Past, Present and Future Development in Mathematical Modeling for Low Temperature Thermochemical Treatments of Stainless Steels for Enhanced Surface Properties

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Abstract. Research development on mathematical modeling for thermochemical treatment especially in low temperature started from the empirical-based research which focused on conducting many experimental studies to gather metallurgical data. Several thermochemical treatments have been developed experimentally using various process parameters such as temperature, treatment time and gas compositions to understand the effect of certain factors towards the resultant layer. The availability of these experimental data was a crucial factor to obtain precise simulation of the diffusion process by thermochemical treatments in the stainless steels which can reduce the trials and errors of the experimental works. However, the lack of the metallurgical data remains an obstacle to correlate the empirical and simulation-based research. The recent additive manufacturing research area is also an attractive challenge to generate a mathematical-based simulation of thermochemical treatments of additive manufactured specimen. In this paper, a historical review in connection with modeling development in low temperature thermochemical treatments is presented including the suggested future works to attain commercial software availability in progressive industrial development.

1. Conceptual Historical Review
Stainless steels are popular for their main characteristic in its resistance towards corrosion due to the high chromium content up to 18 at.%. Since it was first discovered in 1913 [1], the initial use of stainless steels was for cutlery, but as the time goes by, its application widen to various fields such as food and chemical processing, aerospace, appliances, automotive, and also medical. Hence, until now there are more than 100 grades of stainless steels which already available commercially.

According to their metallurgical and crystalline structure, stainless steels are divided into five categories—i.e., martensitic, ferritic, austenitic, duplex and precipitation hardening. Austenitic stainless steels are non-magnetic alloys which are the most frequently used types of stainless steels among others owing to its incredible mechanical properties. In order to fabricate iron alloy with stainless characteristic, only 10.5% chromium is needed, however austenitic stainless steels contain minimum of 15% chromium [2]. AISI 314, 306 and 316 are the most common grades of austenitic stainless steels. Apart from its excellent corrosion resistance, austenitic stainless steels also have good formability, durability and weldability. It is also cost effective compared to other alloys. Unfortunately, it has low hardness and wear resistant because of its austenite microstructure. These drawbacks limit
the use of austenitic stainless steel in certain applications especially those that require high hardness and wear resistant.

A surface engineering method can be used to cope with these limitations which is applied by modifying the surface of the materials or by putting a new layer to cover it. There are some treatments in surface engineering that can alter and even enhance the properties of the materials, such as thermal treatments, thermomechanical treatments and thermochemical treatments. Thermochemical treatments for austenitic stainless steels have been studied for the past decades to improve its surface mechanical properties [3-12]. Among several types of thermochemical treatments such as nitriding, carburizing, nitrocarburizing, carbonitriding, chromizing and boriding, treatments involving nitrogen and carbon atoms are the most leading treatments for stainless steels. These treatments include the diffusion process by incorporating nitrogen and/or carbon interstitial atoms into the solid solution.

In 1959, one of the earliest studies on the thermochemical treatment of stainless steels was conducted using nitriding at 560°C for 48 hours [3]. The study observed the nitrided layer structure of stainless steels to find out the effect of nitriding on the corrosion resistance. During the nitrogen diffusion process, the chromium nitride was formed which reduces the chromium content in the solid solution. Although the surface hardness has increased, a significant degradation in corrosion resistance occurred due to the loss of the chromium content. It also confirmed that the high chromium content in stainless steels makes its characteristic become rustless.

An enhancement of the stainless steels surface hardness of 800-900 HV was achieved by applying thermochemical treatment [3]. Later on, it has been explained that the increased surface hardness was caused by the formation of expanded austenite in the solid solution [4]. This expanded layer also referred to as S-phase.

The reduction in corrosion resistance phenomenon has not been resolved until 1985 although many investigations on that problem has been done. In 1985, a study on nitriding of austenitic stainless steels using plasma technique [5] revealed that as the temperature was set low enough around 400°C, the austenite layer would be free of chromium nitride precipitates, thus no damage in corrosion resistance occurred. Since then until early 2000, many investigations have emerged regarding what is now called low temperature thermochemical treatments which mostly focused on austenitic stainless steels [6]. In that period of time, another classification of stainless steels such as martensitic stainless steels were also used in order to observe its wear behaviour [7].

2. Research Progress and Applications
In the beginning of its applications, low temperature thermochemical treatments were widely carried out in plasma technique such as plasma nitriding and plasma carburizing on austenitic stainless steels [4][5][8]. Through its sputtering behavior, it is believed that plasma process has inherent ability to depassivate the stainless steels surface. The surface alloying processes were also been conducted using other techniques such as salt bath nitriding, salt bath nitrocarburizing, plasma immersion ion implantation, solution nitriding and low pressure plasma [6].

Another alternative to plasma technique is the conventional gaseous process which is more cost effective. It has been proven that conventional gaseous processes were feasible to produce the expanded austenite layer on austenitic [9] and duplex stainless steels [10]. A laboratory fluidized bed furnace has also been used to perform low temperature nitriding on AISI 316L which included particulate alumina as fluidized particles flowing inside the chamber [11].

A relatively new developed process called low temperature hybrid thermochemical treatment has been studied on austenitic stainless steels using plasma technique [12]. The process involves the simultaneous diffusion of nitrogen and carbon interstitial atoms into the substrate which produces a dual layer structure consist of both nitrogen and carbon enriched layers. Recently, as an inexpensive alternative way, the conventional method using gaseous tube furnace was adopted to undertake the hybrid process by employing methane and ammonia gases [9][13]. It is obvious that the cost can be reduced while at the same time producing identical results to the plasma process. The same technique
has also been applied to duplex stainless steel [10]. However, a precipitation of chromium was found at ferrite grain which can reduce the corrosion resistance.

3. Mathematical Modelling Development

Numerous experimental works have been done to comprehend the knowledge in low temperature thermochemical treatments for stainless steels. However, these experimental method-based studies have several constrains in terms of financial effectiveness, trials and errors elimination, and process design accuracies which may lead prolonged learning curve for the implementation in commercial industry. For the past few decades, the development of mathematical model in simulating the low temperature thermochemical treatment derived from Fick’s 2nd law has been growing rapidly. The objective of this method is to provide a model which represent the actual phenomenon with the smallest possible error rate.

The earliest work of modeling was performed in 1970 in which a mechanism of carbon transport in stainless steels at different temperatures was studied using residual activity technique and produced temperature-dependent diffusivity values of carbon in various types of stainless steels [14]. The carbon picks up by stainless steels was predicted which became one of the earliest studies in modeling and simulating certain processes associated with low temperature thermochemical treatment. This temperature-dependent diffusivity term also known as diffusion coefficient at infinite dilution since the diffusion of the interstitial atoms are only influenced by the temperature changes, not concentration as latter also used by other works [15].

The mathematical model and simulation development of thermochemical treatments was initiated using low alloy steels in plasma nitriding atmospheric condition [16]. Several reactions were introduced simultaneously, which include mass transfer mechanism from plasma atmosphere to the specimen surface, nitrogen diffusion phenomenon in the substrate, and alloy nitride precipitation effect to the inhibition of the nitrogen diffusing element.

A decade later, the nitriding process on austenitic stainless steels in low temperature was modeled using gaseous furnace [17]. The nitrogen concentration profiles were obtained by considering several values of nitriding potentials. The study concluded that the kinetic reaction on the surface as well as the stress effect made a big impact on the nitrogen diffusion process, although the distinction between these two factors has not been explained in details. A few years later, the concentration-dependent diffusivity was introduced but yielded erroneous results in low nitrogen content region due to the absence of trapping factor in the analysis [18]. The model derived from the Boltzmann-Matano analysis [19] which assumed concentration dependent-diffusivity is merely binary diffusion couples between the interstitial dissolved atoms and the vacancy sites in a binary system. The concentration-dependent diffusivities of nitrogen and carbon in expanded austenite have been validated experimentally [20][21][22]. These studies demonstrated that the diffusivity of nitrogen and carbon in expanded austenite increase with nitrogen and carbon contents which signified that nitrogen and carbon diffusivities are function of concentrations. Thermogravimetry measurements were both applied to determine the nitrogen and carbon concentration-dependent diffusion coefficient. The discrepancy between theoretical model and experimental study have been further updated in the recent years [15][23][24]. The composition induced residual stresses existing in expanded austenite layers has been included in the diffusion model by several previous works [18][25][26][27]. The existence of residual stresses can enhance the interstitial atom diffusion into the substrate. The prediction to the residual stress-depth profiles have also been proposed based on the composition-induced lattice expansion, and the work suggested this can be applied to the composition-dependent mechanical properties in carbon expanded austenite [28] and nitrogen expanded austenite [23]. The plastic accommodation resulting from the lattice expansion by interstitial atoms diffusion was also convinced.
to become one of the key factors in modeling the behavioral of nitrogen and carbon diffusion in austenitic stainless steels [23][29][24].

The trapping-detrapping model was introduced in modeling the nitrogen transport in austenitic stainless steels [30]. This trapping-detrapping model was adopted from hydrogen transport into metals proposed by the previous work [31], in which hydrogen profiles represented similarities with nitrogen profiles. Several subsequent works also have employed the same trapping-detrapping model with some improvements and modifications. The dimensional swelling effect that occurs during plasma nitrizing has further been suggested in the trapping-detrapping model [32]. The simulation also proposed a new boundary condition which included the gas-solid interface in one-directional inward diffusion. The following work on the nitrogen diffusion model in single-crystalline AISI 316L austenitic stainless steels using plasma nitrizing, the trapping-detrapping mechanism was also studied which involving the sputtering and ion implantation parameters [33]. In the past recent years, the trapping-detrapping model was applied in simulating the carburizing process for austenitic stainless steels [34]. Several improvements in modeling the carburizing process have been made including the composition-induced stress gradient and the carbon activity. These all studies concluded that by considering the composition-induced stress gradient, the nitrogen and carbon diffusions into austenitic stainless steels were accelerated although further explanation was not available.

Recently, the effect of anisotropy on the diffusion process model has attracted many researchers. The penetration depth of the nitrogen interstitial atoms which was influenced by its crystalline orientation had been investigated from the cross-sectional morphology of polycrystalline AISI 316L austenitic stainless steels [32]. In this study different values of diffusivity were used for two different crystalline orientations which represented the anisotropic effect but the results of this early study need further investigations to attain a comprehensive understanding of the above unresolved phenomenon. Following the above early study, the Finite Element Method has been applied to simulate the anisotropic properties of austenitic stainless steels by nitrizing with two different grain orientations were considered <001> <111> [35]. The study found that calculated concentration profiles as a function of orientation dependent were not significant as shown in the experimental works. In addition to the above findings, other works also concluded that the anisotropic internal stresses influence both the depth of diffusion and also the concentration on the surface [36][37]. The most recent experimental study on anisotropic crystal orientations effect in single crystal of AISI 316L austenitic stainless steels has been studied not to influence only the mechanical properties but also the diffusion depth of nitrogen penetration during nitrizing [38]. From three crystal orientations that has been used in this study, i.e.—<100>, <111> and <10 7 2>, <100> crystal orientation produced deepest nitrogen diffusion penetration due to the presence of expanded austenite.

The above series of studies on diffusion model in thermochemical treatments of stainless steels still indicated various arguments on the comprehension in developing the representative model of the actual diffusion process. Thus, further explorations in understanding the diffusion phenomenon of both nitrogen and carbon in austenitic stainless steels with complex parameters during low temperature thermochemical treatments are indeed still necessary.

4. Prospective Research Development

An excessive amount of studies in simulating the low temperature thermochemical treatments particularly for stainless steels have been performed since a few decades ago. The utilization of certain programming software plays an important role in running the simulation by converting such metallurgical phenomenon into a mathematical model solution. Fick’s 2nd law was resolved using mostly finite difference and finite element methods to iterate the diffusion equations layer by layer. Several programming software such as ABAQUS [39][40][35], MATLAB [34] and self-developed programming software [41] were applied to run the simulation processes.
More detailed parameters and boundary conditions were included to generate an accurate model in achieving identical results with the experimental works. Fick’s 2nd law equation has been modified by adding several terms which represent the boundary conditions of the diffusion process. For example, stress gradient effect, concentration-dependent diffusivity, trapping phenomenon, and anisotropy effect have been incorporated as the process parameters in the diffusion equations. However, a gap in correlating the empirical-based research to the simulation-based research using such programming software still exists. There is still an insufficient amount of substantial data from the experimental works which are used for input parameters in simulation to run properly. Thus, a lot of assumptions as well as the use of fitting parameters were applied to fill the gaps in the unavailability of parameters data. This condition may consequently reduce the accuracy of the results while the main objective in the development of the simulation-based research is to generate the results with the lowest possible error rate.

Recently, the application of computer-aided-design (CAD) softwares in additive manufacturing were widely used to produce more precise geometrical shapes of the manufactured stainless steel components by means of using layer by layer development process. While the traditional subtractive manufacturing industries deliver mass production materials, the more complex customized design can be obtained by additive manufacturing in much faster and less expensive. The application of thermochemical treatment especially in low temperature for stainless steel materials produced from additive manufacturing can enhance the development of the additive manufacturing research area in understanding the effect of the treatment to the manufactured components. Moreover, modeling the layer development in the diffusion zone of such materials while implementing the cloud computing to flexible the process control could be the challenge in the next phase of the development in modeling the thermochemical treatments associated with additive manufactured components.

Research investigations on thermochemical treatments of stainless steels were usually conducted on types of stainless steels which need improvements on their mechanical properties such as austenitic and duplex stainless steels. Demand of higher wear and hardness properties as well as corrosion resistance has become the main objective of surface engineering research area. However, further investigations of thermochemical treatments on the other types of stainless steels are necessary to obtain a complete picture of the resulting mechanical properties of all stainless steels types. For example, although martensitic stainless steels have higher hardness compared to other families of untreated stainless steel, but the low temperature thermochemical treatments have the potential to improve the surface hardness of the stainless steels several orders of its martensitic type.

The following future works associated with modeling of low temperature thermochemical treatments of stainless steels are suggested in the following:

• Data acquisition of various experimental studies from the existing literatures
• Further studies on low temperature thermochemical treatments of all stainless steel types
• Implementation of low temperature thermochemical treatments on additive manufactured stainless steel components
• Modeling and simulation by complex parameters
• Software development for commercial application
• Software integration with cloud computing features

The above necessary steps might provide the availability of commercial software in designing the specific thermochemical treatments for stainless steels in the future. It will meet demands on improving the surface mechanical properties of stainless steels in various applications such as medical and biological component, aerospace and automotive parts, which are known as high value-added products. Although presently there are relatively few investigators involved in this related field of thermochemical treatment, the prospect of its implementation in industry is encouraging due to the fact that this surface engineering method can be used as an alternative to improve the surface quality.
of the stainless steels in various application where enhanced properties between corrosion resistance and higher wear resistance are needed.

Acknowledgements
This study was funded by Kementerian Riset Teknologi Dan Pendidikan Tinggi Republik Indonesia through the World Class Research scheme (83.ADD/LL3/PG/2020). The authors declare that they have no conflict of interest.

References
[1] Capus J 2013 *Met. Powder Rep.* 68 12
[2] Michler T 2016 “Austenitic Stainless Steels,” in Reference Module in Materials Science and Engineering, 1–6
[3] Andreeva AG and Gurvich LY 1959 *Met. Sci. Heat Treat. Met.* 34–40
[4] Sun Y, Li X, and Bell T 1999 *Surf. Eng.* 15 49–54
[5] Zhang ZL and Bell T 1985 *Surf. Eng.* 1 131–136
[6] Bell T and Akamatsu K, Eds. 2000 “Stainless Steel 2000,” in International Current Status Seminar on Thermochemical Surface Engineering of Stainless Steel, 2000
[7] Sun Y, Bell T, and Wood G 1994 *Wear* 178 131–138
[8] Rolinski E 1987 *Surf. Eng.* 3 35–40
[9] Adenan MS, Zainal SU, and Haruman E 2019 *Int. J. Eng. Adv. Technol.* 9 5845–5849
[10] Adenan MS, Berhan MN, and Haruman E 2014 *Adv. Mater. Res.* 970 244–247
[11] Haruman E, Sun Y, Malik H, Surjipto AGE, Mridha S, and Widi K 2006 *Solid State Phenom.* 118 125–130
[12] Sun Y and Haruman E 2006 *Solid State Phenom.* 118 85–90
[13] Haruman E, Sun Y, Triwiyanto A, Manurung YHP, and Adesta EY 2012 *J. Mater. Eng. Perform.* 21 388–394
[14] Agarwala RP, Naik MC, Anand MS, and Paul AR 1970 *J. Nucl. Mater.* 36 41–47
[15] Gu X, Michal GM, Ernst F, Kahn H, and Heuer AH 2014 *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 45 4268–4279
[16] Sun Y and Bell T 1996 *Mater. Sci. Eng. A* 224 33–47
[17] Christiansen TL, Dahl KV, and Somers MAJ 2006 *Defect Diffus. Forum* 258–260 378–383
[18] Christiansen TL, Dahl KV, and Somers MAJ 2008 *Mater. Sci. Technol.* 24 159–167
[19] Mandl S, Scholze F, Neumann H, and Rauschenbach B 2003 *Surf. Coatings Technol.* 174–175 1191–1195
[20] Christiansen TL and Somers MAJ 2008 *Int. J. Mater. Res.* 99 999–1005
[21] Hummelsjø T, Christiansen TL, and Somers MAJ 2008 *Defect Diffus. Forum* 273–276 306–311
[22] Ernst F, Avishai A, Kahn H, Gu X, Michal GM, and Heuer AH 2009 *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 40 1768–1780
[23] Jespersen FN, Hattel JH, and Somers MAJ 2016 *Model. Simul. Mater. Sci. Eng.* 24 25003
[24] Küçükyildiz ÖC, Sonne MR, Thorborg J, Somers MAJ, and Hattel JH 2020 *Surf. Coatings Technol.* 381 1–12
[25] Galidakis A and Moskalioviene T 2010 *Comput. Mater. Sci.* 50 796–799
[26] Galidakis A and Moskalioviene T 2011 *Surf. Coatings Technol.* 205 3742–3746
[27] Moskalioviene T and Galidakis A 2012 *Vacuum* 86 1552–1557
[28] Peng Y, Liu Z, Jiang Y, Wang B, Gong J, and Somers MAJ 2018 *Scr. Mater.* 157 106–109
[29] Küçükyildiz ÖC, Rostgaard Sonne M, Thorborg J, Hattel JH, and Somers MAJ 2017 “Integrated Computational Modelling of Thermochemical Surface Engineering of Stainless Steel,” in *Proceedings of the 24th Ifhtse Congress*, 2017
[30] Parascandola S, Möller W, and Williamson DL 2000 *Appl. Phys. Lett.* 76 2194–2196
[31] Myers SM, Richards PM, Wampler WR, and Besenbacher F 1989 *J. Nucl. Mater.* 165 9–64
[32] Moskalioviene T, Galdikas A, Rivière JP, and Pichon L 2011 *Surf. Coatings Technol.* **205** 3301–3306
[33] Martinavičius A, Abrasonis G, and Müller W 2011 *J. Appl. Phys.* **110**
[34] Peng Y, Gong J, Chen C, Liu Z, and Jiang Y 2018 *Metals (Basel).* **8** 1–12
[35] Küçükyıldız ÖC, Sonne MR, Thorborg J, Winther G, Hattel JH, and Somers MAJ 2018 “Numerical modelling of Mechanical Anisotropy during Low Temperature Nitriding of Stainless Steel,” in *European Conference on Heat Treatment*, 2018, 102–108
[36] Moskalioviene T and Galdikas A 2019 *Surf. Coatings Technol.* **366** 277–285
[37] Moskalioviene T and Galdikas A 2020 *Metals (Basel).* **10** 1–13
[38] Küçükyıldız ÖC, Grumsen FB, Christiansen TL, Winther G, and Somers MAJ 2020 *Acta Mater.* **194** 168–177
[39] Agarwal N, Kahn H, Avishai A, Michal G, Ernst F, and Heuer AH 2007 *Acta Mater.* **55** 5572–5580
[40] Hassani-Gangaraj SM and Guagliano M 2013 *Appl. Surf. Sci.* **271** 156–163
[41] Lee SJ, Matlock DK, and Van Tyne CJ 2013 *Comput. Mater. Sci.* **68** 47–54