Arch. Metall. Mater. **66** (2021), 1, 107-111

DOI: 10.24425/amm.2021.134765

SEOK-JAE LEE[1], MINSU JUNG[2*]

PREDICTION OF MARTENSITE START TEMPERATURES OF HIGHLY ALLOYED STEELS

We propose an empirical equation to predict the martensite start temperatures of highly alloyed steels containing more than 3 wt.% of Ni or Cr or 2 wt.% of Mo, W, or Co. The martensite start temperature calculated by the proposed equation was in good agreement with experimental data owing to not only the derivation from experimental data of alloy steels with a wide range of chemical compositions but also the interaction term between carbon and carbide-forming alloying elements.

Keywords: martensite start temperature, empirical equation, highly alloyed steel

1. Introduction

The formation of martensite is necessary to achieve high strength of steels. The martensite transformation begins at the martensite start (M_S) temperature during a continuous cooling by austenite decomposition [1]. Many studies on martensite nucleation at M_S temperature and martensite transformation kinetics below M_S temperature have been reported over the past several decades. Particularly, simple equations to predict M_S temperature were proposed based on experimental data. Most equations were derived in a simple linear form as a function of the chemical composition [2-13]. These equations have different coefficients for alloying elements depending on the experimental data used to derive an individual equation. In addition, the influence of the grain size of prior austenite on M_S temperature has been considered [14,15]. The austenite stability increases with the decrease in the grain size of the prior austenite, leading to a decrease in M_S temperature. However, regardless of the consideration of the austenite grain size effect, the equations used to predict M_S temperature were based mainly on experimental M_S temperature data of low-alloy steels.

Recently, Park et al. [16] reported an equation to predict M_S temperature of cast iron alloys containing carbon contents higher than 2 wt.%. According to the Fe-C phase diagram, the maximum carbon solubility in austenite is approximately 2 wt.% at 1147°C. Cementite (Fe_3C) and some carbide phases are precipitated in austenite in cast iron alloys as the carbon content is higher than its solubility at a given temperature in the austenite region. The solute carbon content in austenite varies depending on the formation of carbide precipitates, which affects M_S temperature. Similarly, a few equations were proposed to predict M_S temperature for stainless steels, typically with Cr and Ni contents higher than those of low-alloy steels [17]. These equations were derived using M_S temperature data of stainless steels consisting of relatively high Cr and Ni contents with limited concentrations of carbon and nitrogen.

However, no equation to predict M_S temperature of highly alloyed steels, different from low-alloy steels, cast iron alloys, and stainless steels, has been reported. In this study, we propose an empirical equation to predict M_S temperature of highly alloyed steels as a function of chemical composition using selected M_S temperature data, different from the experimental data used for the derivation of previous equations. Few information about grain size of prior austenite or austenitizing condition in the experimental data used in the present work, thus no grain size effect of prior austenite was considered in the proposed empirical equation.

2. Experimental data from the literature

The M_S temperature data of highly alloyed steels were obtained from the atlas of time-temperature transformation (TTT) diagrams [18]. The selected M_S temperature data satisfied at least

[1] JEONBUK NATIONAL UNIVERSITY, DIVISION OF ADVANCED MATERIALS ENGINEERING, RESEARCH CENTER FOR ADVANCED MATERIALS DEVELOPMENT, JEONJU, REPUBLIC OF KOREA
[2] KOREA INSTITUTE OF INDUSTRIAL TECHNOLOGY, INTELLIGENT MANUFACTURING R&D DEPARTMENT, SIHEUNG, REPUBLIC OF KOREA
* Corresponding author: mjung@kitech.re.kr

one of the following composition conditions: (1) Ni > 3 wt.%, (2) Cr > 3 wt.%, (3) Mo > 2 wt.%, (4) W > 2 wt.%, (5) Co > 2 wt.%. A total of 203 M_S temperature values were used to derive the new equation in this study. The ranges of chemical composition and M_S temperature for the selected data are presented in Table 1. In general, the M_S temperature is experimentally measured using dilatometric analysis of steel samples. Several studies reported the numerical method to identify the M_S temperature point from dilatation curve obtained during continuous quenching [19,20]. A fast cooling is required to avoid the diffusional transformation above the M_S temperature. In real steel processes, the M_S temperature is affected not only composition or grain size but also the heat treating history of specimen before quenching. For example, Alvarado-Meza et al. [21] investigated the influence of cooling rate and high-temperature deformation on the variation of the M_S temperature in a low carbon stainless steel.

TABLE 1

Chemical composition and experimental M_S temperature data used in this study

□	Minimum	Maximum	Average	Standard deviation
C (wt.%)	0.04	1.26	0.40	0.29
Mn (wt.%)	0.00	1.29	0.40	0.19
Si (wt.%)	0.00	1.05	0.26	0.22
Ni (wt.%)	0.00	10.30	2.45	2.58
Cr (wt.%)	0.00	17.98	3.37	3.93
Mo (wt.%)	0.00	9.50	0.69	1.48
Cu (wt.%)	0.00	0.28	0.03	0.06
V (wt.%)	0.00	2.52	0.30	0.59
W (wt.%)	0.00	19.20	1.84	4.68
Co (wt.%)	0.00	9.66	0.41	1.58
M_S (°C)	35.0	458.0	290.9	89.2

3. Model derivation

Most equations reported previously for alloy steels have been expressed as a simple sum of the alloying element contents:

$$M_S = k_0 + \sum k_i X_i \quad (1)$$

where X_i is the content of the alloy element i (wt.%), k_i (°C/wt.%) is a weight constant of the alloy element i, and k_0 is a constant related to M_S temperature of pure iron. In this study, the new type of empirical equation considered the interaction terms:

$$M_S(^{\circ}\mathrm{C}) = k_0 + \sum k_i X_i + \sum k_{C-i} X_C X_i \quad (2)$$

These terms reflect the interactions between C and strong-carbide-forming elements such as Cr, Mo, V, and W. It is worth noting that no strong carbide precipitates exist at temperatures of the austenite region before the cooling owing to the relatively high contents of strong-carbide-forming elements in highly alloyed steels [22-24]. Owing to the formation of carbides, the exact chemical composition in the solute should be known to investigate the relationship between the composition and M_S temperature to derive an empirical equation. However, no extensive information on the carbide precipitation in austenite are reported in the atlas of TTT diagrams. Therefore, the interaction terms in Eq. (2) are considered practically. The values of k_0, k_i, and k_{C-i} optimized using the M_S temperature data are presented in Table 2. The type of Eq. (2) is similar to the product type equation proposed by Andrew [7] because the effect of carbon addition on the decrease of the M_S temperature is varied non-linearly. Eq. (2) can express a non-linear reduction of the M_S temperature as increasing the C content in the C range we used in Table 1 and is able to be adopted up to the C content of 1.538 wt.% C mathematically. Most of the k_i values in Eq. (2) are negative. This shows the fact that most alloying element lower M_S temperatures except cobalt [1]. In the proposed Eq. (2), the addition of Co shows a positive effect as typically reported. The positive value of k_W is due to the negative value of k_{C-W}, which can express the decrease of M_S temperature as increasing the W content like the C addition effect. A few researchers considered the Si effect since the Si variation might be restricted or its negligible effect on M_S temperatures in low alloy steels [2-13]. In the proposed Eq. (2) the addition of Si increases M_S temperatures. It is thought that Si could influence the formation of carbide precipitate in austenite. Pavlina et al. [25] reported that the increased Si content accelerated the formation of Nb-rich carbonitride precipitates in austenite. We suppose that the M_S temperature increases due to lowering the solute C content because more C atoms are consumed by forming carbides in austenite as increasing the Si level based on experimental data of highly alloyed steels used in this work. Importantly, the approach to derive an empirical equation is directly based on the experimental data, thus the optimized values could have a positive or negative sign. For example, the equation proposed by Capdevila et al. [11] shows positive values for the additions of Mo and W, while other equations show negative values for the same alloying elements.

TABLE 2

Optimized k parameters for Eq. (2)

k_0	523.73
k_C	–521.33
k_{Mn}	–23.18
k_{Si}	20.65
k_{Ni}	–11.93
k_{Cr}	–11.56
k_{Mo}	–7.49
k_{Cu}	–102.20
k_V	–21.80
k_W	8.47
k_{Co}	1.75
k_{C-C}	169.53
k_{C-Cr}	14.33
k_{C-Mo}	2.06
k_{C-V}	36.53
k_{C-W}	–13.69

4. Results and discussion

Figure 1 compares the M_S temperature values predicted by different equations with the measured M_S temperature data from highly alloyed steels. A significant difference between the predicted M_S temperature results and experimental data was observed when the previously reported equations were used. Figure 2 shows the results of a more detailed analysis. The corresponding coefficients of determination (R^2) are compared in Figure 2(a), which are typically used to determine the prediction accuracy. An R^2 value close to 1.0 implies that the prediction result almost matches with the experimental data. R^2 for the results obtained using the equation proposed in this study (Eq. (2)) is higher than those obtained by other equations. The equation proposed by Eicheman and Hull [17] (M14) leads to a higher R^2 than those of other equations reported in the literature, as the equation is derived using the M_S temperature data of stainless steel. The linear-type equation proposed by Andrew [7] (M06) also provides a good R^2 value, although only five alloying ele-

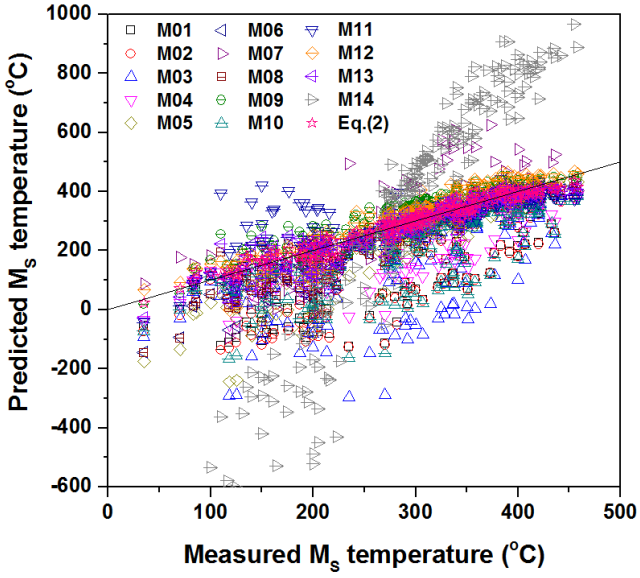

Fig. 1. Calculated M_S temperatures compared with the experimental data presented in Table 1

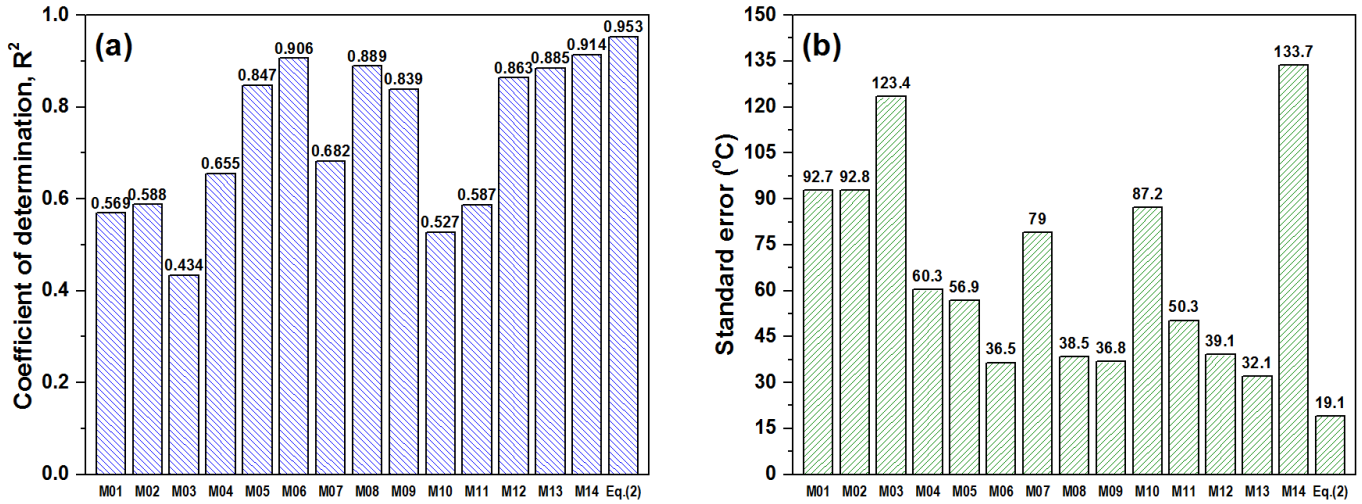

Fig. 2. Comparison of (a) R^2 and (b) standard error values obtained by the equations in Table 3 and proposed equation (Eq. (2)) with experimental data

TABLE 3

Empirical equations for predicting the M_S temperatures of steels

No.	Equation	Ref.
M01	M_S(°C) = (930 – 570C – 60Mn – 20Si – 30Ni – 50Cr – 20Mo – 20W – 32)/1.8	[2]
M02	M_S(°C) = (930 – 600C – 60Mn – 20Si – 30Ni – 50Cr – 20Mo – 20W – 32)/1.8	[3]
M03	M_S(°C) = (1000 – 650C – 70Mn – 35Ni – 70Cr – 50Mo – 32)/1.8	[4]
M04	M_S(°C) = (930 – 540C – 60Mn – 20Si – 30Ni – 40Cr – 20Mo – 32)/1.8	[5]
M05	M_S(°C) = 561 – 474C – 33Mn – 17Ni – 17Cr – 21Mo	[6]
M06	M_S(°C) = 539 – 423C – 30.4Mn – 17.7Ni – 12.1Cr – 7.5Mo	[7]
M07	M_S(°C) = 512 – 453C – 71.5CMn – 16.9Ni + 15Cr – 9.5Mo + 217C^2 – 67.6CCr	[7]
M08	M_S(°C) = 539 – 423C – 30.4Mn – 7.5Si – 17.7Ni – 12.1Cr – 7.5Mo + 10Co	[8]
M09	M_S(°C) = 545 – 330C – 23Mn – 7Si – 13Ni – 14Cr – 5Mo – 13Cu + 4V + 7Co	[9]
M10	M_S(°C) = 520 – 320C – 50Mn – 5Si – 20Ni – 30Cr – 20Mo – 5Cu	[10]
M11	M_S(°C) = 491.2 – 302.6C – 30.6Mn – 14.5Si – 16.6Ni – 8.9Cr + 2.4Mo + 7.4W – 11.3Cu + 8.6Co	[11]
M12	M_S(°C) = 565 – 600(1 – exp(–0.96C)) – 31Mn – 13Si – 8Ni – 10Cr – 12Mo	[12]
M13	M_S(°C) = 545 – 601.2(1 – exp(–0.868C)) – 34.4Mn – 13.7Si – 17.3Ni – 9.2Cr – 15.4Mo + 10.8V + 4.7Co – 16.3Cu	[13]
M14	M_S(°C) = (2381.3 – 3000C – 60Mn – 50Si – 110Ni – 75Cr – 32)/1.8	[17]

ments, C, Mn, Ni, Cr, and Mo are used from low alloy steels. The equation proposed by Grange and Stewart [4] (M03) considered the same five alloying elements, but its R^2 value is the lowest. In addition, the equations proposed by Ishida [9] (M09) and Capdevila et al. [11] (M11) lead to R^2 values lower than that of the equation obtained by Andrew [7] (M06) even though other alloying elements such as Si, Cu, Co, Ti, W, and V are additionally considered. Recently, Barbier [13] (M13) analyzed previously reported equations to predict M_S temperature using almost 1000 M_S temperature values for different compositions to derive the equation. He also employed the exponential carbon dependence on M_S temperature from the study by van Bohemen [12] (M12) to improve the prediction accuracy. The R^2 value obtained using the equation suggested by Barbier is higher.

Similar to R^2, the corresponding standard errors are compared in Figure 2(b). The equation proposed in this study leads to the smallest standard error, which implies that the new equation can most accurately predict M_S temperature of highly alloyed steels (Table 1). Surprisingly, the equation derived by Eicheman and Hull [17] (M14) leads to the worst standard error even though they also used the experimental M_S temperature data from stainless steels. This could be explained as the experimental M_S temperature data used by Eicheman and Hull consisted of a different alloy composition range from the data in Table 1. Among the equations reported in the literature, the equation by Barbier (M13) leads to a smaller standard error. Even though he used a large number of data points and considered many alloying elements to consider the previous equations, the maximum limits of Mo and V contents in Table 1 are significantly higher than those of the experimental data used by Barbier. In addition, the effect of W addition on M_S temperature was not considered in the study by Barbier.

The equations mentioned in this study are derived empirically. All of the equations have similar linear formulas (as for Eq. (1)); each term can be modified, e.g., exponential carbon dependence or interaction term. The most important factor in these types of empirical equation are the experimental data used for the derivation, which are not the same as those in the comparison, as shown in Figure 2. Therefore, a careful analysis should be performed to determine the prediction accuracy and reliability by comparing the equations derived with different source data. In the prediction of M_S temperature of alloy steels with a wide composition range, the equation proposed by Barbier may provide results with higher accuracy and reliability. For highly alloyed steels that satisfy at least one requirement: more than 3 wt.% of Ni or Cr, or 2 wt.% of Mo, W, or Co, the equation proposed in this study provides a better prediction result than those of other equations.

The highest R^2 and lowest standard error obtained by the new equation proposed in this study, as shown in Figure 2, are necessary due to the duplication of the M_S temperature data for the derivation and comparison. Therefore, a total of 13 M_S temperature values, which are not used to derive Eq. (2) and satisfied the requirement of alloying content for highly alloyed steels, are obtained from different studies [19,26-28] to verify Eq. (2). The highly alloyed steels used for the verification are mostly included in the chemical composition range in Table 1, except for two structures. One of them is Fe-0.05C-0.22Si-0.41Mn-13.2Ni-3Cr-0.35Mo [27] with an excess Ni content, while the other is the STD11 steel [28] with an excess C content of 1.5 wt.%. Detailed chemical compositions for 13 M_S temperature data are listed in Table 4. The linear-type equation proposed by Andrew [7] (M06) and equation proposed by Barbier [13] (M13), which provided better R^2 and standard error values, as shown in Figure 2, were used for the verification. Figure 3 compares the M_S temperature values predicted by the two previous equations and Eq. (2) with the experimental data of highly alloyed steels. The two equations proposed by Andrew and Barbier provide well-predicted M_S temperature values; however, underestimated values are obtained for high-C–high-Cr steels, such as the tool steel. This can be attributed to the different content ranges of C and Cr for the alloy steels used to derive

TABLE 4

Chemical composition and M_S temperature data for verification

C (wt.%)	Mn (wt.%)	Si (wt.%)	Ni (wt.%)	Cr (wt.%)	Mo (wt.%)	Cu (wt.%)	V (wt.%)	M_S (°C)	Ref.
0.1312	2.274	0	4.032	0	0	0	0	373	[19]
0.06	0.67	0.53	3.32	0	0	0.06	0	474	[26]
0.04	1.29	0.38	3.58	0	0.08	0.08	0	453	[26]
0.05	0.78	0.66	5.53	0	0.01	0.07	0	447	[26]
0.09	1.05	0.21	3.32	0	0.02	0.20	0	441	[26]
0.04	0.89	0.2	0.3	10	0.04	0	0	416	[27]
0.08	0.89	0.19	0.27	14.7	0.04	0	0	360	[27]
0.04	0.86	0.16	1.7	13	0.04	0	0	301	[27]
0.05	0.41	0.22	13.2	3	0.35	0	0	279	[27]
1.5	0.6	0.4	0	12	1	0	0.35	220	[28]
1.0	0.6	0	0	8	1.3	0	0.2	158	[28]
0.385	0.375	1.00	0	5.15	1.25	0	0.875	324	[28]
0.4	0.6	0.6	0	5	1.3	0	0.7	307	[28]

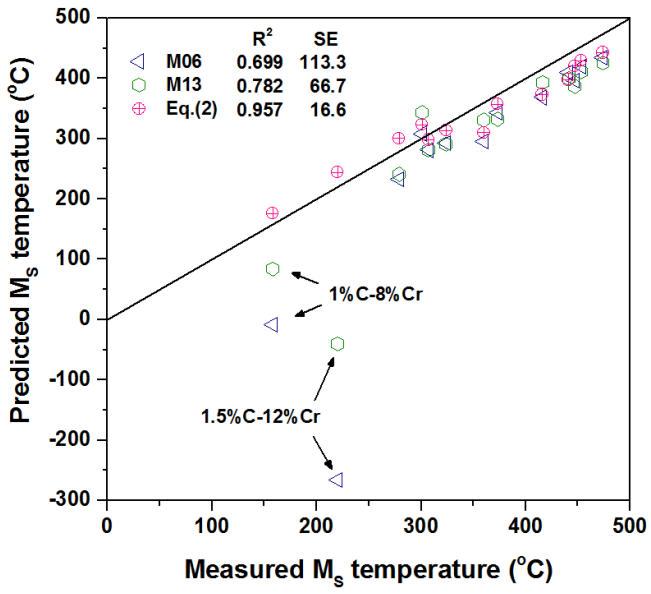

Fig. 3. Verification of the M_S values calculated by the selected equations with the experimental data [19,26-28]. SE means standard error

the previous two equations. On the other hand, the equation proposed in this study provided reliable prediction results for all verification data.

5. Conclusions

An empirical equation was proposed to calculate M_S temperature for highly alloyed steels containing more than 3 wt.% of Ni or Cr or 2 wt.% of Mo, W, or Co. Owing to the high amounts of carbide-forming alloying elements such as Cr, Mo, V, and W, their interactions with C were considered. The proposed equation provided a better accuracy for prediction of M_S temperature than those of existing equations, and thus could be used to design the heat treatment and investigate the phase transformation kinetics for highly alloyed steels.

Acknowledgement

SJL appreciates the financial support by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2016R1D1A1B03935163). MJ appreciates the financial support by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (20182010106480).

REFERENCES

[1] G. Krauss, Steels – Processing, Structure, and Performance, ASM International, Materials Park, OH (2005).
[2] P. Payson, C.H. Savage, Trans. ASM **33**, 261-275 (1944).
[3] E.S. Rowland, S.R. Lyle, Trans. ASM **37**, 27-47 (1946).
[4] R.A. Grange, H.M. Stewart, Trans. AIME **167**, 467-490 (1946).
[5] A.E. Nehrenberg, Trans. AIME **167**, 494-498 (1946).
[6] W. Steven, A.G. Haynes, JISI **183**, 349-359 (1956).
[7] K.W. Andrews, JISI **203**, 721-727 (1965).
[8] C.Y. Kung, J.J. Rayment, Metall. Trans. A **13**, 328-331 (1982).
[9] K. Ishida, J. Alloys Comp. **220**,126-131 (1995).
[10] A.V. Sverdlin, A.R. Ness, Steel Heat Treatment Handbook, G.E. Totten and M.A.H. Howes, Ed., Marcel Dekker Inc., New York, NY (1997).
[11] C. Capdevila, F.G. Caballero, C.G. de Andres, ISIJ Inter. **42**, 894-902 (2002).
[12] S.M.C. van Bohemen, Mater. Sci. Tech. **28**, 487-495 (2012).
[13] D. Barbier, Adv. Eng. Mat. **16**, 122-127 (2014).
[14] S.J. Lee, S. Lee, B.C. De Cooman, Int. J. Mater. Res. **104**, 423-429 (2013).
[15] S.J. Lee, K.S. Park, Metall. Mater. Trans. A. **44**, 3423-3427 (2013).
[16] J. Park, J.H. Shim, S.J. Lee, Metall. Mater. Trans. A. **49**, 450-454 (2018).
[17] A.H. Eichelman, F.C. Hull, Trans. ASM. **45**, 77-104 (1953).
[18] G.F. Vander Voort, Atlas of Time-Temperature Diagrams for Irons and Steels, 4th ed., ASM International, Metals Park, OH (2007).
[19] H.S. Yang, H.K.D.H. Bhadeshia, Mater. Sci. Tech. **23**, 556-560 (2007).
[20] S. Sourmail, V. Smanio, Mater. Sci. Tech. **29**, 883-888 (2013).
[21] M.A. Alvarado-Meza, E. García-Sanchez, O. Covarrubias-Alvarado, A. Salinas-Rodriguez, M.P. Guerrero-Mata, R. Cola, J. Mater. Eng. Perform. **22**, 345-350 (2013).
[22] M. Yaso, S. Hayashi, S. Morito, T. Ohba, K. Kubota, K. Murakami, Mater. Trans. **50**, 275-279 (2009).
[23] M. Nurbanasari, P. Tsakiropoulos, E.J. Palmiere, ISIJ Int. **54**, 1667-1676 (2014).
[24] S. Kang, M. Kim, S.J. Lee, Metals **7** (2017), 12(1)-12(7).
[25] E.J. Pavlina, C.J. Van Tyne, J.G. Speer, Mater. Charac. **102**, 35-46 (2015).
[26] Z.Y. Zhang, R.A. Farrar, An atlas of continuous cooling transformation (CCT) diagrams applicable to low carbon low alloy weld metals, 1st ed., Maney Publishing, CRC Press (1995).
[27] M.C. Payares-Asprino, H. Katsumoto, S. Liu, Weld. J. **87**, 279S-289S (2008).
[28] http://www.seahss.co.kr/eng/pr/brochure.jsp, SeAH Changwon Integrated Special Steel, Tool & Mold Steel, Product Catalog (2017).