of dotted lines in Fig. 1(a)). Taking the standard error of the ANN model, the standard error of the K-R method is 20.4°C when applied to the current test alloys.

Employing a similar linear dependence of the Ms upon the chemical composition as in the K-R model, the ANN predicted results are represented more accurately by the linear equation obtained by linear regression analysis

$$Ms = 545 - 470.4w_C - 3.96w_{Si} - 37.7w_{Mn} - 21.5w_{Cr} + 38.9w_{Mo}, \quad ^\circ\text{C}. \quad (4)$$

Note that the influence of neither Ni nor Co has been considered. The Ms temperatures calculated from eq. (4) are plotted versus those predicted by the ANN model in Fig. 1(b). As was expected, eq. (4) gives a better prediction than the original K-R parameters.

Table 1 Parameters of empirical methods for predicting the Ms temperature.

Methods	Equation types	$k_0/^\circ\text{C}$	$\Delta \bar{k}/^\circ\text{C}$	$\sigma_1/^\circ\text{C}$	$\sigma_2/^\circ\text{C}$
Steven-Haynes ⁹⁾		561	11.7	37.4	39.3
Grange-Stewart ³⁾		538	-5.1	27.8	30.3
Payson-Savage ⁶⁾		499	-15.9	33.8	35.9
Nehrenberg ⁵⁾		499	-5.0	22.4	25.4
Rowland-Lyle ⁸⁾		499	-21.7	38.9	40.7
Andrews ¹⁾		539	13.1	26.1	28.7
Kung-Rayment ⁴⁾		539	2.9	16.5	20.4
Current linear		545	0.0	8.1	14.5
Carapella ²⁾	$Ms = k_0 \prod_i (1 - k_i w_i)$	496	-14.6	34.0	36.0
Andrews ¹⁾	$Ms = k_0 + \sum_i k_i w_i + \sum_{i,j} k_{ij} w_i w_j$	512	12.2	28.7	31.1
Interaction model	$Ms = k_0 + \sum_i k_i w_i + \sum_{i \neq j} k_{ij} w_i^{0.5} w_j^{0.5}$	540	0.0	4.2	12.7
Semi-physical	$Ms = A + B \cdot T_0$	640	0.0	15.3	19.4

Fig. 1 M_s temperatures predicted by different models. (a) Kung and Rayment's¹⁾ prediction versus ANN prediction. (b) New linear equation's prediction, showing clearly the improvement of linearity over K-R method.

3.2 A new empirical model taking into effects of binary interactions

Note that no interaction has been incorporated in eq. (4), or more accurately, all interactions have more or less been attributed to various single alloying elements. It is worthwhile to statistically separate the role of interactions from that of single alloying elements. By adding interaction terms into eq. (4) for C–Si, C–Mn, C–Cr, C–Mo, Si–Mn, Si–Cr, Si–Mo, Mn–Cr, Mn–Mo, and Cr–Mo, a more accurate regressive equation has been obtained

$$\begin{aligned}
 M_s^{BR} = & 540 - 584.9w_C - 23.1w_{Si} - 117.7w_{Mn} - 42.5w_{Cr} \\
 & + 49.9w_{Mo} - 62.5w_{C-Si} + 178.3w_{C-Mn} \\
 & - 10.0w_{C-Cr} + 52.5w_{C-Mo} + 117.2w_{Si-Mn} \\
 & + 50.9w_{Si-Cr} - 142.2w_{Si-Mo} - 29.2w_{Mn-Cr} \\
 & - 9.7w_{Mn-Mo} + 69.9w_{Cr-Mo}, \quad ^\circ\text{C}
 \end{aligned} \quad (5)$$

w_i s have the same meaning as those given in eq. (1). The nominal concentration of binary terms are defined as the square root of the products of two chemical compositions

$$w_{i-j} = \sqrt{w_i \cdot w_j}. \quad (6)$$

Thus, the general form of eq. (5) for binary interactions is

$$M_s = k_0 + \sum_{i,j} k_{ij} \sqrt{w_i w_j}. \quad (7)$$

Following this method, the interactions amongst more than two elements can be easily taken into consideration. Furthermore, the choice of square or n th root is helpful when the concentrations of various alloying elements are of different order. Note that eq. (7) has the different form from Andrews¹⁾ product equation. eq. (7) uses the product of square root of the concentrations instead of the direct product, and only considers the interactions while Andrews' equation also includes the C–C interaction term. In addition, Andrews' product formula only considered the C–C, C–Mn, C–Cr interactions. Using eq. (5), the standard error in M_s prediction is as low as 4.2°C. Incorporated with that introduced by the ANN model, the overall standard error due to eq. (5) amounts up to 12.7°C. Apparently, the introduction of binary interaction terms improves the prediction accuracy; but more importantly, this analysis proves helpful for the physical understanding of the influence of alloying elements on M_s , as will be discussed in the coming sections.

3.3 Semi-physical determination of M_s from T_0

T_0 is defined as the temperature at which the ferrite and austenite phases with the same composition have an equal Gibbs free energy. It describes the critical temperature for athermal decomposition of austenite, and thus the corresponding critical chemical driving force, ΔG_{Ch}^* , at this temperature equals zero. For the martensitic transformation, further cooling is required to obtain enough chemical driving force to overcome the resistance barrier, *i.e.*, elastic (transformation) strain energy, frictional work required by the glissile interface, additional interfacial energy, *etc.* If an intrinsic correlation between ΔG_{Ch}^* and M_s exists, T_0 is expected to be properly related to M_s , too. The T_0 temperature of a given steel can be estimated directly by thermodynamic methods. In this study, MTDData was used to calculate the Gibbs free energies of both austenite and ferrite at different temperature and to determine the T_0 temperatures. It should be pointed out the Zener ordering energy has been neglected.²⁰⁾ Figure 2 shows the correlation between T_0 and M_s . The relation can be statistically represented by equation

$$T_0 = 0.845M_s + 367, \quad ^\circ\text{C}. \quad (8)$$

The standard error of this method is 15.3°C and the total error amounts up to 19.4°C. Note that unlike any empirical methods, the critical temperature is “physically” determined by a thermodynamic program. In case where T_0 can be obtained, the M_s temperature may be easily calculated from eq. (8). Compared to the standard error introduced by the KR method (20.4°C), a simple linear equation (14.5°C) and a binary interaction model (12.7°C), the semi-physical method is very attractive. Moreover, eq. (8) is based on the assumption that

Fig. 2 Prediction of M_s from critical temperature (T_0): Critical temperature is thermodynamically calculated by setting chemical driving force as zero; the linearity is very clear over all the studied M_s temperature range.

the M_s only depends on the T_0 . It is apparent that if a separate effect of steel chemistry can be properly incorporated into this equation, the accuracy of the prediction is expected to be improved. Efforts to correlate the M_s temperature with the degree of undercooling, $\Delta T = T_0 - M_s$, gave no clear relation so far.

4. Discussion

4.1 M_s temperature of pure iron

The reproducibility of the offset value, k_0 , irrespective of the regressive methods involved, is shown in Table 1, where regressions have been made over various sources experimental data. For the more realistic models, the K-R model, the linear model, the interaction model and A_3 model (to be discussed), the offset parameter is not sensitive to the steel chemistry. It is reasonable to relate this constant to the M_s temperature of pure iron. In fact, there is considerable doubt concerning the M_s temperature of pure iron. The previously published values include 500°C,^{21,22)} 520°C,²¹⁾ 545°C,²³⁾ 550°C,²⁴⁾ 560°C,¹⁰⁾ 680°C,²⁵⁾ 700°C,²⁶⁾ 740°C,²⁷⁾ and 750°C.²⁸⁾ These values are based on the extrapolation of the M_s in either the substitutional binary Fe-X alloys, or interstitial Fe-C or Fe-N alloys. Nevertheless, Table 1 strongly indicates that the M_s of "pure" iron is around 540°C. Consequently, the so-called "pure" iron is not of chemical purity because the concentrations of inclusions, or trace elements are neglected and not reported in most of the published CCT diagrams, which are the basis of the statistical equations.

4.2 Influence of carbon on the M_s temperature

Figure 3(a) shows how an individual element affects the M_s temperature. Undoubtedly, carbon plays the strongest role in decreasing the M_s . Compared to its effect on A_3 , the influence of carbon upon the M_s is significant, especially in eq. (5), in which effects of apparent interactions have been statistically excluded. It is worthwhile to discuss if this ten-

Fig. 3 Effect of alloying elements on M_s temperatures. (a) Effect coefficients of unary single alloying elements (for more details regarding factors for A_3 temperatures, see Fig. 5). (b) Phenomenological influence of C in two series of alloys predicted by ANN; Fe-xC-0.5Si-0.5Mn-0.5Cr-0.1Mo (Base A) and Fe-xC-0.5Si-1.0Mn-1.0Cr-0.5Mo (Base B). The non-linear dependence of M_s on C mass% is clear according to the ANN predictions.

dency is correct. The scale factor for carbon has been reported²⁹⁾ to amount up to 788°C/mass%C in the carbon variation range of 0.02 to 0.16 mass% in 12 mass%Cr steel grades. Eichelmann and Hull¹⁰⁾ even set a factor for carbon that is twice this value for an 18-8 stainless steel. These results imply that at very low carbon concentration, where the C-X interactions are very weak, the carbon-influencing factor tends to increase. In other words, if the influence of the interactions is excluded, the effect of C in decreasing the M_s is expected to be more significant. This is consistent with results shown in Fig. 3(a).

The phenomenological influence of carbon upon the M_s temperature is shown in Fig. 3(b) according to the ANN model. In the case of base A (Fe-C-0.5Si-0.5Mn-0.5Cr-0.1Mo) system, the decrease rate of M_s temperature reduces when the C concentration in the alloy increases, which is implied by the decrease in the slope of the M_s -C (mass%) line

(shown by solid circles) in Fig. 3(b). If compared with the two lines corresponding to bases A and B, it is shown in Fig. 3(b) that the decrease rate is again reduced by increasing the amount of other (substitutional) alloying elements. The two lines indicated by solid and open circles have fitting equations of $M_s = 534.3 - 512.2C$ [mass%], °C and $M_s = 497.3 - 444.4C$ [mass%], °C. That is, the rate of decrease reduces from about 512°C/mass%C to 444°C/mass%C, again supporting the statistical result discussed above.

4.3 Statistical interactions of C with substitutional alloying elements

A more likely explanation for the statistical and phenomenological effects mentioned in the previous section can be obtained by assuming that the influence of carbon is partially masked by interactions of C with some substitutional alloying elements. This is supported by the evidence shown in Fig. 4(a). The first group of columns in Fig. 4(a) shows the influence of C–X interactions predicted by eq. (5). The effect of C is moderated by C–Mn and C–Mo interactions, which, as shown in the above equation, tend to increase the M_s temperature. The C–Si interaction, however, enhances the role of carbon because of its negative coefficient. The C–Si and C–Mo interactions are comparable in strength but opposite in direction. The C–Cr interaction can be neglected. The overall apparent effect of C depends on the effect of all these factors. The factors of the interactions for other elements are also shown in Fig. 4(a).

The phenomenological influence of the binary C–X interactions can be visualized in Fig. 4(b). Four solid lines corresponding to four carbon levels represent the change of the Si-influencing factor. The four lines are nearly straight and parallel to each other, indicating that the C–Si interaction is very weak. If the vertical axis is chosen as the decrease in M_s temperature, as shown in Fig. 4(c), it is clear that the increase in Si will strengthen the role of C in decreasing the M_s temperature. The effect of the C–Cr interaction is also very weak but complicated in nature, as shown by the four dashed lines. Here the interaction is not independent of composition. Furthermore, the dotted lines in Fig. 4(b) show that the influence of Mn depends clearly on the C concentration. At the carbon level of 0.2 mass%, the role of Mn is significantly higher than at higher C concentration, where the influence of Mn decreases. With C content over 0.4 mass%, the effects of Mn and Cr are similar and weak.

It is possible to get a physical understanding of the above statistical and phenomenological results. According to their chemical properties, the alloying elements involved can be classified as strong carbide-formers (Mn and Mo), intermediate carbide former (Cr) and non-carbide former (Si). The above behavior of interactions may be attributed to the influence of alloying elements on the activity of carbon in the solid solution. Keeping this in mind, we can expect that interactions between carbon and carbide-forming elements, e.g., that between Mn and Mo, tend to weaken the role of carbon, and give rise to an increase in M_s ; the interaction of carbon with non-carbide forming elements, such as Si, may enhance the role of C, and lead to a further decrease in M_s . This is in full consistence with the statistical and phenomenological results

Fig. 4 Effects of binary interactions on M_s temperatures. (a) Effect factors for binary interactions: corresponding unary factors are given in Fig. 3(a). (b) Phenomenological influence of binary C–X interactions predicted by ANN; Base alloy: Fe–x C–(0.5 or y) Si–(0.5 or y) Mn–(0.5 or y) Cr–0.1 Mo. (c) The influence of C–Si interaction on the decrease of M_s temperature.

shown in Figs. 4(a) and (b). An exception is Cr, an intermediate carbide-forming element, as the interaction strength of C and Cr appears constant and weak. For future studies, it is then interesting and worthwhile to check if these rules hold for the interactions of carbon with other alloying elements, such as Al, V, and Ni.

4.4 Influence of single substitutional alloying elements

Now, let us discuss the influence of single substitutional alloying elements upon the M_s temperature. Figure 3(a) indicates that Mn plays an important role in decreasing M_s temperature. Cr and Si also decrease the M_s temperature. The predictions of the effect of Mo are ambiguous. To gain the understanding of this effect, the influence of alloying elements on the A_3 temperature in pure binary systems of Fe–X has also been considered. Figure 5(a) gives the influence of alloying elements on the A_3 temperature in the pure Fe–X binary systems within the relevant composition range. The equilibrium temperatures for the binary test alloys were determined by the thermodynamic program MTDData. Apparently, Mo and Si are ferrite stabilizers while C and Mn are austenite forming elements. Regarding Cr, its behavior again appears complicated. Figure 5(a) shows that it is a weak austenite stabilizer though it has been reported to be a ferrite stabilizer.³⁰⁾ This ambiguity is an explanation for the phenomenological results shown in Fig. 4(b). The offset values of all these linear equations are 909.35°C, A_3 , which is the equilibrium temperature of austenite and ferrite of pure iron according to MTDData. The unary linear coefficients represent the influence of single alloying elements upon A_3 . As shown in Fig. 4(a), the unary coefficients of C, Mn and Cr are negative. Comparison between coefficients for martensite and proeutectoid ferrite transformations indicates that alloying elements have a similar effect on both M_s and ferrite formation. Notice the difference of the predictions regarding the role of Mo. Following K-R's equation, Mo is expected to decrease M_s temperature while, in eqs. (4) and (5), it appears to increase M_s temperature. In accordance with the result of the thermodynamic model predicting the influence of alloying elements upon A_3 , as shown in Fig. 5(a), as well as in Fig. 5(b), which is part of the binary Fe–Mo system, that Mo slightly increases the A_3 temperature, a positive coefficient for Mo is seemingly understandable. Figure 5(c) shows the influence of Mo on the driving force of athermal decomposition of austenite to martensite calculated by the thermodynamic model based on the SGTE database. It is clear that Mo increases the transformation driving force, and thus increases the M_s temperature if the increase in driving force is large enough to balance the solid solution strengthening of the austenite matrix.³¹⁾ With respect to the role of silicon, all statistical methods give a prediction of negative coefficient for Si. This is contradicted with the theoretical expectation based on the similar influence of alloying elements upon the A_3 temperatures. Similar to Mo, Si, as a ferrite stabilizer, is bound to increase the chemical driving force for martensite reaction. In fact, eq. (4) implies a weak influence of Si. Considering all the predictions in Fig. 3(a), we know that eq. (4) gives an adequate prediction for almost all alloying elements though the binary interactions have been neglected.

Fig. 5 Thermodynamic analysis of the influence of alloying elements. (a) Influence of alloying elements on A_3 temperature in pure binary Fe–X systems predicted by MTDData: The linearity holds only for Fe–Si, Fe–Mo, Fe–Cr, and Fe–Mn. Average slope for the Fe–C system is 304°C per C mass%. (b) Part of binary Fe–Mo phase diagram showing that Mo is a ferrite stabilizing element. (c) Increase in chemical driving force for the athermal decomposition of austenite with the increase of Mo concentration.

4.5 Apparent interactions between substitutional alloying elements

It is also interesting to investigate the influence of various interactions between substitutional alloying elements, which have apparently been successfully incorporated into eq. (5). The second group of columns in Fig. 4(a) summarizes the role of interactions of Si with other elements. The strongest interactions occur between Si-Mn and Si-Mo. From Fig. 4(a), we also know that Si-Cr and Cr-Mo interactions are significant while those of Mn-Cr and Mn-Mo are very weak. There is no proper physical explanation for the surprisingly strong interactions of Si-Mn, and Si-Mo, yet. However, supportive evidence has been obtained from a phenomenological analysis. Figure 6 shows the overall influence of Si and Mn upon the M_s temperature. Apparently, the effects of Si and Mn can be by no means added up linearly. Another interesting result is the negligible interaction between the two strong carbide-forming elements, Mn and Mo. Actually, this means that the roles of Mn and Mo may be linearly added up.

With the help of eq. (5), we may reconsider the overall apparent influence of single alloying elements on the M_s temperature. C decreases the M_s temperature and has strong interactions with substitutional atoms. Its role may be enhanced by Si, but weakened by Mn and Mo. Si has such a weak influence that it may be overturned by the strong binary interaction of Si-Mn, and strengthened by that of Si-Mo. Thus, the overall effect of Si depends ultimately on the concentrations of other alloying elements. Similar to C, Mn decreases M_s . Its influence will be partially masked by the interactions of C-Mn and Si-Mn. Cr has moderate interactions with all other elements. As a weak ferrite stabilizer, Mo would increase M_s temperature. However, the strong interaction of Si and Mo could change the sign of the role of Mo.

It is clear that the statistical analysis is accurate enough for the determination of the M_s temperature in the Fe-C-Mn-Si-Cr-Mo system. However, in addition to chemical composition, M_s of a steel is also sensitive to the processing and

microstructure. For example, sub-critical austenitization, external stress, and abnormal grain size have significant influence on the M_s temperature. These factors can only be fully taken into consideration by a physical model, which will be discussed in the accompanying paper.¹⁴⁾

5. Conclusions

(1) Nine empirical methods for predicting the M_s temperature of engineering steels have been evaluated using the predictions of a large validated ANN model. It is concluded that the Kung and Rayment method gives the best results. Two new statistical formulas and a semi-physical model have been derived for predicting the M_s temperature in the Fe-C-Si-Mn-Cr-Mo system. The former is based on the full dependency of the M_s temperature upon the steel chemistry while the latter is to correlate the M_s with critical temperature, T_0 . Both give satisfactory predicting results.

(2) The M_s temperature of engineering pure iron is estimated as 540°C. C, Mn, Mo, Cr and Si decrease the M_s while Mo increases the M_s . The analysis indicates that most alloying elements have similar effects upon the M_s and A_3 temperatures.

(3) The influence degree of carbon depends on the C-X interactions. C-Mn, and C-Mo interactions weaken the effect of carbon while the C-Si intensifies the role of C. This is supported by the phenomenological results and has been physically interpreted.

(4) The interactions between substitutional alloying elements can play an important role in changing the M_s temperature. The Si-Mn interaction strongly increases the M_s , while Si-Mo interaction significantly decreases the M_s . So far, there is no proper physical explanation for this though supportive evidence has been obtained from phenomenological result. Mn and Mo have the weakest interaction. Si and Mo themselves have weak influence but their overall effect depends further on the concentration of other alloying elements because of the strong interactions found with other alloying elements.

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Fig. 6 Phenomenological influence of the Si-Mn interaction predicted by ANN. Base alloy: Fe-0.4C-xSi-yMn-1.0Cr-0.5Mo.

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