

# **Facilitating the Formation of Intermetallic Compounds in Al-Si Coatings on Steel during Hot Stamping**

by

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## **Author's Declaration**

This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## Statement of Contributions

Prof. Rodney Smith and Prof. Kyle Daun assisted in the theoretical development of this project. The first draft of the accepted manuscript (Chapter 3) was authored by Jixi Zhang. Prof. Rodney Smith provided assistance in data analysis, writing, and revising the manuscript, as well as submitting it to a peer-reviewed journal. Prof. Kyle Daun also contributed to the revisions of the paper. Jason Boettger and Cyrus Yau assisted in the development of the patent application, which was based on the content in Chapter 5. Jixi Zhang is the sole author of the rest of the thesis.

Part of the work described in **Chapter 3** has been published by ACS Omega as:

*“Raman Spectroscopic Analysis of the Reaction Between Al-Si Coatings and Steel”*

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- Jixi Zhang performed all synthesis and characterization of materials.
- Prof. Rodney Smith and Jixi Zhang performed the data analysis.
- Prof. Rodney Smith, Prof. Kyle Daun, and Jixi Zhang completed the final draft.

Part of the work described in **Chapter 5** is patent pending as:

*“COATED STEEL, HOT STAMPING PARTS FORMED THEREFROM, AND HOT STAMPING METHOD”*

Jason BOETTGER, Cyrus YAU, Kyle DAUN, Rodney D. L. SMITH, Jixi ZHANG

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- Jason Boettger and Cyrus Yau are in charge of the patent document preparation.
- Prof. Kyle Daun, Prof. Rodney Smith, and Jixi Zhang contributed to the conception of the patent.
- Jixi Zhang performed the sample synthesis and characterization of the samples.

## **Abstract**

Hot-stamped ultrahigh strength steel (UHSS) components are pivotal to automotive light-weighting. Steel blanks, often coated with an aluminum-silicon (Al-Si) layer to protect them from oxidation and decarburization, are austenitized within a furnace and then simultaneously quenched and formed into shape. The Al-Si coating melts within the furnace and reacts with iron from the steel to yield an intermetallic phase that provides some long-term corrosion protection. During the intermediate liquid phase, some of the coatings may transfer to the furnace components, leading to maintenance costs and operational downtime. This document describes the development of a rapid analysis method using Raman microscopy mapping to investigate the reaction mechanisms of Al-Si coating and steel during heating. A new surface modification strategy was applied on the Al-Si coating to facilitate intermetallic phase formation. This strategy provides the possibility of expediting the solidification during the heating, thus providing a method to mitigate furnace rollers' contamination caused by melted high-temperature liquids in the industrial hot stamping process.

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## List of Abbreviations

**UHSS:** Hot-stamped Ultrahigh Strength Steel

**BCC:** Body-centered Cubic

**FCC:** Face-centered Cubic

**BCT:** Body-centered Tetragonal

$\tau_5$ :  $\text{Al}_7\text{Fe}_2\text{Si}$

$\eta$ :  $\text{Al}_5\text{Fe}_2$

**SEM:** Scanning Electron Microscope

$\theta$ :  $\text{Al}_3\text{Fe}$  or  $\text{Al}_{13}\text{Fe}_4$

$\tau_6$ :  $\text{Al}_{4.5}\text{FeSi}$

$\alpha_2$ :  $\text{AlFe}$

$\alpha_1$ :  $\text{AlFe}_3$

$\xi$ :  $\text{Al}_2\text{Fe}$

$\epsilon$ :  $\text{Al}_8\text{Fe}_5$

$\rho$ :  $\text{FeSi}$

$\omega$ :  $\text{FeSi}_2$

$\tau_1$ :  $\text{Al}_2\text{Fe}_3\text{Si}_3$

$\tau_2$ :  $\text{Al}_3\text{FeSi}$

$\tau_3$ :  $\text{Al}_2\text{FeSi}$

$\tau_4$ :  $\text{Al}_3\text{FeSi}_2$

$\tau_7$ :  $\text{Al}_3\text{Fe}_2\text{Si}_3$

$\tau_8$ :  $\text{Al}_2\text{Fe}_3\text{Si}_4$

$\tau_{10}$ :  $\text{Al}_{57-59}\text{Fe}_{24-25}\text{Si}_{17-18}$

$\tau_{11}$ :  $\text{Al}_4\text{Fe}_{1.7}\text{Si}$

$\alpha$ :  $\text{AlFe}$  or  $\text{AlFe}_3$  or body-centered cubic iron

**EDS:** Energy Dispersive X-ray Spectroscopy

**EBSD:** Electron Back-Scattering Diffraction

**XRD:** X-Ray Diffraction

**P-XRD:** Powder X-ray Diffraction

**ICSD:** Inorganic Crystal Structure Database

**2-D:** Two-Dimensional

# Chapter 1

## Introduction

### 1.1 Hot Stamping

Hot stamping is one of the main techniques used to manufacture automotive parts, such as bumpers, roof rails, tunnels, and other chassis components.<sup>1</sup> The use of hot stamped steel can significantly increase the passengers safety and the vehicle crashworthiness qualities, also reduce the vehicle weight and fuel consumption.<sup>1-3</sup> Different types of steel plates, such as, 20MnB5, 22MnB5, 8MnCrB3 and 27MnCrB5, are used in industrial production, of which 22MnB5 is the most common.<sup>1,2,4</sup> The steel plates used in the thesis are all 22MnB5. As shown in **Table 1.1**, the 22MnB5 is an iron (Fe) based alloy with manganese (Mn) as the main alloying element and small amounts of carbon (C), silicon (Si), aluminum (Al), chromium (Cr), titanium (Ti), phosphorus (P), sulfur (S), copper (Cu), niobium (Nb), and boron (B).<sup>1,2,5-10</sup>

**Table 1.1** The minimum alloy composition of 22MnB5 steel in weight%.<sup>10</sup>

| Element | C    | Si  | Al  | Mn  | Cr   | Ti   | P    | S    | Cu  | Nb   | B     | Fe   |
|---------|------|-----|-----|-----|------|------|------|------|-----|------|-------|------|
| wt.%    | 0.25 | 0.4 | 0.1 | 1.4 | 0.35 | 0.05 | 0.03 | 0.01 | 0.2 | 0.01 | 0.005 | Bal. |

Bal. = balance compositions of alloy.

**Figure 1.1** illustrates a full hot stamping process. The steel blanks are first passed through a furnace on ceramic rollers. The furnace has different temperature zones to gradually ramp the temperature to approximately 950 °C. This high temperature is critical so that the steel plates can finish the austenitization process, followed by the transferring of austenitized steel plates to a press for shaping while quenching to drive a martensitization process.<sup>1,2,5</sup> As shown in **Figure 1.2**, the crystal structure of steel undergoes a transformation from a body-centered cubic (BCC) arrangement, as observed in the original ferritic steel state, to a face-centered cubic (FCC) structure known as austenite following the austenitization process. Subsequently, during the martensitization process, the austenite structure transforms into a body-centered tetragonal (BCT) configuration, resulting in the formation of hot-stamped martensite. It is worth noting that a cooling rate of 27 °C·s<sup>-1</sup> is the slowest rate at which 22MnB5 steel can achieve a complete martensite microstructure.<sup>1,4,11</sup>

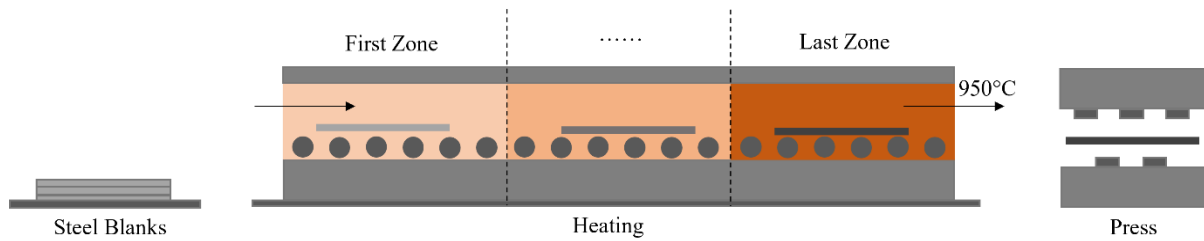


**Figure 1.1** Schematic illustration of a typical hot-stamping line.

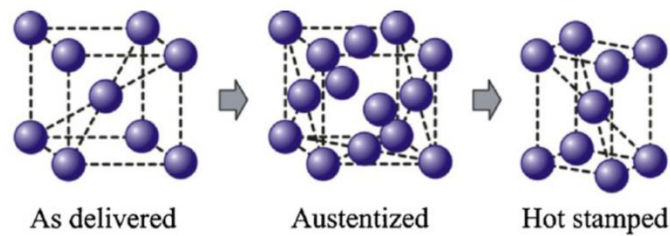


**Figure 1.2** Structure change of steel during hot stamping. During hot stamping, the BCC as delivered ferritic steel will first transform to FCC austenitized steel, then transform to BCT hot stamped martensitic steel. Figure adapted with permission from Elsevier.<sup>1</sup>

Since the steel blanks are heated to a high temperature during hot stamping process in the atmosphere containing oxygen, bare steel would oxidize and decarburize.<sup>7,12,13</sup> This would affect both the appearance of steel surface and the mechanical properties of final products.<sup>2,5</sup> Hence, coated steels are widely used to protect the steel during hot stamping process.

## 1.2 Al-Si Coating

Al-Si coatings have become the most widely used coating to prevent oxidation and decarburization of steel during hot-stamping process due to their high oxidation resistance performance.<sup>2,6,12,14–16</sup> The Al-Si coatings also provide good corrosion resistance, paintability, and weldability.<sup>2,13,16,17</sup>

### 1.2.1 Component of Al-Si Coating

In the industrial process, the Al-Si coatings are deposited to the bare steel by hot dipping.<sup>2,8,18–20</sup> The bare steel is immersed in molten near-eutectic Al-Si alloy with a composition of approximately 88 wt% Al, 9 wt% Si, and 3 wt% Fe at about 675 °C.<sup>2,5,8,13</sup> The hot-dipped aluminized coating typically consists of approximately 90 wt% Al and 10 wt% Si, with a thickness ranging from 10 to 33  $\mu\text{m}$  and a weight from 60 to 200  $\text{g/m}^2$ .<sup>2,21–23</sup> During the hot dipping process, intermetallic layers are generated

in the interface between the coating and the bare steel as shown in **Figure 1.3**.<sup>2,8,9,12,24</sup> The formation of a  $\tau_5$  ( $\text{Al}_7\text{Fe}_2\text{Si}$ ) inhibition layer is able to prevent the rapid formation of  $\eta$  ( $\text{Al}_5\text{Fe}_2$ ) layer during the hot dipping process.<sup>2,21</sup>

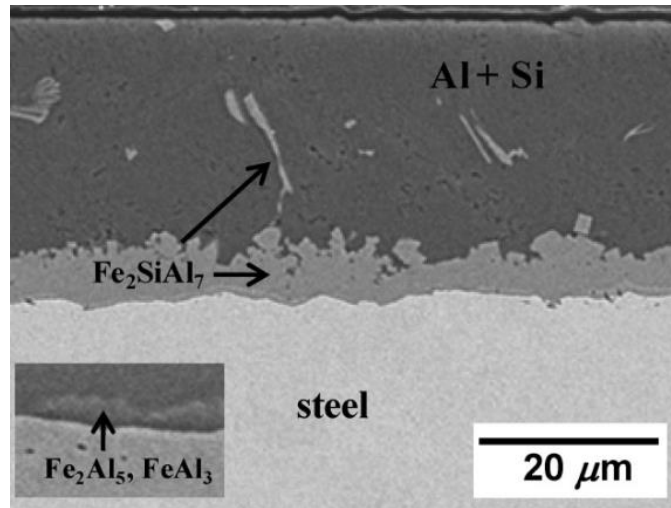


**Figure 1.3** The cross-sectional view of phase distribution in the Al-Si coating after hot dipping. This is the scanning electron microscope (SEM) image of hot dipped Al-Si coating microstructure, containing Al-Fe-Si ternary phases and Al-Fe binary phases in the interface steel/coating. Figure reprinted with permission from John Wiley and Sons.<sup>2</sup>

The Al-Si coating is known to have two layers.<sup>5,12</sup> The thinner layer of coating is the intermetallic layer, which is near the steel and contains the iron-enriched phases like  $\eta$ ,  $\theta$  ( $\text{Al}_3\text{Fe}$  or  $\text{Al}_{13}\text{Fe}_4$ ), and  $\tau_5$ .<sup>2,5,25</sup> The thicker layer is composed of pure Al, Si, and floating Fe-Al-Si ternary phases, like  $\tau_5$  and  $\tau_6$  ( $\text{Al}_{4.5}\text{FeSi}$ ).<sup>2,12,25</sup> During the hot stamping process, the coating reacts with the substrate steel and absorbs Fe to generate Al-Fe binary phases, Fe-Si binary phases, and Al-Fe-Si ternary phases. These reactions are affected by the heating time and temperature. The coating thickness grows with heating time and temperature.<sup>2</sup>

### 1.2.2 The Build-up of Melted Al-Si Coating during Hot-Stamping

The Al-Si coatings are viable to protect the bare steel during and after hot stamping process. However, the Al-Si coating melts at around  $577^\circ\text{C}$  (**Figure 1.4**), which is far below the temperature used in the hot stamping process.<sup>26,27</sup> The melted coatings cause issues during industrial production of automotive parts. The molten Al-Si coating transfers to the furnace rollers, leading to the

contamination, degradation, or even failure of the rollers.<sup>2,28,29</sup> The build-up of melted Al-Si coating on furnace rollers causes blanks to shift, complicating the automated transfer process after heat treatment.<sup>25</sup> **Figure 1.5** illustrates the contaminated rollers obtained from industrial production line, showing the melted liquid generated coating layer (**Figure 1.5A**) or particulates (**Figure 1.5B**) on the surface of rollers and penetrated the rollers (**Figure 1.5B**). The companies' profits decrease with the low transferring efficiency, replacement of degraded rollers, and the downtime of replacing rollers.

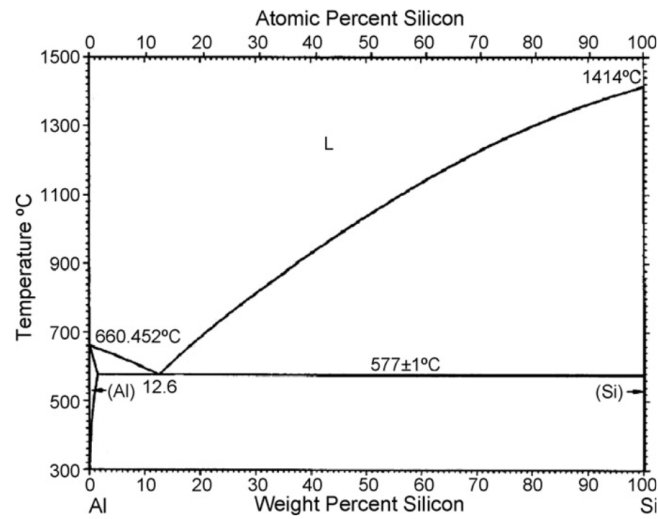


**Figure 1.4** Al-Si binary phase diagram. Reprinted with permission from Elsevier.<sup>27</sup>

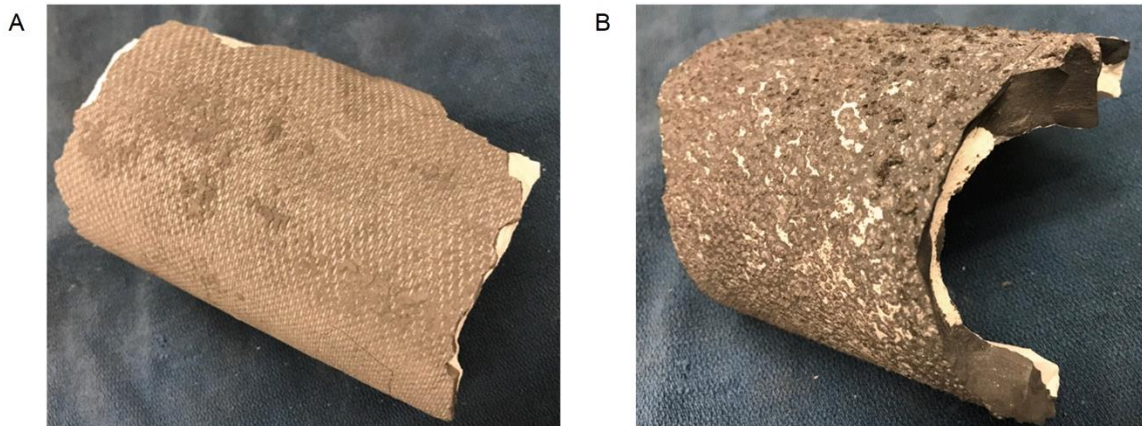


**Figure 1.5** Images of contaminated furnace rollers. (A) and (B) are different contaminated rollers.

### 1.3 Intermetallic Compounds

As mentioned previously, the transfer of Fe from the steel to the Al-Si coating generates a series of Al-Fe-Si or Al-Fe intermetallic compounds during the hot stamping process. In **Table 1.2**, we list all the reported intermetallic compounds in the Al-Fe, Al-Si, Fe-Si, and Al-Fe-Si systems.<sup>5,30-44</sup> As shown for each compound, many compounds are non-stoichiometric and are stable with compositional variations, with the unit cell defining the structure type.

**Table 1.2** The list of binary and ternary phases in the Al-Fe, Al-Si, Fe-Si, and Al-Fe-Si system.<sup>5,30,31</sup>

| Intermetallic Compounds                                              | Structure Type                                   | Crystal System | Space Group  |
|----------------------------------------------------------------------|--------------------------------------------------|----------------|--------------|
| AlFe ( $\alpha_2$ )                                                  | CsCl/B2                                          | Cubic          | $Pm\bar{3}m$ |
| AlFe <sub>3</sub> ( $\alpha_1$ )                                     | BiF <sub>3</sub> /D0 <sub>3</sub>                | Cubic          | $Fm\bar{3}m$ |
| Al <sub>2</sub> Fe ( $\xi$ )                                         | Al <sub>2</sub> Fe                               | Triclinic      | $P\bar{1}$   |
| Al <sub>3</sub> Fe ( $\theta$ )                                      | Al <sub>3</sub> Fe                               | Monoclinic     | $C2/m$       |
| Al <sub>5</sub> Fe <sub>2</sub> ( $\eta$ )                           | Al <sub>5</sub> Fe <sub>2</sub>                  | Orthorhombic   | $Cmcm$       |
| Al <sub>13</sub> Fe <sub>4</sub> ( $\theta$ )                        | Al <sub>13</sub> Fe <sub>4</sub>                 | Monoclinic     | $C2/m$       |
| Al <sub>8</sub> Fe <sub>5</sub> ( $\epsilon$ )                       | Cu <sub>5</sub> Zn <sub>8</sub> /D8 <sub>2</sub> | Cubic          | $I\bar{4}3m$ |
| HT-FeSi <sub>2</sub> (Fe <sub>2</sub> Si <sub>5</sub> )              | FeSi <sub>2</sub>                                | Tetragonal     | $P4/mmm$     |
| LT-FeSi <sub>2</sub>                                                 | FeSi <sub>2</sub>                                | Orthorhombic   | $Cmca$       |
| Fe <sub>2</sub> Si                                                   | Fe <sub>2</sub> Si                               | Hexagonal      | $P6_3/mmc$   |
| Fe <sub>5</sub> Si <sub>3</sub>                                      | Mn <sub>5</sub> Si <sub>3</sub>                  | Hexagonal      | $P6_3/mcm$   |
| FeSi ( $\rho$ )                                                      | FeSi                                             | Cubic          | $P2_13$      |
| FeSi <sub>2</sub> ( $\omega$ )                                       | FeSi <sub>2</sub>                                | Orthorhombic   | $Cmca$       |
| Al <sub>2</sub> Fe <sub>3</sub> Si <sub>3</sub> ( $\tau_1$ )         | Al <sub>2</sub> Fe <sub>3</sub> Si <sub>3</sub>  | Triclinic      | $P\bar{1}$   |
| Al <sub>21.5-45</sub> Fe <sub>36.5-37.5</sub> Si <sub>8.5-41.5</sub> |                                                  |                |              |
| Al <sub>3</sub> FeSi ( $\tau_2$ )                                    | Al <sub>3</sub> FeSi                             | Monoclinic     | -            |

---

|                                                                                    |                                       |              |                 |
|------------------------------------------------------------------------------------|---------------------------------------|--------------|-----------------|
| $\text{Al}_{53.9-65.3}\text{Fe}_{19.5-20.5}\text{Si}_{15.2-25.6}$                  |                                       |              |                 |
| $\text{Al}_2\text{FeSi}$ ( $\tau_3$ )                                              | $\text{Al}_2\text{FeSi}$              | Orthorhombic | <i>Cmma</i>     |
| $\text{Al}_{53-56}\text{Fe}_{23.5-24.5}\text{Si}_{20.5-22.5}$                      |                                       |              |                 |
| $\text{Al}_3\text{FeSi}_2$ ( $\tau_4$ )                                            | $\text{GaPd}_5$                       | Tetragonal   | <i>I4/mcm</i>   |
| $\text{Al}_{45.5-54}\text{Fe}_{15.5-16.5}\text{Si}_{30.5-38}$                      |                                       |              |                 |
| $\text{Al}_{7.4}\text{Fe}_2\text{Si}/\text{Al}_7\text{Fe}_2\text{Si}$ ( $\tau_5$ ) | $\text{Al}_{7.4}\text{Fe}_2\text{Si}$ | Hexagonal    | <i>P6_3/mmc</i> |
| $\text{Al}_{68-72}\text{Fe}_{18-19.5}\text{Si}_{10-12.5}$                          |                                       |              |                 |
| $\text{Al}_{4.5}\text{FeSi}$ ( $\tau_6$ )                                          | $\text{Al}_9\text{Fe}_2\text{Si}_2$   | Monoclinic   | <i>C2/m</i>     |
| $\text{Al}_{64.5-67.5}\text{Fe}_{15.5-16.5}\text{Si}_{17-19}$                      |                                       |              |                 |
| $\text{Al}_3\text{Fe}_2\text{Si}_3$ ( $\tau_7$ )                                   | $\text{Al}_3\text{Fe}_2\text{Si}_3$   | Monoclinic   | <i>P2_1/n</i>   |
| $\text{Al}_{39.2-48.7}\text{Fe}_{23.5-24.5}\text{Si}_{27.8-36.3}$                  |                                       |              |                 |
| $\text{Al}_2\text{Fe}_3\text{Si}_4$ ( $\tau_8$ )                                   | $\text{Al}_2\text{Fe}_3\text{Si}_4$   | Orthorhombic | <i>Cmcm</i>     |
| $\text{Al}_{24.1-28.6}\text{Fe}_{31.9-32.9}\text{Si}_{39.5-43}$                    |                                       |              |                 |
| $\tau_{10}$ ( $\text{Al}_{57-59}\text{Fe}_{24-25}\text{Si}_{17-18}$ )              | -                                     | Hexagonal    | -               |
| $\text{Al}_4\text{Fe}_{1.7}\text{Si}$ ( $\tau_{11}$ )                              | $\text{Co}_2\text{Al}_5$              | Hexagonal    | <i>P6_3/mmc</i> |
| $\text{Al}_{64-66.5}\text{Fe}_{24-25}\text{Si}_{9.5-11}$                           |                                       |              |                 |

---

The materials of interest here are viewed as intermetallic compounds, which are distinct from metallic alloys. Both intermetallic compounds and alloys are composed of two or more metallic elements, but they differ in their structures.<sup>45</sup> The intermetallic compounds exhibit within a crystalline predetermined atomic positions for each constituent element. Alloys are a random mixture of metals, with one of the constituent elements' crystal structures adopted. In this project, some samples suggest the possibility of Si dissolution in the intermetallic compounds, which makes us uncertain about the terminology for such phases. To avoid ambiguity, we intend to call them intermetallic phases instead of intermetallic compounds or alloys.

## 1.4 Phase Transformation Mechanisms

### 1.4.1 Al-Fe-Si Ternary System

Understanding the Al-Fe-Si ternary system forms the foundation for comprehending the phase transformation mechanisms that occur during the hot stamping process (**Figure 1.6**).<sup>46,47</sup> In the phase diagram, each area represents one phase and is shown as different symbols, as defined in **Table 1.2**. Each univariant line represents the equilibrium between liquid and two crystalline phases. The invariant reactions inferred from the phase diagram are listed in **Table 1.3**.<sup>46-48</sup>

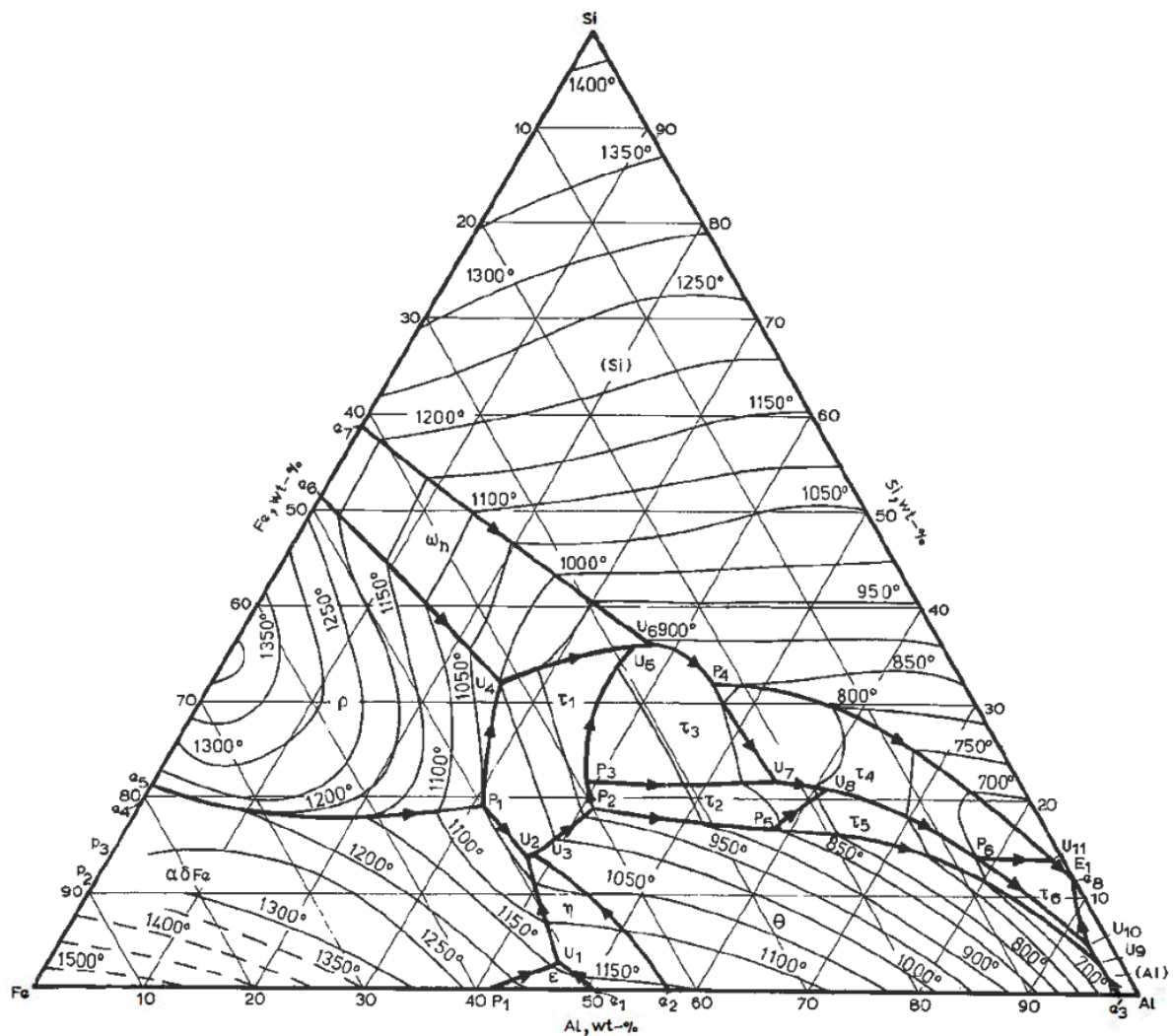


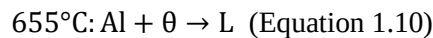
**Figure 1.6** The liquid projection of the Al-Fe-Si ternary system. Reprinted with permission from Taylor & Francis.<sup>46</sup>

**Table 1.3** Selected invariant reactions in ternary Al-Fe-Si system.<sup>46,48</sup>

| Symbol          | Temperature (°C) | Invariant reaction                              | Equation |
|-----------------|------------------|-------------------------------------------------|----------|
| E <sub>1</sub>  | 577              | $L \rightleftharpoons \tau_6 + (Al) + (Si)$     | 1.1      |
| U <sub>11</sub> | 600              | $L + \tau_4 \rightleftharpoons \tau_6 + (Si)$   | 1.2      |
| U <sub>10</sub> | 615              | $L + \tau_5 \rightleftharpoons (Al) + \tau_6$   | 1.3      |
| U <sub>9</sub>  | 620              | $L + \theta \rightleftharpoons (Al) + \tau_5$   | 1.4      |
| U <sub>8</sub>  | 790              | $L + \tau_2 \rightleftharpoons \tau_4 + \tau_5$ | 1.5      |
| U <sub>7</sub>  | 835              | $L + \tau_3 \rightleftharpoons \tau_2 + \tau_4$ | 1.6      |
| P <sub>5</sub>  | 855              | $L + \theta + \tau_2 \rightleftharpoons \tau_5$ | 1.7      |
| U <sub>4</sub>  | 1000             | $L + \rho \rightleftharpoons \omega + \tau_1$   | 1.8      |
| U <sub>3</sub>  | 1020             | $L + \eta \rightleftharpoons \theta + \tau_1$   | 1.9      |

#### 1.4.2 Phase Transformation Mechanisms

The Al-Si coating undergoes a series of complex liquification-solidification reactions during the hot stamping process.<sup>5,21,49</sup> As Grigorieva *et al.* indicated, based on the Al-Fe-Si phase diagram and Al-Si phase diagram, the initial mechanism is the melting of Al-Si coating and intermetallic phase in equation (1.1) from **Table 1.3**. Grauer *et al.* also found the proof of melting at 575°C using a differential scanning calorimetry experiment.<sup>50</sup> With increasing temperature, Rivlin *et al.* described the phase transformation of  $\tau_6$  to  $\tau_5$  in equation (1.3) from **Table 1.3**. Barreau *et al.* used SEM with a heating stage to monitor the specific reactions occurring at the surface during heating, and they found the proof of equation (1.3) happening.<sup>5</sup> With the support of electron microscopy measurements and the Al-Fe-Si phase diagram, Grigorieva *et al.* indicated the phase change of  $\tau_5$  to  $\theta$  in equation (1.4). Barreau *et al.* also observed a melting process in between 650 and 690°C,<sup>5</sup> with support of the Al-Fe binary phase diagram,<sup>33,44</sup> shown in equation (1.10):



At higher temperatures, Barreau *et al.* and Grigorieva *et al.* observed the transformation of  $\tau_5$  to  $\tau_2$  and  $\theta$ ,<sup>5,12</sup> which indicated equation (1.7) occurring. These five reactions give us a general

understanding of the mechanism that happens on Al-Si coating and steel interface during the heating process.

## 1.5 Characterization Methods

There are various characterization methods applied to identify intermetallic compounds generated in Al-Si coating during the heating process. The most frequently used characterization technique for intermetallic compound identification is SEM, combined with energy dispersive X-ray spectroscopy (EDS).<sup>8,12,21,25,51–55</sup> SEM-EDS suffers from slow measurement, low quantitative accuracy, and the risk of misleading results due to the measured signal originating from a volume that encompasses approximately 3  $\mu\text{m}$  of sample below the surface.<sup>56</sup> Electron backscatter diffraction (EBSD) has been applied to confirm the identity of intermetallics by their crystal structures.<sup>8,9,22,52,53,57–62</sup> A well-prepared sample is needed for EBSD due to its sensitivity to sample orientation and surface condition.<sup>63</sup> Another common technique applied to detect the identity of compounds is X-ray diffraction (XRD), which can detect the types of compounds in the given sample without specifying their exact location.<sup>8,9,24,30,31,55,64,65</sup> A new technique, Raman microscopy, is applied to characterize intermetallic phases in Al-Si coated steels under in situ high-temperature conditions.<sup>49</sup> This work indicates the effectiveness of Raman microscopy as a powerful technique for confirming the identity of intermetallic phases.

## 1.6 Research Motivation

The understanding of reaction mechanisms occurring in Al-Si coating during the hot stamping process was based on the invariant reactions inferred from Al-Fe-Si ternary phase diagram and Al-Fe binary phase diagram.<sup>5,12,50</sup> By only considering the invariant reactions from Al-Fe-Si phase diagram, the lowest temperature at which  $\eta$  initially appears is 1020 °C based on  $U_4$  from **Table 1.3**. However, previous research has shown that  $\eta$  can appear on samples at lower temperatures, such as, 600, 700, 882, 900, 905, and 907 °C.<sup>13,25,59</sup> This discrepancy suggested that considering only the invariant reactions cannot fully explain the mechanisms that happened on Al-Si coating and steel interface during the heating process. Other reactions must occur during the process in addition to the invariant reactions. Additionally, a more rapid, chemically specific, simple, and location-specific characterization technique is needed to identify intermetallic compounds due to the limitations of

previous characterization methods. Thus, this thesis introduces Raman spectroscopy for phase evolution mechanisms study on Al-Si coating and steel interface during heating process.

This thesis primarily focuses on the contamination of the furnace rollers by the melted Al-Si coating. A novel surface modification strategy, coating Fe-containing source on the surface of Al-Si coated steel, is applied to facilitate the growth of intermetallic layers, thereby mitigating furnace roller contamination during the hot stamping process. The developed Raman microscopic method is employed to study reaction mechanisms. It can test the impact of surface modification on mechanisms to assess the effectiveness of the Fe-containing source addition method in alleviating furnace roller pollution.

## 1.7 Thesis Overview

This work focuses on the phase evolution at the interface of Al-Si coating and the 22MnB5 steel during the heating process, which is the basic knowledge for alleviating the contamination problems of Al-Si coated 22MnB5 steel during the hot-stamping process.

**Chapter 2** describes the experimental methods used in this project, including sample preparation and characterization techniques.

**Chapter 3** introduces Raman mapping microscopy as a useful tool to infer the reaction mechanisms taking place at the interface of Al-Si coating and steel with increasing heating temperature. Samples were made by heating 12 Al-Si coated specimens at different temperatures for 10 minutes under air. The cross-section of heated samples and one as-received sample were characterized and analyzed to infer the reactions that happened with elevated temperatures.

**Chapter 4** expands the scope of the Raman mapping microscopy approach to provide more detailed insight into phase transition mechanisms by combining heating temperature and duration. A total of 72 samples were made by heating at variable temperatures and times to reveal the nature of reactions at the interface of Al-Si coating and steel during the heating process. The map distribution results of heated samples indicate that the diffusion of Fe is the primary driven for intermetallic phase reactions and growth.

**Chapter 5** provides a surface modification method to alleviate the contaminations that happened during the hot stamping process. The iron containing source were coated on the top of Al-Si coated steel, and then the Raman microscopic mapping was used to infer the influence on reaction

mechanisms during the heating process. The viability of this Fe coating was assessed by comparing the Fe-coated sample mechanisms and no Fe-coated sample mechanisms. The results indicate that the samples with the addition of Fe elements on the surface undergo the phase transition at lower temperatures within the same heating duration and shorter heating time within the same heating temperature. This rapid phase transition effectively reduces the time during which the liquid phase exists, leading to a decrease in the generation of pollution.

**Chapter 6** summarizes the results of this project and suggests future works.

## Chapter 2

### Methodology

#### 2.1 Sample Preparations

##### 2.1.1 Synthesis of Intermetallic Standards

A series of binary Al-Fe and ternary Al-Fe-Si phases were synthesized for use as characterization standards by combining appropriate molar ratios of pure Al granules (Puratronic, 99.999%), Fe powder (Alfa Aesar, 98%), and Si powder (Alfa Aesar, 99.9%) and melting them together using an electric arc under an Argon atmosphere.<sup>66</sup> The ingot obtained upon cooling was crushed using an iron mortar and pestle, then subsequently ground to a powder using an agate mortar and pestle. Targeted samples include  $\tau_2$ ,  $\tau_3$ ,  $\tau_4$ ,  $\tau_5$ ,  $\tau_6$ ,  $\eta$  and  $\theta$ .

##### 2.1.2 Synthesis of Cross-sectional Al-Si Coated Steel Samples

Furnace-heated specimens were prepared using Al-Si coated 22MnB5 steel from a commercial supplier (AS150 Usibor 1500, ArcelorMittal).<sup>10</sup> The Al-Si coating has a nominal composition of 10% (wt.) Si and a weight of 1.28 g/cm<sup>2</sup>, corresponding to an as-received thickness of approximately 25  $\mu\text{m}$ . The specimens were cut into 38 mm  $\times$  19 mm pieces and degreased and cleaned with ethanol and then deionized water. Cleaned samples were heated under different heating conditions and then removed from the furnace and allowed to passively cool to room temperature in the air. Cross sections of each sample were mounted and polished for further characterization.

##### 2.1.3 Surface Modification

Coupons measuring around 20 mm  $\times$  20 mm  $\times$  1.7 mm were cut from Al-Si coated 22MnB5 steel blanks and used as the substrate for Fe-rich coating electrodeposition using chronopotentiometry technique. The specimens were cleaned using mili-Q water (18.2 M $\Omega$ ), soapy water, and ethanol. The Fe electrodeposition method followed previous studies.<sup>67,68</sup> The electrolyte solution was prepared with a concentration of 0.143 M iron(II) sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ , Fisher Chemical),  $6.2 \times 10^{-3}$  M citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , Fisher Chemical), and mili-Q water. A Bio-logic SP-300 potentiostat was used for Fe electrodeposition. An around 150 mL electrolyte was heated and kept at 50 °C with mechanical stirring. The electrodeposition was carried out at a constant current density of 0.03 A/cm<sup>2</sup> for 10 minutes. A platinum (Pt) mesh was used as counter electrode and a cleaned steel plate as

working electrode. The reduction of  $\text{Fe}^{2+}$  occurred at working electrode, resulting in the deposition of a Fe-rich coating on the steel plate. The electrodeposited samples are stored under air, leading to the oxidation of Fe-rich coating.

## **2.2 Characterization Methods**

### **2.2.1 Raman Microscopy Measurements**

Raman microscopy measurements were performed using a Renishaw inVia Reflex system equipped with a sample stage capable of 100 nm positioning in three dimensions. A 532 nm (Renishaw DPSSL laser, 50 mW) laser filtered to 10% intensity was focused on the samples using a 50 $\times$  objective, with a 2400 lines/mm grating used to analyze Raman scattered light. This provided a Raman shift spacing of 1.2  $\text{cm}^{-1}$  between individual data points and a maximum spatial resolution of approximately 650 nm. Spectra on characterization standards were acquired between 111 and 1370  $\text{cm}^{-1}$  with a total acquisition time of 20 seconds. The surface area of powders was sampled to ensure representative spectra were obtained. Spectra on heat treated steel plates were acquired across using a two-dimensional (2-D) grid with 1  $\mu\text{m}$  spacing between spectra acquired in the x and y dimensions with the same acquisition settings used on measurement standards. Grid size is variable per sample, but typically on the order of 5  $\mu\text{m}$  by 30  $\mu\text{m}$ . All spectra were acquired and analyzed using the Renishaw 5.5 software package. Spectra were prepared for analysis by simple normalization of the data between 111 to 500  $\text{cm}^{-1}$  for intermetallic phases and data between 111 to 800  $\text{cm}^{-1}$  for iron oxides to span zero to unity.

### **2.2.2 Powder X-ray Diffraction**

Powder X-ray diffraction (P-XRD) was performed on the synthesized standards using either an INEL X-ray diffractometer ( $\tau_2$ ,  $\tau_3$ ,  $\tau_5$ ,  $\tau_6$ , and  $\theta$ ) or a PANalytical Empyrean X-ray diffractometer ( $\tau_4$  and  $\eta$ ) at room temperature. Diffraction patterns for each intermetallic standards were compared with previously published structures found in the Inorganic Crystal Structure Database (ICSD).<sup>69</sup> Rietveld refinements were performed using the GSAS-II software package.<sup>70</sup>

## Chapter 3

# Raman Mapping Spectroscopic Analysis of the Reactions Between Al-Si Coating and Steel

### 3.1 Introduction

The transfer of Fe from the steel substrate to the Al-Si coating induces a sequence of complex liquefaction-solidification reactions within the coating.<sup>5,21,49</sup> Efforts to identify the chemical reaction steps associated with the overall reaction have largely focused on ex situ electron microscopic analysis of specimens heated within furnaces at different temperatures.<sup>12,21,48,50,51,59,71,72</sup> In as-received samples, there is typically an Al-Si matrix present on top of a thin intermetallic layer at the steel-coating interface. This intermetallic interface is formed during the dip-coating process, and components such as  $\tau_5$  and  $\tau_6$  are commonly observed in this context.<sup>2,5,12,49,73</sup> SEM-EDS and EBSD have been used to identify a range of intermetallic compounds that emerge during the coating transformation process, including the ternary Al-Fe-Si compounds commonly denoted  $\tau_1$  through  $\tau_6$ , and the binary phases  $\eta$ ,  $\theta$ ,  $\alpha_2$ , and  $\zeta$ .<sup>2,12,21,51,59</sup> The Al-rich corner of the ternary Al-Fe-Si phase diagram is complex, with numerous invariant reactions linking together three or more phases.<sup>41,46,48</sup> The gradual conversion of the Al-Si coating to a complete Al-Fe-Si intermetallic coating requires an increase in the Fe-content of the coating, which means that the coating composition must change with time and temperature. The alteration in coating composition gives rise to the potential for partial solidification and localized reactions specific to the interface. Consequently, questions arise concerning the mechanistic and kinetic significance of the individual phases that form within the coating as its structure undergoes evolution. In-situ light reflection measurements made by shining a laser onto the surface of a heated specimen indicate a multistep liquefaction-resolidification process occurs between *ca.* 570 and 700 °C,<sup>73</sup> with coating thickness affecting times required for complete conversion of the coating.<sup>25</sup>

Raman microscopy is frequently used to characterize solid-state materials, but it has seen little application in the analysis of Al-Si coatings and Al-Si-Fe intermetallics. Performing Raman microscopy on solids can be a challenging task due to weak signals and potential fluorescence interference. However, the measurement of vibrational frequencies within the lattice offers a chemical fingerprint that allows for species identification with higher confidence compared to techniques such

as EDS.<sup>74–78</sup> Klassen *et al.* recently pioneered the application of Raman microscopy to Al-Si coated steels under in-situ high temperature conditions.<sup>49</sup> The analysis identified several distinct spectra that appeared at specific temperature thresholds. These spectra were assigned based on ex-situ analysis of cooled specimens using EDS and by comparing them with previously published reaction mechanisms. This study demonstrated the effectiveness of Raman microscopy in detecting intermetallic phases formed in the Al-Fe-Si system. However, the sampling approach employed limited the extraction of detailed mechanistic information, and the lack of crystalline standards for comparison resulted in tentative assignments of Raman spectra. A more comprehensive understanding of the spatial distribution of phases throughout the coating can be achieved through a systematic spectroscopic analysis of cross-sections of the thin coatings. By expanding this systematic approach to cover a range of temperatures has the potential to provide broader insights into the mechanisms underlying the evolution of the coating structure.

Herein, we present a new approach using cross-sectional Raman microscopic mapping to investigate the mechanism of the conversion of Al-Si coatings to intermetallic coatings on steel substrates. We synthesized and characterized intermetallic phases using Raman spectroscopy and XRD measurements to establish their Raman vibrational fingerprints. By comparing the Raman spectra obtained from a series of Al-Si coated steel sheets heated at temperatures ranging from 570 to 900 °C with these fingerprints, we were able to identify the temperature-dependent composition of the Al-Si coating. The spatial information obtained through this spectroscopic mapping technique revealed that the coating structure undergoes a series of interface-specific chemical reactions, with  $\tau_5$ ,  $\eta$  and  $\tau_2$  playing crucial roles in the overall transformation.

## 3.2 Results

### 3.2.1 Characterization of Intermetallic Standards

A series of intermetallic standards ( $\tau_2$ ,  $\tau_3$ ,  $\tau_4$ ,  $\tau_5$ ,  $\tau_6$ ,  $\theta$ , and  $\eta$ ) were synthesized by arc melting method and characterized to identify the Raman spectra for structures of interest. Powder X-ray diffraction patterns (P-XRD) indicate that a single phase is present for the binary compositions  $\theta$  and  $\eta$ , but contaminants in all ternary phases ( $\tau_2$  -  $\tau_6$ ; **Figure 3.1A**). Such impurities in the ternary phases are to be expected given the complex interaction between many phases in the aluminum-rich corner of the ternary phase diagram for Al-Fe-Si.<sup>41,46,48</sup>

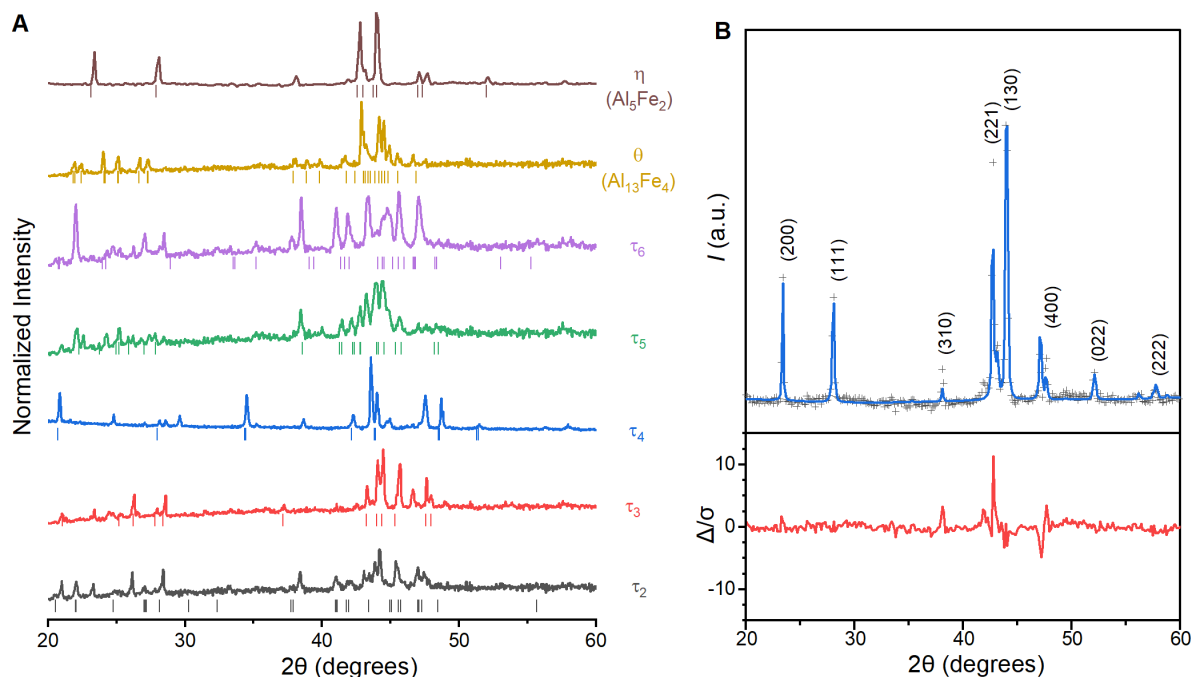


**Figure 3.1** Powder X-ray diffraction patterns for synthesized intermetallic phases. **(A)** Experimental patterns (solid lines) compared to Bragg peaks predicted by ICSD structures cited in the text (vertical dashes). **(B)** Sample Rietveld refinement performed on synthesized  $\eta$ . Remaining samples are provided in **Figures A.1-A.6**.

Each diffraction patterns were compared with previously published structures in ICSD.<sup>69</sup> Rietveld refinements were applied on each synthesized intermetallic phases (**Figures A.1-A.6**), and refinement for  $\eta$  is shown in **Figure 3.1B**. Rietveld refinements on each XRD pattern nonetheless confirm that the majority component of each characterization standard is the desired phase:  $\theta$  can be refined to the  $C2/m$  space group (ICSD 57795),<sup>79</sup>  $\eta$  to  $Cmcm$  (ICSD 57796),<sup>80</sup>  $\tau_2$  to  $R-3$  (ICSD 99169),<sup>81</sup>  $\tau_3$  to  $Cmma$  (ICSD 40317),<sup>37</sup>  $\tau_4$  to  $I4/mcm$  (ICSD 199347),<sup>82</sup> and  $\tau_5$  to  $P63/mmc$  (ICSD 422224).<sup>83</sup> Refinements on attempted syntheses of  $\tau_6$  showed a small amount of the expected  $A2/a$  (ICSD #54050) phase (**Figure A.5**),<sup>84</sup> but always as a minor component. Metallic Al was found in  $\tau_2$ ,  $\tau_4$ ,  $\tau_5$  and  $\tau_6$ , seen as Bragg peaks that match those expected for the  $Fm-3m$  space group (ICSD 18839).<sup>85</sup> According to refinements, minor side products except for the mentioned Al can be inferred for each synthesized samples: synthesized  $\tau_2$  has  $\tau_3$  as a minor side product,  $\tau_3$  has  $\tau_2$ ,  $\tau_4$  has  $\tau_3$ , and  $\tau_5$  has  $\theta$

and  $\tau_2$ . These characterization standards provide sufficient purity for the purposes of Raman microscopic characterization.

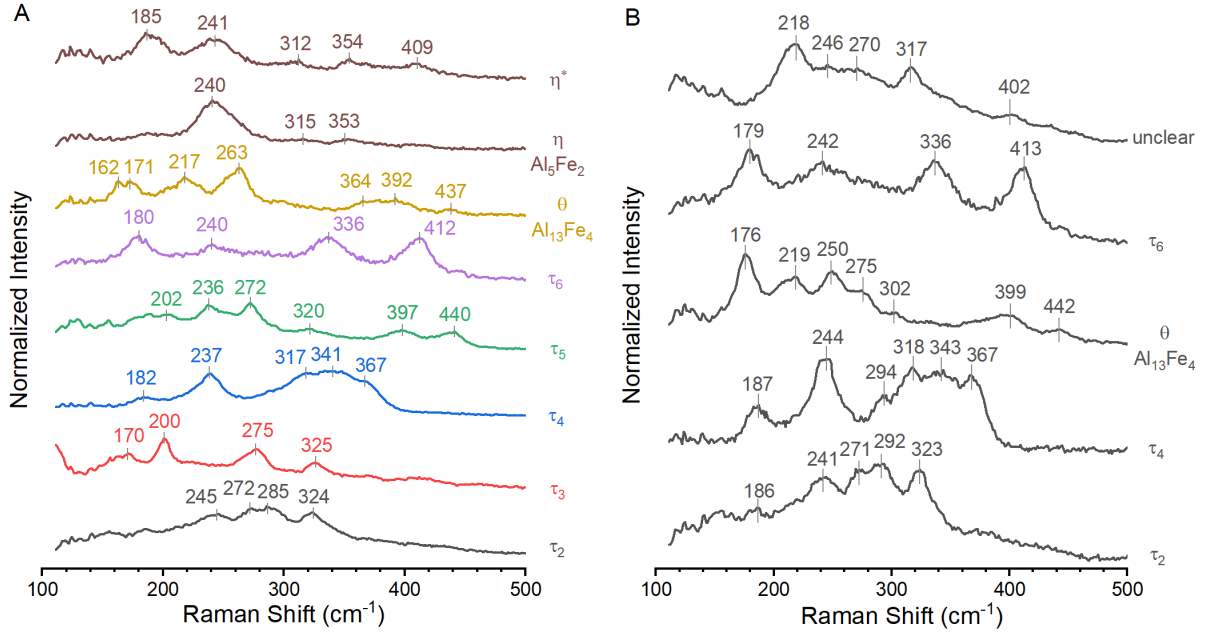


**Figure 3.2** Raman spectra for synthesized intermetallic standards. **(A)** Raman spectra assigned to each phase using characterization standards. **(B)** All unique Raman spectra observed within sample following attempted synthesis of  $\tau_6$ . The bottom three match  $\tau_2$ ,  $\tau_4$  and  $\theta$ . The identity of top spectrum remains unassigned and the second from top is assigned to  $\tau_6$ .

Spectroscopic analysis of the characterization standards with a Raman microscope identified the major components and impurities. A series of at least 15 Raman spectra were acquired across the surface of each characterization standard. Spectra that were mutually consistent for each characterization standard were averaged together to enhance the single-to-noise ratio. These spectra show distinctive vibrational fingerprints in the region between 100 and 500  $\text{cm}^{-1}$ ; the Raman spectrum for the Al-Si mixture was consistent with that of elemental silicon, with a single strong peak at *ca.* 520  $\text{cm}^{-1}$ . The assignment of each individual spectrum to a given intermetallic phase (**Figure 3.2A**) was performed by considering the prevalence of each type of Raman spectrum for a given standard, then cross-comparing with spectra acquired on the other standards. This approach confirmed pure phases of  $\theta$  and  $\eta$ , albeit with  $\eta$  showing variations in intensity of peaks that may indicate strain or lattice defects. Ternary samples identified the phase of interest plus contaminant phases:  $\tau_2$  contained

contributions from  $\tau_6$ ,  $\tau_3$  contained  $\tau_2$ ,  $\tau_4$  contained  $\tau_3$ , and  $\tau_5$  contained  $\tau_2$  and  $\theta$ . The purity of  $\tau_6$  is lowest for all synthesized samples, as seen with XRD, yielding five unique Raman spectra within the samples (**Figure 3.2B**). Three of these spectra can be assigned as  $\tau_2$ ,  $\tau_4$  and  $\theta$ . One of the remaining two spectra is tentatively assigned as  $\tau_6$  based on emergence of this spectrum in the coating at temperatures expected for  $\tau_6$ , and on previous assignment.<sup>49</sup> Spectrum assignments for  $\tau_5$ ,  $\tau_6$ ,  $\eta$  and  $\theta$  agree with past assignments.<sup>49</sup> To the best of our knowledge, the remaining spectra have not been previously reported.

### 3.2.2 Structural Evolution of Coatings

The time required for Al-Si coated 22MnB5 steel coupons to attain a stable temperature was determined by measuring temperature as a function of time. Significant structural evolution of the Al-Si coatings is known occur between 570 and 670 °C.<sup>5,25,73</sup> A furnace was pre-heated to each selected set-point temperature before placing a steel sample with an attached thermocouple within the center of the furnace. Temporal temperature measurements indicate that the steel samples reach the furnace set point temperature between 5-7 minutes, depending on the set-point temperature (**Figure 3.3**). While both time and temperature variables are important to completely describe evolution of the coating structure, a single heating period of 10 minutes was used for all samples in order to establish the viability of cross-sectional spectroscopic analysis.

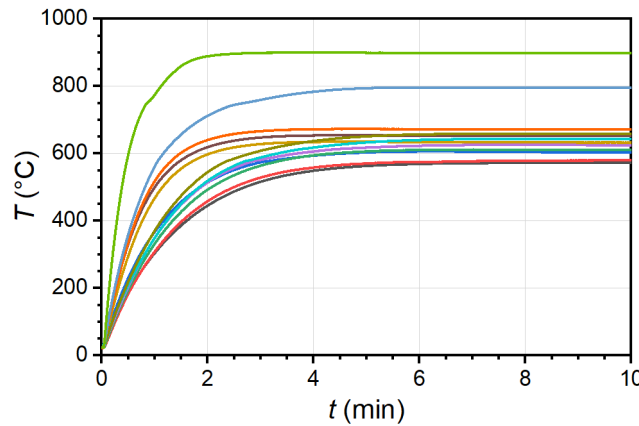


**Figure 3.3** Temperature profiles acquired on aluminum silicon coated 22MnB5 steel coupons placed in a tube furnace. Set-point temperatures are in 10 °C steps from 570 to 670 °C (without 590 °C), plus 800 and 900 °C.

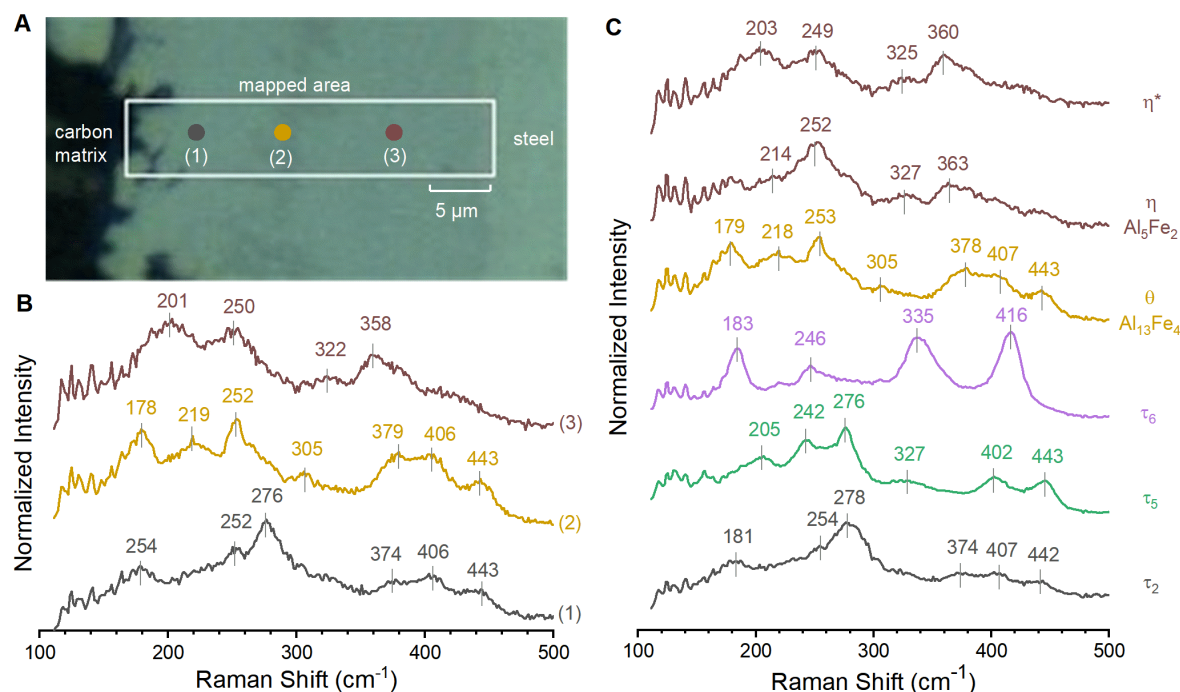


**Figure 3.4** Cross-sectional Raman microscopic mapping of a heat-treated aluminum silicon coated 22MnB5 steel coupons. **(A)** A white light microscope image of the mapped area, with a box around the mapped area. Sample shown corresponds to heat treatment at 800 °C for 10 minutes. **(B)** Raman spectra acquired at the positions in the white light image indicated. **(C)** All unique spectra identified across all 4098 spectra in 13 cross sectional Raman microscopic maps on temperature treated samples.

A total of 12 cleaned specimens were heated for 10 mins in a muffle furnace at a set point temperature and then removed from the furnace and allowed to passively cool to room temperature. Set-points of 570, 580, 600, 610, 620, 630, 640, 650, 660, 670, 800, and 900 °C were selected to capture temperature ranges where significant structural evolution has been previously noted.<sup>25,49,73</sup> Cross sectional Raman microscopic mapping was used to identify intermetallic phases present in Al-Si coated 22MnB5 after heating at temperature set points. Cooled specimens were mounted within carbon pucks and polished to a mirror finish to expose a cross section of the steel coupon and the coating. Raman microscopic mapping was performed by acquiring discrete spectra in 1 μm steps to generate a 2-D map. Map sizes vary slightly due to variations in thickness of the Al-Si coatings, but each map was at least 26 μm by 6 μm. These maps extend from the top of the Al-Si coating to the steel interface. A sample of the mapping procedure shows the area mapped for the sample heated at

800 °C (**Figure 3.4A**) and the three unique spectra observed within this sample (**Figure 3.4B**). This treatment at 800 °C yields a layered structure, where a continuous layer of  $\eta$  sits atop the steel substrate and is followed by alternating layers of  $\theta$  and  $\tau_2$ . Inspection of all 4098 spectra obtained across the 13 Raman microscopic maps identified a total of 6 unique spectra that are presented as an average spectrum on a per-phase and per-sample basis (**Figure A.7**) and as the overall average across all samples on a per-phase basis (**Figure 3.4C**). In addition, spectra for the Al-Si mixture and elemental silicon were observed as a single, strong peak at *ca.* 520  $\text{cm}^{-1}$ . Comparison of these unique spectra to the characterization standards shows that the dominant components of these heat-treated samples are  $\tau_2$ ,  $\tau_5$ ,  $\tau_6$ ,  $\theta$ ,  $\eta$ .

Cross-sectional Raman microscopic mapping enables identification of the temperature thresholds and location at which major chemical reactions take place during structural evolution of the Al-Si coatings. As-received samples have a single layer of  $\tau_5$  on top of the steel substrate, beneath a layer of Al-Si containing elemental Si particles (**Figure 3.5A**).<sup>73</sup> It is well established that the Al-Si mixture melts at 577 °C, and has been demonstrated for Al-Si coated 22MnB5 steel.<sup>5,25,49,73</sup> Raman maps indicate that the structure and composition of the coating remains stable up to 580 °C (**Figures 3.5B-3.5C**), despite the melting of the Al-Si overlayer. A chemical reaction then begins at approximately 600 °C, with a thin layer of  $\theta$  forming at the interface between  $\tau_5$  and the steel substrate (**Figure 3.5D**). At 610 °C the  $\theta$  layer remains approximately static while the intermetallic layer on top of it grows and transforms from  $\tau_5$  into  $\tau_6$  (**Figure 3.5E**). Heating to 620 °C converts the  $\theta$  layer to  $\eta$  (**Figure 3.5F**), leading to subsequent formation of  $\tau_5$  at the interface between  $\eta$  and  $\tau_6$  (**Figure 3.5G**). The thickness of the  $\tau_5$  and  $\eta$  layers begin to increase at 640 °C (**Figure 3.5H**). Full conversion of  $\tau_6$  into  $\tau_5$  is achieved at 650 °C, with concomitant growth of the  $\tau_5$  layer (**Figure 3.5I**). The Raman spectra for  $\eta$  transform to that designated as  $\eta^*$  at 660 °C, with the layer significantly increasing in thickness. This  $\eta^*$  layer then persists above 670 °C (**Figures 3.5J-3.5K**). The greater intensity and better-defined peak shapes in the Raman spectra (**Figure 3.2A**) suggest that this transformation results in a higher degree of crystallinity. Growth of  $\theta$  at the interface between  $\eta^*$  and  $\tau_5$  is then observed at 800 °C, along with formation of  $\tau_2$  atop the  $\theta$  layer (**Figure 3.5L**). Transformation of  $\theta$  to  $\tau_2$  at 900 °C (**Figure 3.5M**) suggests that a  $\tau_5$  to  $\theta$  transformation precedes a  $\theta$  to  $\tau_2$ .

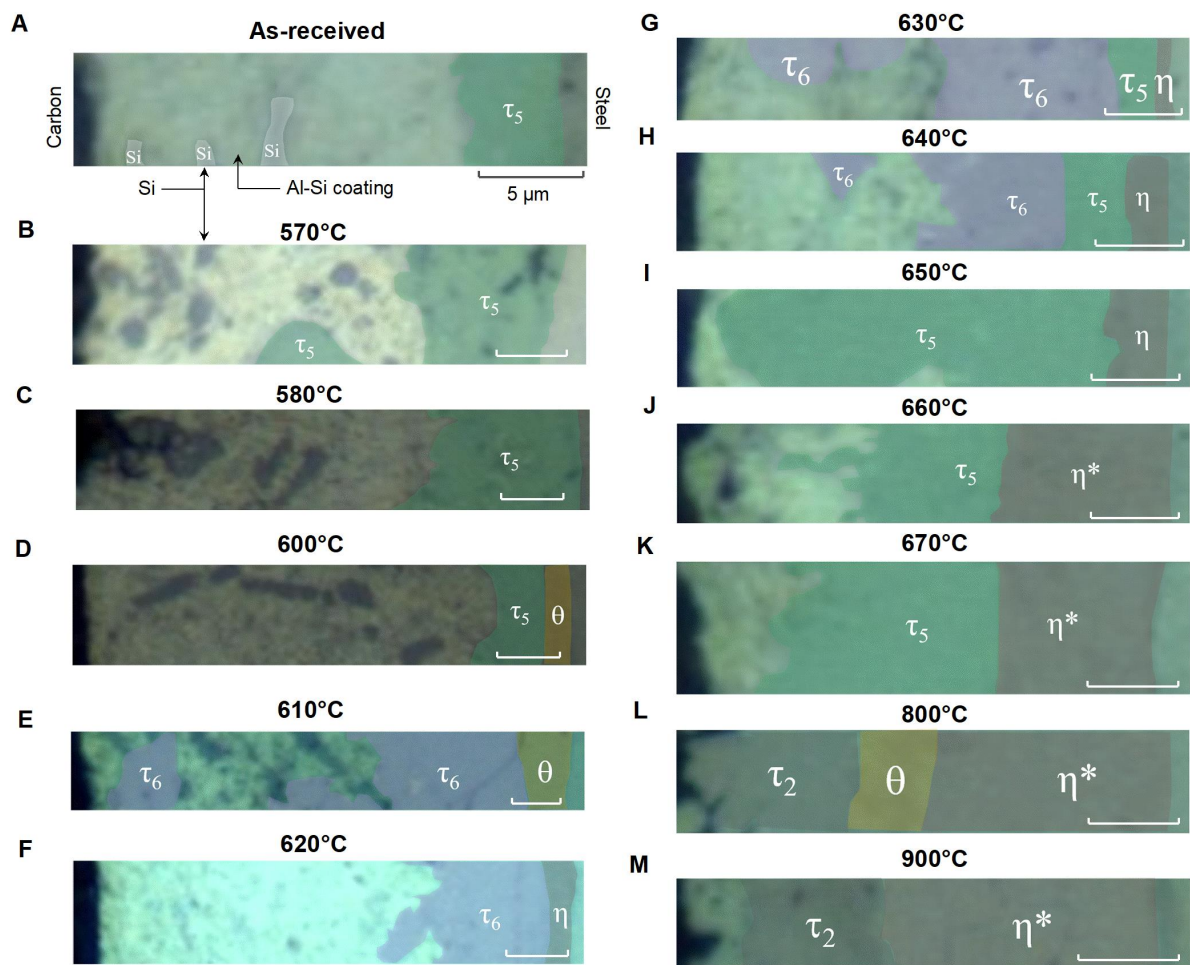


**Figure 3.5** Chemical maps derived from Raman microscopic mapping of Al-Si coatings on steel substrates. **(A)** An as-coated sample is labeled with carbon matrix, Si, Al-Si coating,  $\tau_5$ , and steel to show the layout of the maps. Additional maps for samples heated for 10 minutes at **(B)** 570, **(C)** 580, **(D)** 600, **(E)** 610, **(F)** 620, **(G)** 630, **(H)** 640, **(I)** 650, **(J)** 660, **(K)** 670, **(L)** 800, and **(M)** 900 °C have the similar layout with the as-received sample. The scale bar in each panel corresponds to 5  $\mu\text{m}$ .

### 3.3 Discussion

Raman microscopic mapping shows the emergence of intermetallic phases at temperatures that are consistent with observations in previous studies. In the case of the as-received steel, for example, the dip coating process is known to produce a layer of  $\tau_5$  at the steel interface.<sup>2,12,18,52,60</sup> This layer acts as a barrier between the Al-Si coating and the Fe in the substrate steel, thereby inhibiting further

transformation of the Al-Si coating up to 580 °C.<sup>2,53</sup> Other compounds that have been identified as minority components after the hot-dipping process include  $\tau_1$ ,  $\tau_6$ ,  $\eta$  and  $\theta$ .<sup>12,21,22,25</sup> Previous studies have reported that  $\theta$  and  $\eta$  form at *ca.* 650 °C,<sup>50</sup>  $\tau_2$  at 830 °C,<sup>12</sup> AlFe at 882 °C,<sup>59</sup> and  $\tau_1$  at 900 °C.<sup>13,59</sup> AlFe and Al<sub>2</sub>Fe<sub>2</sub>Si emerge at higher temperatures, around 900 °C.<sup>13,59</sup> Some EDS and electron back-scattering diffraction measurements suggest that Al-Si coated steel heated to 900 °C contain mixtures of  $\tau_1$ ,  $\tau_2$ , and  $\omega$ ,<sup>46</sup> while others show  $\tau_1$ ,  $\tau_5$ , AlFe, Al<sub>2</sub>Fe,  $\theta$ , and  $\eta$ .<sup>13,22,25,49,59</sup> Variations in the composition of the Al-Si-Fe layer may arise due to variations in heating time. The temperatures at which Raman spectra identify new phases here are consistent with these observations, attesting to the accuracy of the Raman spectroscopy-based assignment.

Spectra within the Raman maps show no contributions from common oxide compounds of Si, Al or Fe. Electron microscopy has shown that such Al-Si coatings form a *ca.* 10 nm thick coating of Al<sub>2</sub>O<sub>3</sub> on the outer interface that limits oxidation into the bulk of the coating.<sup>5</sup> Aluminum oxide is most common in the corundum ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) structure, which yields 8 strong peaks in Raman spectra;<sup>86</sup> iron oxides tend to form hematite at temperatures above 500 °C, which also adopts the corundum structure and exhibits 7 strong Raman peaks.<sup>87</sup> A total of six well defined peaks are expected for SiO<sub>2</sub>.<sup>88</sup> The fingerprints for these oxides are not observed in any of the spectra obtained. Any oxide coatings present are therefore believed to be restricted to surface coatings on the scale of tens of nanometers.

Past analyses of Al-Fe-Si ternary compositions have identified at least 11 invariant reactions involving intermetallic phases in the 573 to 900 °C temperature range.<sup>46,48</sup> A sample of the low temperature reactions include: equilibria between  $\tau_6$  and an Al-Si mixture at 573 °C; between  $\tau_4$  and  $\tau_6$  at 600 °C; between  $\tau_5$  and  $\tau_6$  at 620 °C; and between  $\tau_4$ ,  $\tau_5$  and  $\tau_6$  at 700 °C.<sup>46–48</sup> The complete conversion of the Al-Si coating to an intermetallic coating (**Figure 3.5**), however, necessitates that Fe content within the coating increases with time and temperature. The chain of reaction steps needed to achieve this overall conversion is therefore tied to a line traversing the initial Al-Si binary composition in the Al-rich corner of the ternary phase diagram to the Fe-rich corner. The observed evolution of Al-Si coatings in a layered fashion creates local reaction environments and local diffusion conditions that may result in divergence from these invariant reactions.

Five major chemical reactions appear sufficient to describe the overall macroscopic coating transformation process observed here, which align with mechanisms proposed in previous studies.<sup>5,12</sup> We note that the intermetallic phases appear stable to small degrees of non-stoichiometry, as

evidenced by variability in the stoichiometry for multiple crystal structures published.<sup>5,31,48</sup> The five reactions include: equation (3.1) precipitation of  $\tau_5$  upon Fe contacting with the liquid Al-Si mixture; equation (1.4) removal of Si from  $\tau_5$  to yield  $\theta$ ; equation (1.3) interconversion between  $\tau_5$  and  $\tau_6$  by changes in Fe:Si content; equation (3.2) adjusting the Fe-content to convert between relatively Fe-deficient  $\theta$  and Fe-rich  $\eta$ ; and equation (3.3) accumulation of Si to convert  $\theta$  to  $\tau_2$ :



The consistent thickness of the  $\tau_5$  layer up to 600 °C confirms that equation (3.1) is self limiting within the liquid Al-Si medium, implying that leeching of Fe into  $\tau_5$  is extremely slow. Formation of  $\theta$  at the internal  $\tau_5$ |steel interface requires depletion of Al and Si, as represented by equation (1.4). It is notable that this region is spatially isolated from the liquid-phase Al-Si mixture and the 600 °C temperature is below any reported invariant reactions involving  $\tau_5$ .<sup>5,12,46,48</sup> The excess Al and Si must therefore be transferred into the  $\tau_5$  overlayer – this is visible with the conversion of  $\tau_5$  to  $\tau_6$  through equation (1.3) at 610 °C. The 620 °C conversion of  $\theta$  to the more Fe-rich  $\eta$  phase at the steel interface is attributed to equation (3.2), driven by a localized increase in rate of Fe leeching. Previous studies have demonstrated that the appearance of  $\eta$  is critical for growth in the thickness of the intermetallic layer,<sup>89</sup> which suggests that  $\eta$  facilitates both dissolution of Fe from the steel substrate and diffusion into the depth of the coating. Evidence for  $\eta$  facilitating Fe leeching and diffusion is seen here as a reappearance of  $\tau_5$  at 630 °C at the internal  $\tau_6$ | $\eta$  interface and its subsequent growth until 650 °C. This reaction proceeds via Fe enrichment of  $\tau_6$  to  $\tau_5$  through equation (1.3). Growth in the thickness of  $\eta$  with further temperature increase likely proceeds through a sequence of reactions (1.4) and (3.2), which would involve diffusion of Si towards the exterior of the coating and diffusion of Fe from the steel substrate to the resultant  $\eta$ | $\theta$  interface with paired Al diffusion towards the steel. Evidence for such a two-step process is seen in the data at 800 °C, where a layer of  $\theta$  sits atop  $\eta$ , and the data at 900 °C, where  $\theta$  is converted to the Si-rich  $\tau_2$  phase through equation (3.3). This analysis suggests that three of the phases are critical for structural evolution of the coating:  $\tau_5$  appears to be the preferred product until Fe-content becomes too high;  $\eta$  is critical for facilitating the leeching of Fe

from the steel substrate; and  $\tau_2$  becomes the phase where all Si from the initial Al-Si mixture is accumulated.

The Raman microscopic mapping protocol developed here provides a rapid analysis that is complimentary to traditional analyses previously employed to study the evolution of Al-Si coatings. The structural evolution of these coatings has been most frequently studied using cross sectional SEM-EDS analysis, where morphology and elemental composition enable distinction of different phases.<sup>49</sup> This approach has high spatial resolution but phase identification relies upon an approach that lacks chemical specificity. Specifically, SEM provides visualization of a surface while EDS probes elemental composition within a volume that typically spans several micrometers in three dimensions. Consequently, it is necessary to assume that the sample is homogeneous across its depth, and that the volume being probed does not extend to neighboring compounds. Raman microscopic mapping sacrifices some spatial resolution, but vibrational fingerprints provide chemical specificity that boosts confidence in identification of chemicals of interest. The dispersion of sub-micrometer particles of secondary phases throughout the coating cannot be excluded, but bulk phase transitions such as those observed here can be tracked with high confidence. The Raman microscopic mapping process developed here not only provides insight into the mechanism by which aluminum silicon converts to intermetallic phases, but also an accessible tool that facilitates confident phase identification. This will enable the development of strategies capable of rapidly analyzing structural evolution in such coatings, such as through combination of image segmentation and machine learning protocols to study semi-automate structure analysis. This will, for example, expedite analysis of how structural evolution mechanisms change with changing heating duration, temperature, coating formulation, or heating rate. These results provide the possibility for optimizing industrial production.

### 3.4 Conclusions

The structural evolution of Al-Si coatings on a 22MnB5 steel alloy during heating was analyzed using cross-sectional Raman microscopic mapping. The Raman spectroscopic fingerprints for individual intermetallic phases were identified by synthesizing and characterizing the compounds of interest. This information was used to identify the components present in 13 specimens that were heated to different set-point temperatures. Spectroscopic mapping demonstrated that the coating structure evolved in a layered fashion, consistent with past observations. The bulk structural evolution under our heating conditions consists of a sequence of reaction mechanism steps that occur at discrete

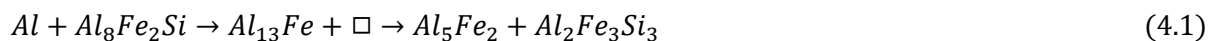
interfaces. Analysis of the nature of these transitions leads us to propose that structural evolution is dominated by five critical reaction steps, with each step driven by gradual diffusion of Fe and Si towards the exterior interface, and aluminum towards the inner interface. Important roles are observed for  $\eta$ , which facilitates transfer of Fe from the steel substrate to the coating and subsequent diffusion outwards, and  $\tau_2$ , which is the ultimate destination of Si from the original Al-Si mixture. These insights build on past studies, which have also shown that both the rate of heating and the temperature dwell time can affect observed structures. The low cost and rapid analysis of thin coatings demonstrated here can be applied to build a comprehensive understanding of the interfacial reaction mechanisms; the technique can also be applied to quantitatively test strategies to manipulate how the structure of such Al-Si coatings evolve. It is expected that this will facilitate the development of strategies to speed up the solidification of Al-Si coatings, which would significantly decrease furnace maintenance fees in the global automotive hot-stamping industry.

## Chapter 4

### Investigating the Reaction Mechanisms of Al-Si Coating and Steel through Variations in Heating Time and Temperature

#### 4.1 Introduction

Researchers have conducted various studies on the reactions that occur between Al-Si coating and steel during the heating process.<sup>5,9,12,25,49–51,59,73,90–92</sup> In addition to studying the temperatures at which reactions occur,<sup>5,12,21,49,50</sup> researchers also investigated the influence of heating time or heating rate on the reactions.<sup>5,9,12,25,50,51,59,73,90–92</sup> One approach is to control specific heating profiles and study the phase transformations of the coating at a particular state within the heating profile.<sup>5,50,51,91,92</sup> Jenner *et al.* used this method to describe the Al-Si coating evolution during the heating process with a 10 °C/s or 5 °C/s heating rate.<sup>51</sup> Barreau *et al.* used an in-situ characterization method to investigate the influence of different rates on the surface morphology for Al-Si coating heating to 900 °C.<sup>5</sup> Another research method involves placing the samples in a furnace set at a predetermined temperature and heating them for different durations, followed by studying the phase transformations.<sup>9,12,25,59,73,90</sup> Grigorieva *et al.* placed Al-Si coated steel samples in a furnace at 900 °C and extracted them at different heating times, obtaining samples heated at 615, 830, and 900 °C, thereby inferring the occurrence of equation (1.1), equation (1.4), and equation (1.7).<sup>12</sup> Windmann *et al.* heated steel samples at 920 °C for different heating time to investigate the phase evolutions.<sup>9</sup> Within first 2 minutes, the phase evolution can be described by:



where  $\square$  represent an unidentified phase. After 2 mins dwell time, all the intermetallics have the trend to transform to AlFe with the extent of transformation varying with different heating times. Another study focused on the influence of heating time at 600 and 800 °C, which indicates that Fe diffusion occurs more rapidly for samples heated under 800 °C.<sup>73</sup> The previous studies provide a general and preliminary understanding of the influence of heating time and temperature on phase transition mechanisms. A more comprehensive analysis of time and temperature on reaction is enabled by the Raman microscopic mapping approach. This will provide finer details than have already been established.

This chapter expands the application of Raman microscopic mapping technique and studies the influence of heating time and temperature on the reaction mechanisms of Al-Si coatings with steel. Samples were heated between 570 and 900 °C for 1, 2, 4, 6, 8, and 10 minutes, and the resulting phase distributions were studied and compared. The results indicate that a series of reactions occurred between the Al-Si coating and the steel under heating, and these reactions are influenced by both the heating time and temperature. One Al-Si coated sample was subjected to heating at 590 °C for 3 days, and the results showed the presence of  $\theta$  and  $\eta$  on the heated sample. According to the invariant reactions (**Table 1.3**), the formation temperatures for  $\theta$  and  $\eta$  are 620 and 1020 °C, respectively, which are both higher than 590 °C. This suggests that, with sufficient heating time, a phase transition can occur even at a low heating temperature. These systematic observations demonstrate that the reactions occurring are more complex than simply the invariant reactions, provide insights into the nature of the reaction mechanisms involved and offer guidance for addressing furnace rollers' contamination.

## 4.2 Results

A total of 72 cleaned Al-Si coated 22MnB5 steel specimens were heated at setpoints of 570, 580, 600, 620, 630, 640, 650, 660, 670, 800, or 900 °C in a tube furnace for 1, 2, 4, 6, 8, or 10 minutes and then removed from furnace and cool down to room temperature in air. As the phase distribution of Al-Si coating is related to heating time, various heating durations were selected to capture the structural evolution changes with increasing heating time.<sup>58</sup> The cross section of each heated sample was then mounted and polished for Raman microscopic mapping characterization. Similar to Chapter 3, a 2-D grid was chosen on the top of the steel to capture the phase distribution in the Al-Si coating after the heating process. Our previous study in Chapter 3 revealed the standard Raman spectra for a series of intermetallic phases in the Al-Fe-Si system. By comparing the Raman spectra in all 72 cross section maps (16106 spectra) and the standards, the dominant intermetallic phases of these heated samples are  $\tau_2$ ,  $\tau_5$ ,  $\tau_6$ ,  $\theta$ , and  $\eta$  (**Figure 4.1**).

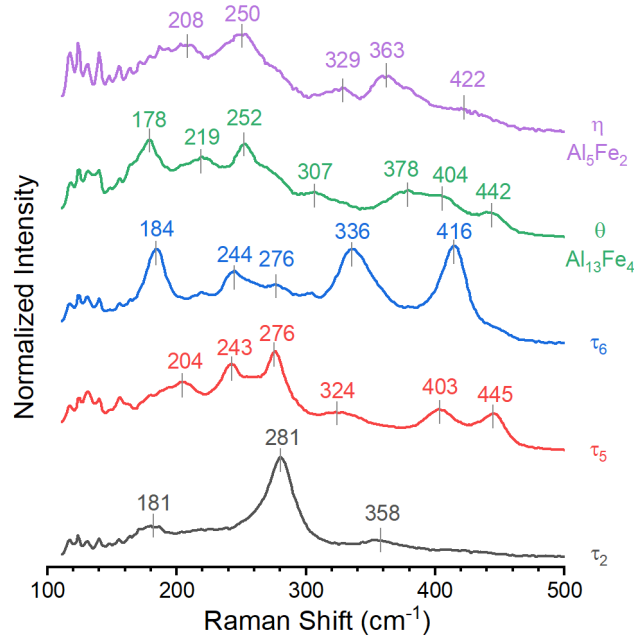


**Figure 4.1** The averaged Raman spectra for heated Al-Si coated 22MnB5 steel samples. All unique spectra were identified across all 16106 spectra in 72 cross sectional Raman microscopic maps of heat-treated samples.

The Raman microscopic mapping provided the technique to identify the location and the identity of intermetallic phase distributions. Among all 72 samples, 12 samples heated for 2 minutes were selected to show the nature of the data in **Figure 4.2**.  $\tau_5$  was the common intermetallic phase that exists in all maps, and  $\tau_5$  was the only intermetallic when heating at temperatures of 570, 610, 620, 650, 670, and 800 °C for 2 minutes (**Figures 4.2A, 4.2D-4.2E, 4.2H, 4.2J-4.2K**). As heating temperature increased from 570 to 580 °C, an  $\eta$  layer formed between  $\tau_5$  and steel (**Figure 4.2B**), and a  $\theta$  layer emerged between the  $\eta$  and  $\tau_5$  layer (**Figure 4.2C**). As the temperature continued to rise,  $\eta$  and  $\theta$  layers continuously appeared and disappeared with the continuous presence of the  $\tau_5$  layer until 900 °C, where the majority of the coating was  $\eta$  with a small amount of  $\tau_2$  (**Figures 4.2 D-4.2L**). In a particular case at 660 °C, a  $\tau_6$  intermetallic phase formed at the top of  $\tau_5$  layer, near the Al-Si coating side (**Figure 4.2I**). The thickness of intermetallic layers slightly grew from 570 to 800 °C, and there was no remaining Al-Si coating when the heating temperature increased to 900 °C (**Figure 4.2**).

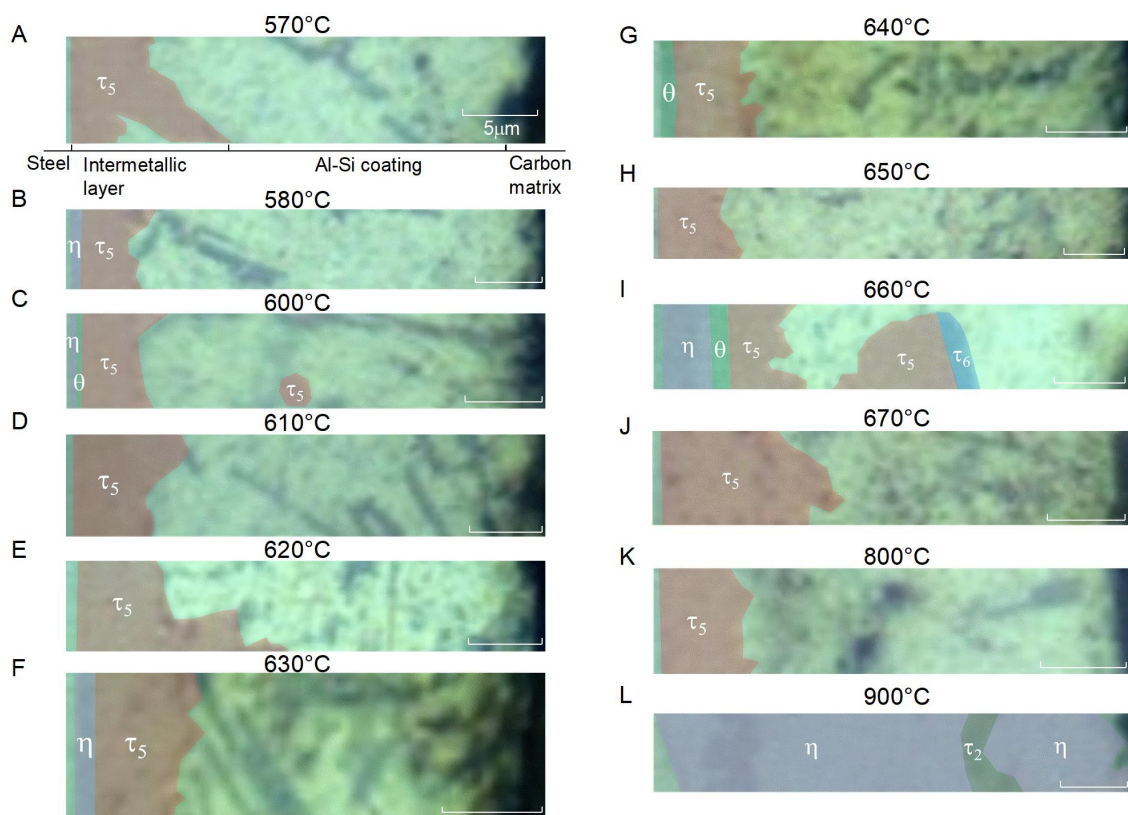


**Figure 4.2** Cross sectional maps of 22MnB5 samples heated at varied temperatures for 2 minutes. **(A)** The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled to illustrate the layout of the map. Additional maps are from samples heated for 2 minutes at **(B)** 580, **(C)** 600, **(D)** 610, **(E)** 620, **(F)** 630, **(G)** 640, **(H)** 650, **(I)** 660, **(J)** 670, **(K)** 800, and **(L)** 900 °C. All have a similar layout with 570 °C sample. A 5  $\mu\text{m}$  scale bar is labeled on each map to show the size of the maps.

The phase transition behavior changed when the heating time increased to 6 minutes (**Figure 4.3**). As the  $\tau_5$  was the primary phase in as-received state samples, a new  $\eta$  layer appeared between  $\tau_5$  and the steel when the heating temperature increased to 570-580 °C (**Figures 4.3A-4.3B**). A new  $\tau_6$  layer formed on top of the  $\tau_5$  layer as the heating temperature increased to 600-610 °C (**Figures 4.3C-4.3D**). With the heating temperature increased to 620-640 °C, the  $\tau_6$  layer disappeared, allowing the growth of  $\eta$  and  $\tau_5$  layers (**Figures 4.3E-4.3F**). A  $\theta$  layer occurred between  $\eta$  and  $\tau_5$  layers when the heating temperature increased to 650-670 °C (**Figures 4.3H-4.3J**). The  $\tau_2$  phase first appeared at 800 °C for samples heated for 6 minutes (**Figure 4.3K**), which was at a lower temperature compared to samples heated for 2 minutes (**Figure 4.2L**). The types of intermetallic phases remained consistent as

the heating temperatures increased from 800 to 900 °C, but the distribution of these phases shifted (**Figures 4.3 K-4.3L**).

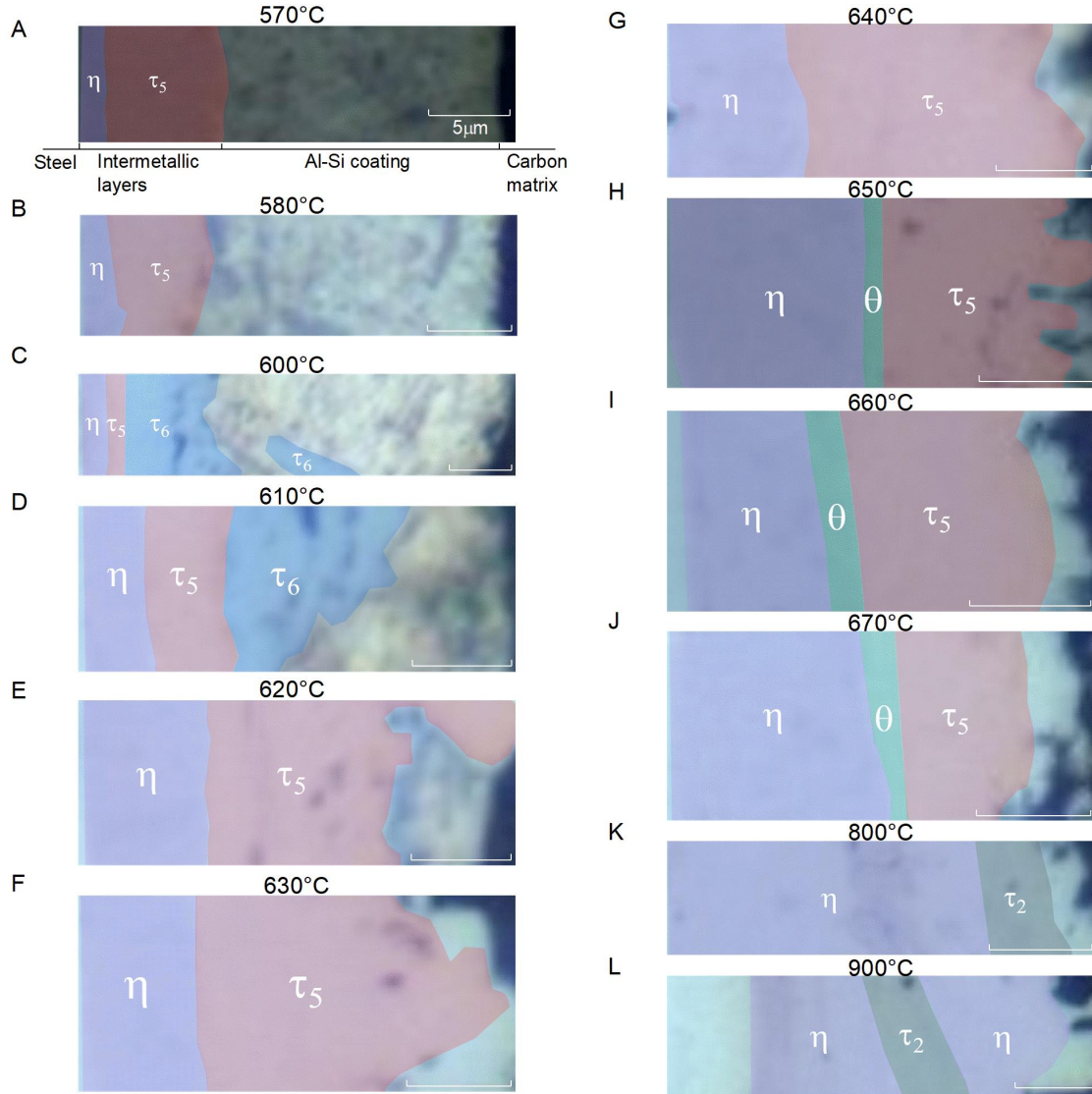


**Figure 4.3** Cross-sectional map of chemical species distributions of 22MnB5 samples that were heated at varied temperatures for 6 minutes. **(A)** The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled to illustrate the layout of the map. Additional maps are from samples heated for 6 minutes at **(B)** 580, **(C)** 600, **(D)** 610, **(E)** 620, **(F)** 630, **(G)** 640, **(H)** 650, **(I)** 660, **(J)** 670, **(K)** 800, and **(L)** 900 °C. All have a similar layout with 570 °C sample. A 5 µm scale bar is labeled on each map to show the size of the maps.

When the heating time was extended to 10 minutes, the intermetallic layers grew deeper into the Al-Si coating relative to shorter heating times. The maps revealed no significant changes in interface composition for samples heated from 570 to 580 °C, as they consisted of layers of  $\eta$ ,  $\theta$ , and  $\tau_5$  (**Figures 4.4A-4.4B**). As temperature increased to 600 and 610 °C, a  $\tau_6$  layer generated at the top of the intermetallic layers (**Figures 4.4C-4.4D**). The  $\tau_6$  layer transformed into  $\tau_5$  with the temperature increase to 620 °C (**Figure 4.4E**). The composition of intermetallic layers remained stable between 620 to 670 °C, with only a slight change in the ratio of each intermetallic phase (**Figures 4.4E-4.4J**). When the temperature reached 800 °C,  $\tau_5$  transformed to  $\tau_2$ ,  $\theta$  and  $\eta$  remained as intermetallic layers (**Figure 4.4K**). Only  $\eta$  was left in the intermetallic layer when the temperature increased to 900 °C (**Figure 4.4L**). From previous studies,  $\eta$  is known as the dominant component during interface growth.<sup>25,93</sup> This is similar to our results that all the maps contained a  $\eta$  layer in the interface (**Figures 4.3-4.4**). For other samples heated for 1, 4, and 8 minutes, the map distributions are shown in **Figures B.1-B.3**.

With the observations from all the 72 samples,  $\tau_5$  was the main intermetallic phase in the phase transition reactions. The transformation from  $\tau_5$  to  $\tau_6$  occurred, but the presence of  $\tau_6$  was not persistent. This phase transformed back to  $\tau_5$  with increasing heating temperature or prolonged heating time. The diffusion of Fe contributed to phase growth, typically forming the  $\eta$  phase. The  $\theta$  phase appeared between  $\eta$  and  $\tau_5$ , with mutual transformations observed among  $\eta$ ,  $\theta$ , and  $\tau_5$ . The presence of  $\tau_2$  depended on the heating conditions, as it was only observed at temperatures of 800 °C and higher, with a heating time of 2 minutes or longer. If continuous heating were applied, the  $\tau_2$  phase would disappear. Given sufficient heating time, all phases would transform into the  $\eta$  phase, resulting in the complete transformation of all Al-Si coatings into intermetallic layers.

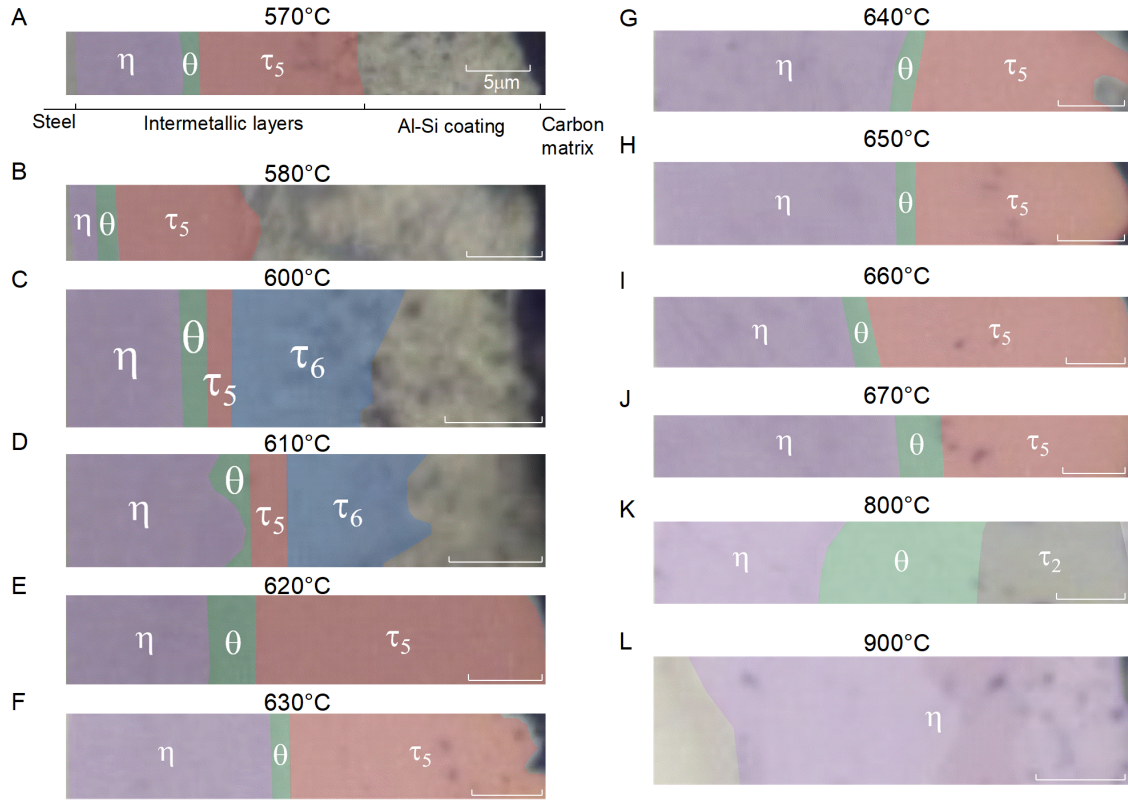


**Figure 4.4** The cross-sectional view of the samples heated for 10 minutes with intermetallic phase distributions. **(A)** The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled with steel, intermetallic layers, Al-Si coating, and carbon matrix to illustrate the layout of the map. Additional maps are from samples heated for 10 minutes at **(B)** 580, **(C)** 600, **(D)** 610, **(E)** 620, **(F)** 630, **(G)** 640, **(H)** 650, **(I)** 660, **(J)** 670, **(K)** 800, and **(L)** 900 °C. All have a similar layout with the 570 °C sample. A 5 μm scale bar is labeled on each map to show the size of the maps.

## 4.3 Discussion

### 4.3.1 Intermetallic Phase Distributions

From the Raman microscopic mapping 2-D grid, we can calculate the ratio of each intermetallic phase or element in relation to the distance. The thickness of the coating layer, including the intermetallic layer and the Al-Si coating, varied among all the samples due to the growth of the intermetallic layer during the heating process. To study the growth behaviour of the intermetallic phases, the normalized distance was calculated based on the distance to steel. As shown in **Figure**

4.5, a normalized distance of 0 represented the steel surface, and a normalized distance of 1 represented the top of the Al-Si coating. In **Figure 4.5**, each intersection point has a corresponding spectrum, enabling us to infer the identity of each point. The ratio of each intermetallic phase at a certain normalized distance can be calculated by dividing the number of points for each intermetallic phase at this distance by the total number of points at this distance. The calculation of each element ratio at a certain distance can be determined by multiplying the ratio of calculated intermetallic phases at this distance by the proportion of each element within the intermetallic phases. By comparing the relationship between the ratio and distance change among different samples, we are able to visually understand the positional information of the growth of each intermetallic phase or element as the heating condition changes (**Figures 4.6-4.7**).

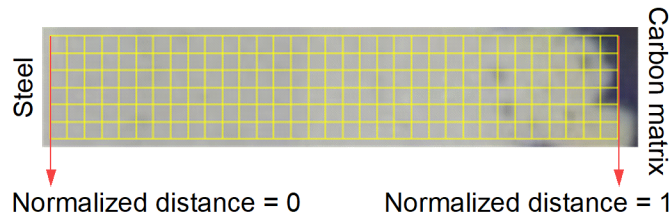


**Figure 4.5** A 2-D grid illustration for ratio calculation and distance normalization. The Raman microscopic mapping 2-D grid is from a sample that heated under 630 C for 10 minutes.

**Figure 4.6** shows the ratio changes for each species in a sample that was heated at 660 °C. With increasing heating duration,  $\tau_5$  gradually grew from steel and increased its ratio and thickness (**Figure 4.6A**). The growth behavior of  $\theta$  and  $\tau_6$  was not obvious, and they only occupy a small portion of the coating (**Figures 4.6B-4.6C**).  $\theta$  is always observed in between  $\tau_5$  and  $\eta$ , and  $\tau_6$  is always observed in between  $\tau_5$  and the Al-Si coating.  $\eta$  had a significant growth with increasing heating duration, similar to  $\tau_5$ , which had an obvious increase in proportion and thickness (**Figure 4.6D**). During growth,  $\eta$  remained close to the side adjacent to the steel.<sup>22,73</sup> The Al-Si coating sat on top of intermetallic phases and gradually moved further away from the steel substrate until it eventually disappeared completely with increasing heating duration (**Figure 4.6E**). In **Figure 4.6G**, it is evident that as heating time increased, Fe diffusion from steel to the Al-Si coating resulted in a rising concentration of Fe elements in the coating. The decreasing trend of the Fe ratio from steel to the top was noticeable, which was consistent with previous studies.<sup>12,24,50,59,73,90,94,95</sup> Other series of heating

temperatures for intermetallic phases and elements ratios change with distance are shown in **Figures B.4-B.14**.

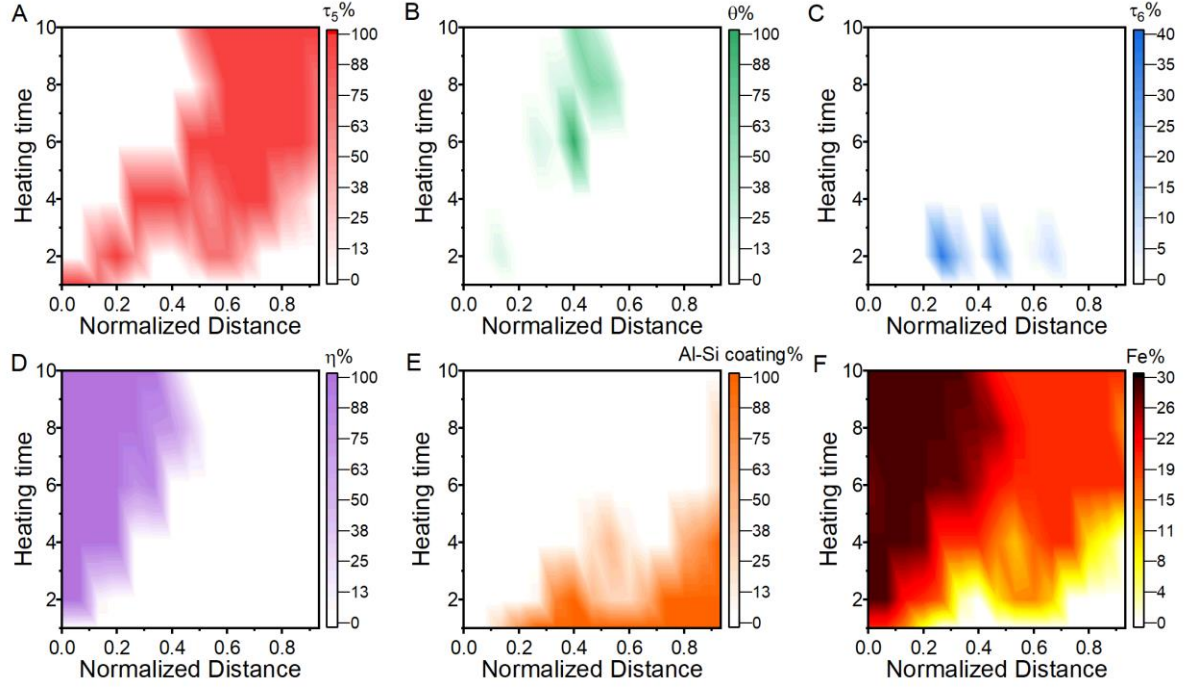


**Figure 4.6** Contour plots of the proportion of individual intermetallic phases for samples heated under 660 °C as a function of normalized location within the coating and heating time. The location within the coating is based on the normalized distance to the steel, where a normalized distance of 0 represents the steel surface and a 1 represents the top of the Al-Si coating. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratios, **(E)** Al-Si coating ratio, and **(F)** Fe element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 660 °C heating temperature.

From the heating profile (**Figure 3.3**), it is evident that the temperatures of samples with heating times of 1, 2, and 4 minutes may be lower than the furnace temperature. **Table 4.2** summarizes the estimated sample temperatures at different heating times through the measured heating curves in **Figure 3.3**. This table allows us to analyze the effects of sample temperature variation on the phase distribution at a fixed heating time.

**Table 4.1** Estimated sample temperatures from heating profile under various heating conditions.

| Estimated sample temperature (°C) |    | Furnace set temperature (°C) |     |     |     |     |     |     |     |     |     |     |     |
|-----------------------------------|----|------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|                                   |    | 570                          | 580 | 600 | 610 | 620 | 630 | 640 | 650 | 660 | 670 | 800 | 900 |
| Heating time (minutes)            | 1  | 300                          | 310 | 370 | 330 | 350 | 470 | 350 | 500 | 470 | 520 | 560 | 775 |
|                                   | 2  | 445                          | 460 | 515 | 500 | 515 | 600 | 520 | 620 | 545 | 640 | 710 | 890 |
|                                   | 4  | 550                          | 560 | 590 | 590 | 605 | 630 | 620 | 650 | 640 | 670 | 780 | 900 |
|                                   | 6  | 570                          | 580 | 600 | 610 | 620 | 630 | 640 | 650 | 660 | 670 | 800 | 900 |
|                                   | 8  | 570                          | 580 | 600 | 610 | 620 | 630 | 640 | 650 | 660 | 670 | 800 | 900 |
|                                   | 10 | 570                          | 580 | 600 | 610 | 620 | 630 | 640 | 650 | 660 | 670 | 800 | 900 |

The changes in ratios as a function of location in the film and sample temperature for the samples heated for 4 minutes are shown in **Figure 4.7**. With increasing sample temperature, the growth of  $\tau_5$  in both thickness and ratio became more apparent, but  $\tau_5$  was no longer observed for samples heated at 900 °C (**Figure 4.7A**). There were no significant changes in the distribution of  $\theta$  and  $\tau_6$  with increasing sample temperature, as they consistently occupied a small portion of the coating (**Figures 4.7B-4.7C**).  $\eta$  remained the phase closest to the steel throughout the temperature range.<sup>22,73</sup> The  $\eta$  exhibited the widest distribution and gradually became dominant in the coating as the temperature increased (**Figure 4.7C**). The appearance of  $\tau_2$  was observed in the topmost region of the intermetallic layer when heated to 900 °C (**Figure 4.7E**). The main distribution of Al-Si coating was concentrated at lower sample temperatures and away from the steel region (**Figure 4.7F**). The changes in elemental distribution with respect to distance and sample temperature were also included. Al element is distributed throughout the whole coating layer, with a denser concentration observed away from the steel and at lower sample temperatures (**Figure 4.7G**). Fe exhibited a diffusional pattern, with a clear decrease from the steel to the top of the coating with increasing sample temperature (**Figure 4.7H**). Si showed the lowest concentration near the steel interface and increased as the distance away from the steel (**Figure 4.7I**). For the sample heated for 10 minutes at 900 °C, the final film contains only  $\eta$ , which has no forward Si content (**Figure 4.4L**). The Si must still be within the system which means it must be dissolved in the  $\eta$  crystal structure. Such an occurrence is known

to occur.<sup>9,96-98</sup> The specific Si concentrations could not be calculated in this study by Raman microscopic mapping. Other series of heating times for intermetallic phases and elements ratios change with distance results were shown in **Figures B.15-B.19**.

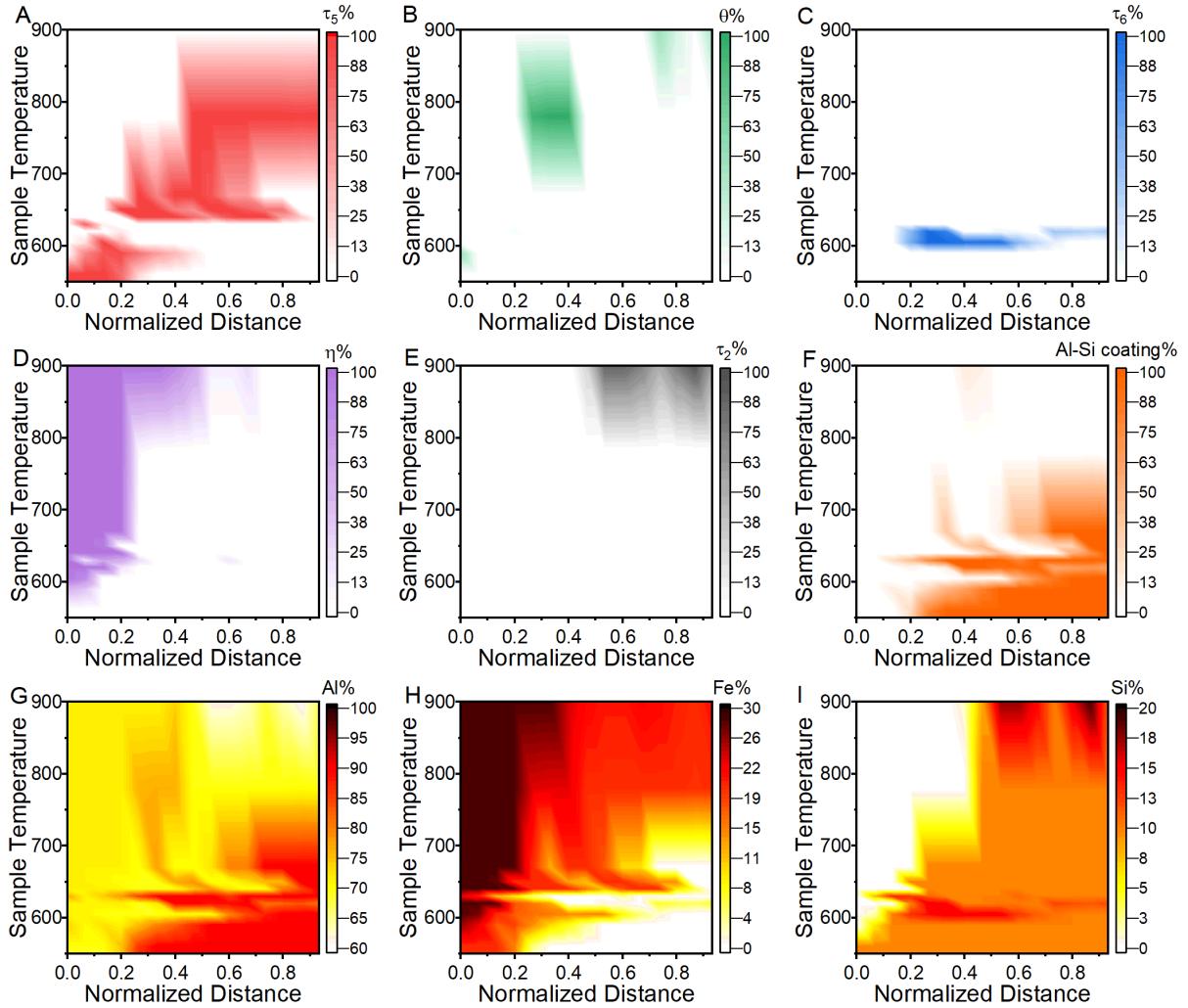


**Figure 4.7** Contour plots of ratio changes for samples heated for 4 minutes as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)**  $\tau_2$ , **(F)** Al-Si coating, **(G)** Al element, **(H)** Fe element, and **(I)** Si element, were listed as a function of heating temperature and normalized distance.

In addition to the distance-related phase distribution, the overall phase in the coating distribution can also be studied. The ratio of each intermetallic phase can be calculated by dividing the number of

data points in the 2-D grid representing the intermetallic phase by the total number of data points in the 2-D grid (**Figure 4.5**). The ratio of the intermetallic layer can be calculated by summing up the ratios of each individual intermetallic phase. These ratios effectively illustrated the distribution of each intermetallic phase or the entire intermetallic layer with increasing heating times and sample temperatures (**Figure 4.8**). In **Figure 4.8A**, intermetallic phases are shown in different colors: grey represents  $\tau_2$ , red represents  $\tau_5$ , blue represents  $\tau_6$ , green represents  $\theta$ , and purple represents  $\eta$ . Using sample temperature as the y-axis resulted in two absences of data for plotting the contour plot: the white area on the bottom right corner and the top left corner.  $\tau_5$  is the most common phase during the heating process, primarily concentrated at low sample temperatures and shorter heating times, while  $\eta$  is predominantly found at higher sample temperatures and longer heating times.  $\tau_6$  is mainly distributed around a sample temperature of approximately 600 °C, with its concentration increasing as heating time extends.  $\theta$  is primarily distributed at lower sample temperatures with longer heating times, as well as at higher sample temperatures with shorter heating times.  $\tau_2$  only appears near a sample temperature of 800 °C and disappears at 900 °C. The invariant reactions can be linked to sample temperature in **Figure 4.8A**. As we proposed in Chapter 3,  $\tau_5$  continuously grows with the melting of the Al-Si coating at 577 °C (equation 3.1), consistent with the growth of  $\tau_5$  along the 577°C isothermal line in **Figure 4.8A**. The invariant reaction  $U_{10}$  (equation 1.3) suggests that  $\tau_6$  will transform to  $\tau_5$  at 615 °C, which is very close to the temperature observed here. The invariant reaction  $U_9$  (equation 1.4) indicates that  $\theta$  will be generated from  $\tau_5$  at 620 °C, but the formation of  $\theta$  occurs at much sample temperatures in the plot. Another invariant reaction,  $U_8$  (equation 1.5), reveals that the generation of  $\tau_2$  occurs at 790 °C, similar to the distribution of  $\tau_2$  observed in **Figure 4.8A**. Due to the absence of samples heated between 670 and 800 °C, we cannot determine the specific minimum temperature of  $\tau_2$  generation. Among all our samples,  $\tau_2$  only appeared at sample temperatures of 800 °C and above. According to invariant reaction  $U_3$  (equation 1.9), the minimum temperature for  $\eta$  to occur is 1020 °C, while  $\eta$  appeared at even 610 °C in **Figure 4.8A**. These results are partially described by the invariant reactions in the Al-Fe-Si phase diagram, but there are clearly more reactions that need to be considered. In **Figure 4.8B**, it is seen that the growth of intermetallic layers became more pronounced with increasing sample temperature or heating dwell time. At the same sample temperature, a longer heating time allows the sample to absorb more Fe from the steel into the coating. By increasing the localized concentration of Fe at the interface, interfacial reactions present a

microenvironment that is different than a bulk phase that is thermodynamically equilibrated. Such environments appear to promote interfacial reactions that regulate the growth of intermetallic layers. At the same heating time, the growth of intermetallic layers becomes more obvious at higher sample temperatures with all the invariant reactions happening.

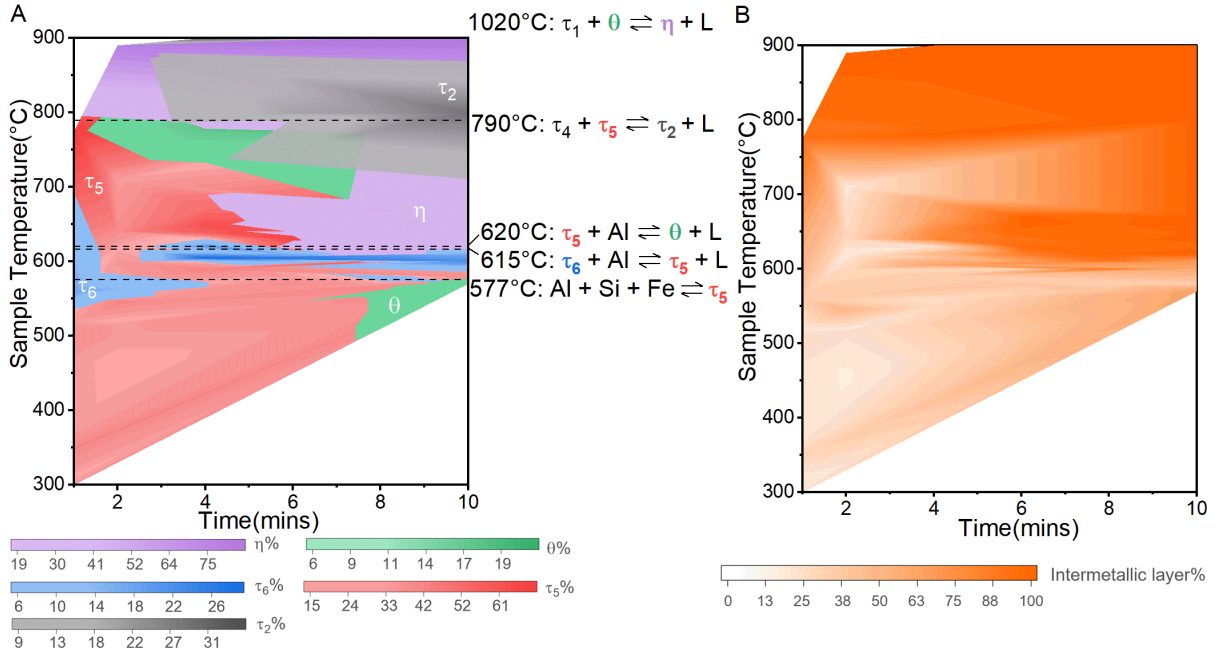


**Figure 4.8** The contour maps of intermetallic phases as a function of heating times and sample temperatures. **(A)** Five different types of intermetallic phases,  $\eta$ ,  $\theta$ ,  $\tau_6$ ,  $\tau_5$ , and  $\tau_2$ , are listed in different colors. **(B)** The contour map of the ratio of intermetallic layer growth.

#### 4.3.2 Inferred Mechanisms

Five major chemical reactions appear sufficient to describe the overall coating transformation process observed in all 72 samples. Two of these five reactions are the same as the reactions (1.3 and 1.4) in the previous study.<sup>5,12,46</sup> The five reactions include: (equation 1.3) the interconversion between  $\tau_6$  and  $\tau_5$ ; (equation 1.4) the transformation between  $\tau_5$  and  $\theta$ ; (equation 3.1) the generation of  $\tau_5$  upon Fe reacting with melted Al-Si coating; (equation 3.2) the interconversion between  $\eta$  and  $\theta$ ; and (equation 3.3) the transformation between  $\theta$  and  $\tau_2$ .

The equation (3.1) reveals the initial reactions with the Al-Si coating melting at 577 °C, which generates  $\tau_5$ . With an increase in heating time, Fe diffuses from steel into  $\tau_5$  to make  $\theta$  (equation 1.4).

Further diffusion converts  $\theta$  into  $\eta$  (equation 3.2). From the maps, the appearance of  $\tau_6$  requires sufficient heating time for the sample temperature to reach around 600 °C. As shown in equation (1.3),  $\tau_5$  and  $\tau_6$  can transform to each other, which aligns with mechanisms proposed by other researchers before.<sup>5,46</sup> The local microenvironments are important in determining the direction of reaction, as both  $\tau_5$  to  $\tau_6$  and  $\tau_6$  to  $\tau_5$  are observed. When the heating temperature reaches at least 800°C and the heating time is at least 2 minutes,  $\theta$  will transform to  $\tau_2$ , which aligns with the equation (3.3). The  $\eta$  to  $\theta$  conversion occurs throughout the 570-900 °C range (equation 3.2). According to our data,  $\eta$  becomes the final and only intermetallic phase when a sufficiently long heating time or sufficiently high heating temperature is applied. This contrasts with the ternary phase diagram, where  $\eta$  first appears at 1020 °C.

#### 4.3.3 Nature of Reactions

According to the chemical speciation maps, there are several specific phase distribution combinations that continually emerge, which are steel| $\eta$ | $\theta$ | $\tau_5$ |Al-Si coating, steel| $\eta$ | $\theta$ | $\tau_5$ | $\tau_6$ |Al-Si coating, and steel| $\eta$ | $\theta$ | $\tau_5$ |Al-Si coating. To understand the reason behind these phase distribution combinations, we calculated the Fe composition ratio for each intermetallic phase. The chemical formula for  $\eta$  is  $\text{Al}_5\text{Fe}_2$ , which contains around 29% Fe. Using the same method, we calculated that  $\theta$  contains 24% Fe;  $\tau_5$  contains 20% Fe;  $\tau_6$  contains 15% Fe; and  $\tau_2$  contains 20% Fe. In each combinations, the increasing trend of Fe from steel to Al-Si coating clearly indicates that the growth of intermetallic phase is governed by Fe diffusion.<sup>8,9,13,22,62,99</sup>

In **Figure 4.9**, the Raman microscopic maps of samples heated under different conditions are presented. The thickness of the intermetallic layer increases as the Fe diffuses from steel to the Al-Si coating. By comparing the phase distributions of samples heated for the same duration, such as 1 minute, 4 minutes, or 8 minutes, the growth of intermetallic layers becomes more obvious with increasing sample temperatures (**Figure 4.9**). Similarly, when we compare samples at the same temperature, the growth of intermetallic layers becomes more pronounced with increasing sample time (**Figure 4.9**). Thus, the degree of Fe diffusion is influenced by the heating times and sample temperatures. Fe diffuses to the interface and generates  $\eta$ , which accelerates the diffusion of Fe within  $\eta$  until it is blocked by the inhibition layer of  $\tau_5$ .<sup>2</sup> As seen in **Figure 4.9**, the  $\eta$  phase is often observed at the steel interface and clearly promotes Fe diffusion.

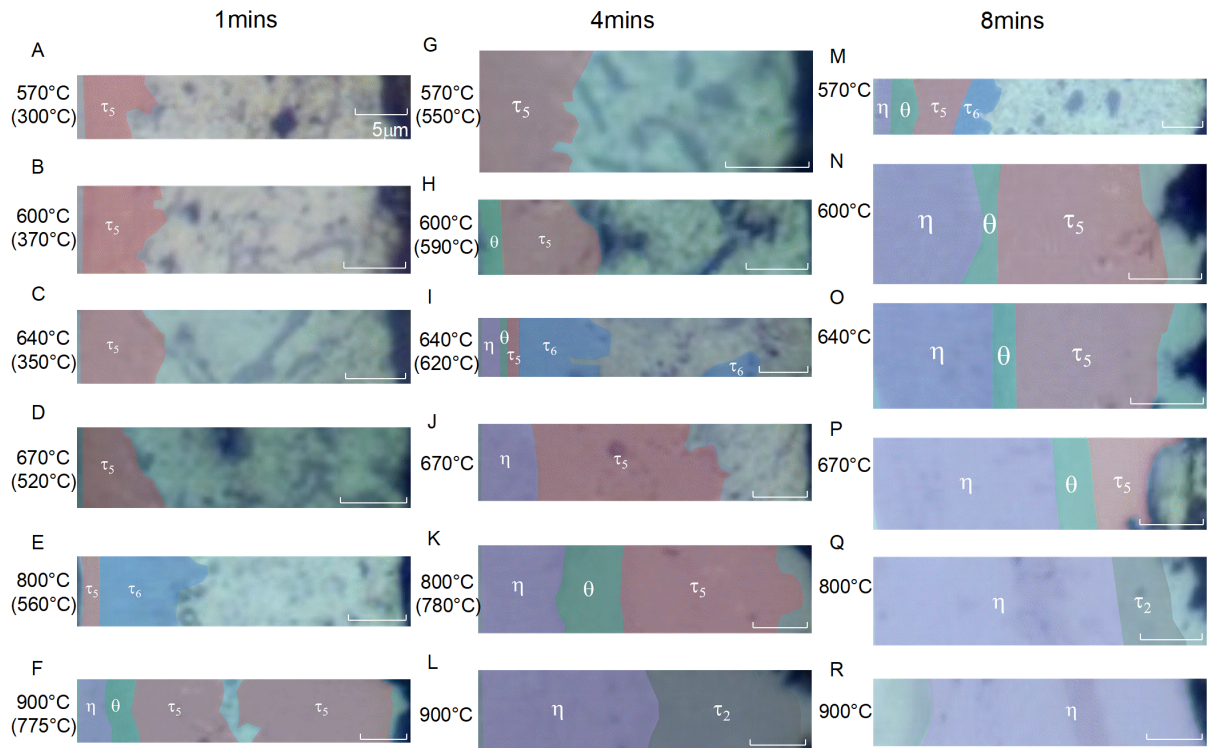


**Figure 4.9** Comparison of cross-sectional map phase transitions between different samples. The maps distribution of samples heated for 1 minute at **(A)** 570, **(B)** 600, **(C)** 640, **(D)** 670, **(E)** 800, and **(F)** 900 °C. The temperatures inside the brackets represent the estimated sample temperatures, while those maps with only one temperature present mean the estimated sample temperature is the same as the furnace set temperatures. Cross-sectional views with maps distribution for samples heated for 4 minutes at **(G)** 570, **(H)** 600, **(I)** 640, **(J)** 670, **(K)** 800, and **(L)** 900 °C. And the maps distribution for samples heated for 8 minutes at **(M)** 570, **(N)** 600, **(O)** 640, **(P)** 670, **(Q)** 800, and **(R)** 900 °C are also shown here. A 5 μm scale bar is attached near each map.

To test the role of Fe diffusion on the overall process and investigate the phase transition during low temperatures, an Al-Si coated 22MnB5 steel sample was heated at 590 °C for 3 days in a tube furnace and then cooled down to room temperature in air (**Figure 4.10**). Then the cross section of the heated sample was mounted and polished for Raman microscopic mapping characterization. After 3 days of heating, the growth of intermetallic layers reached 100% and consisted of η and θ (**Figure 4.10A**), where the Raman spectra of them are shown in **Figure 4.10B**. Similar to what was mentioned earlier, θ and η are expected to initially generate at 620 and 1020 °C, respectively, which are higher

than the heating temperatures. This demonstrates that the Fe was gradually diffused to the coating and promoted interfacial reactions, which means that reactions outside of the invariant reactions within the ternary phase diagram must occur.

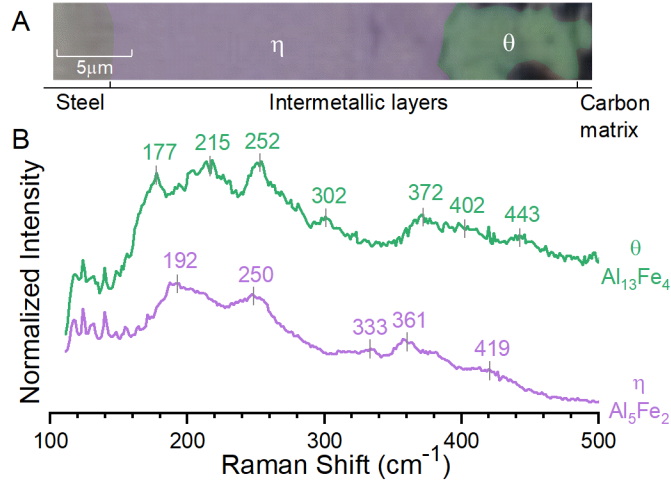


**Figure 4.10** Cross-sectional Raman microscopic mapping of an Al-Si coated 22MnB5 steel specimen heating under 590 °C for 3 days. **(A)** The cross section of heated Al-Si coated 22MnB5 steel, with the distribution of intermetallic phases labeled. The scale bar corresponds to 5 μm. **(B)** Raman spectra for θ and η were obtained by averaging the spectra from the region indicated in the above image.

The emergence of the binary η and θ phases at temperatures below those expected in the ternary phase diagram is attributed to the formation of local reaction environments. A high concentration of Fe can be readily established at the interface of steel and Al-Si coating, creating a microenvironment rich in both Fe and Al. Under such conditions, reactions found in the binary Al-Fe phase diagram may become dominant. The binary reaction of Al and Fe can readily yield θ and η at low temperatures (**Figure 4.11**). During heating, the Fe diffusion from the steel therefore generates the lower Fe-content θ phase. As time progresses, greater Fe diffusion enables θ to grow further to solution while greater diffusion from the steel converts the layers closer to the surface into the more Fe-rich η phase. According to the Al-Fe binary phase diagram, these phase formations can be achieved at temperatures as low as 400 °C, much lower than indicated in the Al-Fe-Si ternary phase diagram.

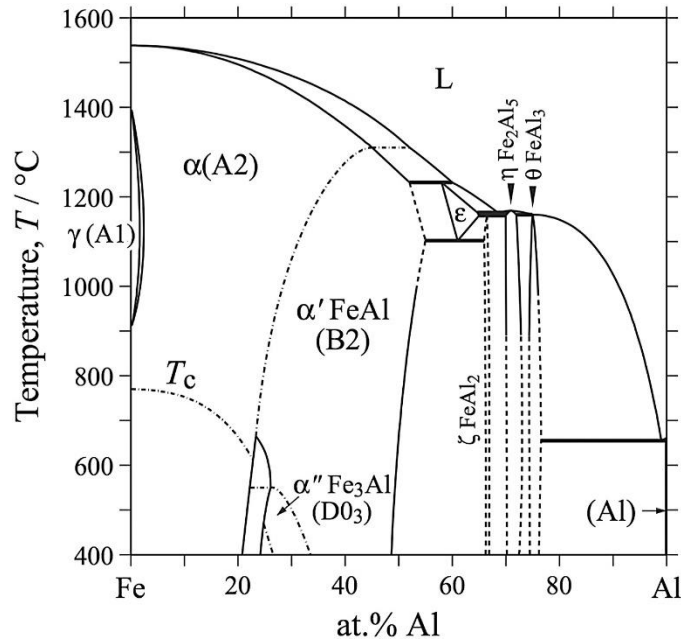


**Figure 4.11** The Al-Fe binary phase diagram. Reprinted with permission from Elsevier.<sup>100</sup>

#### 4.4 Conclusions

Cross-sectional Raman microscopic mapping was applied to conduct a detailed and systematic analysis of the reaction mechanisms for Al-Si coating on 22MnB5 steels during heating. A total of 72 specimens of steel samples were heated under 12 different heating temperatures for 6 different heating durations to compare the behavior of phase evolution and the degree of intermetallic phase growth. The comparison revealed that the phase transitions become more pronounced with increased sample temperatures and heating durations. Five reaction mechanisms were proposed to describe the interface reactions of Al-Si coating and steel that happened during the heating process, with most reactions being governed by Fe diffusion from steel to Al-Si coating. The majority of the reactions can occur without a specific heating temperature requirement, except for  $\tau_2$ , which is observed at temperatures above 800 °C and with a minimum heating time of 2 minutes. Furthermore, the results obtained from heating a sample at 590 °C for 3 days demonstrated that reactions outside the invariant reactions in ternary phase diagrams must occur. Due to the high concentration of Fe at the interface of steel and the intermetallic layer, we are dealing with a Fe-rich and Al-rich system, where the Al-Fe binary phase was introduced to explain the formation of both  $\theta$  and  $\eta$  at lower temperatures. Therefore, the local microenvironments at the interfaces can drive the coating formation under

conditions less demanding than those required in the ternary situation. With our understanding of phase transformations, we can provide guidance for future research. For example, modifications can be made to the heating process or the sample itself to optimize industrial production, thereby achieving improved performance and mitigating issues related to roller contamination.

## Chapter 5

### Facilitating Intermetallic Layer Growth by Surface Modification on Al-Si Coating

#### 5.1 Introduction

It is well known that the primary reason for pollution in the furnace rollers is the melting and transfer of the coating during the heating process.<sup>2,28,29</sup> To alleviate pollution on the furnace rollers, it is essential to minimize the quantity and existing time of high-temperature molten liquids. The majority of these molten high-temperature liquids originate from the melting of the Al-Si coating, with a smaller portion resulting from the reactions of intermetallic phases.<sup>26,27,29</sup> Therefore, it is crucial to expedite the conversion of the Al-Si coating into non-molten intermetallic phases. Based on our previous research in Chapters 3 and 4, the diffusion of Fe is the main driver for Al-Si coating transformation to intermetallic phases. This process can be visually explained using an Al-Fe-Si ternary phase diagram in **Figure 5.1**.<sup>46</sup>

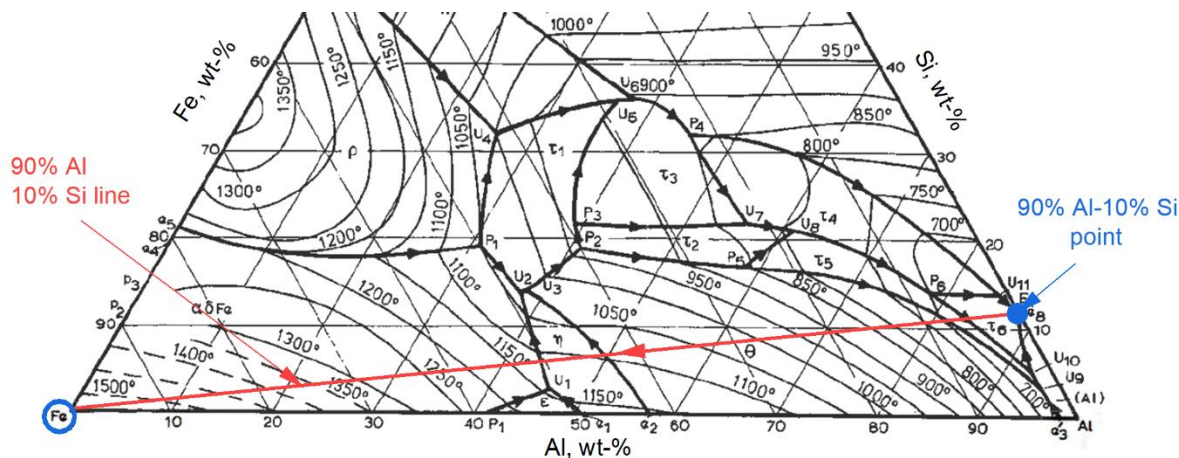


**Figure 5.1** Partial Al-Fe-Si phase diagram focusing on the Al-Fe-rich region with illustrations showing the theoretical reaction path. Reprinted with permission from Taylor & Francis.<sup>46</sup>

The blue point on the right, the 90% Al-10% Si point, represents the approximate position of the initial Al-Si coating on the phase diagram. During the heating process, Fe leeches from the steel,<sup>8,9,22,62</sup> which can be represented by linking the initial point with 100% Fe (**Figure 5.1**; red line). This line tracks where the relative Al-Si coating is 90-10, providing the approximate reaction trend. As the composition of the coating shifts from right to left along the red line, signifying the growth of

the intermetallic layer, the molten liquid gradually solidifies and decreases. Thus, in order to alleviate the pollution resulting from molten liquids, it is necessary to expedite the growth of the intermetallic layer. This can be accomplished by accelerating the rate at which the Fe content of the coating increases.

To facilitate the phase evolution of intermetallic phases, it is necessary to consider the principles underlying the phases' transformation. Previous studies have indicated that the increase in Fe content in the Al-Si coating stems from the diffusion of Fe from steel. This diffusion process is affected by heating time and temperature (**Figure 5.2A**). To achieve the phase transformation in a lower heating temperature or in a shorter heating time, an additional Fe-containing source could be provided to the top of the Al-Si coated sample, promoting Fe diffusion from both sides. This would accelerate intermetallic layer growth (**Figure 5.2B**). Furthermore, a melting event would result in the Fe source suddenly dispersing in the molten liquid, which could be expected to rapidly induce intermetallic formation. Thus, if the addition of a secondary Fe source is effective, the time for the Fe addition sample to achieve 100% intermetallic layer growth ( $t_2$ ) should be much shorter than the time for the uncoated sample ( $t_1$ ).

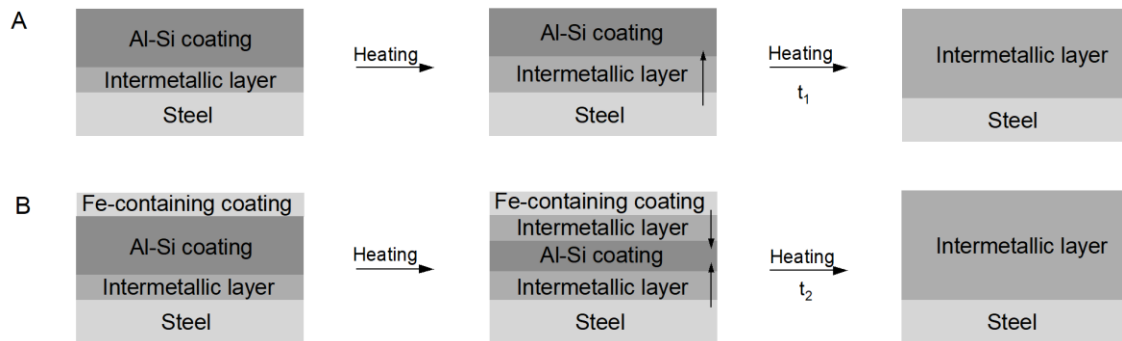


**Figure 5.2** The illustrations of phase transition mechanisms during the heating process for both the original sample and the Fe-containing source coated sample. **(A)** The illustration of the original phase transition mechanism during heating, in which the intermetallic layer will grow from the steel and will take  $t_1$  time for all Al-Si coating to undergo transformation into intermetallic phases. **(B)** The illustration of the Fe-containing source coated sample's phase transition mechanism during heating, in which the intermetallic layers will grow from both the Fe coated side and the steel side and takes  $t_2$  time for all Al-Si coating to transform into intermetallic phases.

This chapter demonstrates the facilitated growth of the intermetallic layers during the heating process by modifying the surface of the Al-Si coating on 22MnB5 steel. A Fe layer was coated on top of the Al-Si coating using the electrodeposition method, followed by the coated layer being oxidized by air to form a  $\text{Fe}_3\text{O}_4$  layer. Then the coated samples were heated for 2 minutes at various temperatures from 570 to 900 °C to investigate the phase evolution during the hot stamping heating temperatures. By comparing the map distribution results of Fe source coated samples with those of no Fe source coated samples, we are able to assess the effectiveness of our surface modification method. The results indicate that the Fe-containing source significantly accelerates the formation of intermetallic layers and does so at lower heating temperatures.

## 5.2 Results

Raman microscopic mapping was used to confirm the identity of compounds in cross-sectional maps of each surface Fe-coated 22MnB5 sample. The surface of Al-Si coated coupons was modified by cathodic electrodeposition from a  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  solution with a constant current density of 0.03 A/cm<sup>2</sup> for 10 minutes.<sup>67,68</sup> An electrodeposited steel sample is shown in **Figure 5.3**.



**Figure 5.3** The image of an Fe-containing source coated steel sample after electrodeposition.

The Fe source coated steel specimens were then heated at setpoints of 570, 580, 600, 620, 630, 640, 650, 660, 670, 800, or 900 °C in a tube furnace for 2 minutes, then cooled naturally in ambient air. Heated samples and one without heat treatment were mounted into a carbon matrix and polished for cross-sectional Raman measurements. Similar to Chapters 3 and 4, a 2-D grid was selected to capture the phase distributions in the Al-Si coating and Fe source coating. Previous studies in Chapter 3 demonstrated the Raman spectra of intermetallic phases of Al-Fe-Si and the oxides of Fe as references.<sup>87,101–106</sup> By comparing the Raman spectra from all 13 Fe coated samples (3477 spectra) and

reference Raman spectra in previous studies, we found the dominant phases of these samples are  $\tau_2$ ,  $\tau_5$ ,  $\tau_6$ ,  $\theta$ ,  $\eta$ ,  $\text{Fe}_3\text{O}_4$  (magnetite), and  $\alpha\text{-Fe}_2\text{O}_3$  (hematite). All Raman spectra of individual phases were averaged to obtain higher quality spectra, and the Raman spectrum range for the intermetallic phase was focused on 111 to 500  $\text{cm}^{-1}$ , while the iron oxide was focused on 111 to 800  $\text{cm}^{-1}$  to obtain the desired peaks of interest (**Figure 5.4**). The Raman spectra of  $\alpha\text{-Fe}_2\text{O}_3$  contained the expected vibrations at *ca.* 227, 247, 297, 412, 500, 614, and 663  $\text{cm}^{-1}$ ,<sup>87,103–106</sup> and Raman spectra of  $\text{Fe}_3\text{O}_4$  contained the expected vibrations at *ca.* 306, 544, and 668  $\text{cm}^{-1}$  (**Figure 5.4B**).<sup>101–104</sup> The expected Raman peaks for  $\gamma\text{-Fe}_2\text{O}_3$  (maghemite) are at *ca.* 348, 498, 707  $\text{cm}^{-1}$ ,<sup>103–105</sup> which were not observed in any sample here. As Fe is Raman inactive, there are no expected peaks in the Fe Raman spectrum.

The cross-sectional Raman microscopic mapping identified the location of each phase's distribution (**Figure 5.5**). The Fe coated sample without heat treatment contained a single layer of  $\tau_5$  at the interface of the Al-Si coating and the steel and a layer of Fe and  $\text{Fe}_3\text{O}_4$  on top of the Al-Si coating (**Figure 5.5A**). The samples heated at 570 and 580 °C showed no obvious changes in the intermetallic phases or Fe coated layer on top of the Al-Si coating (**Figures 5.5B-5.5C**). Layers of  $\tau_6$  emerged on the top and bottom of the Al-Si coating when heated to 600 °C, confirming that the intermetallic layer can simultaneously grow from the Fe-containing coating and the steel (**Figure 5.5D**). Similar to the sample heated at 600 °C, the samples heated from 610 to 620 °C also indicated intermetallic layer growth from the Fe source coated layer (**Figures 5.5E-5.5F**). The phase distribution of intermetallic layers changed for samples heated at 620 °C, where the  $\tau_5$  and  $\tau_6$  layers exchanged positions near the steel interface and the  $\text{Fe}_3\text{O}_4$  converted to  $\alpha\text{-Fe}_2\text{O}_3$ . At 630 °C, there was no Al-Si coating remaining, as the entirety of the Al-Si coating transformed to  $\tau_5$  (**Figure 5.5G**). The Fe source layer showed some residual  $\text{Fe}_3\text{O}_4$  beneath  $\alpha\text{-Fe}_2\text{O}_3$  for samples heated at 630 and 640 °C (**Figures 5.5G-5.5H**). Some residual  $\tau_6$  was observed for the sample heated at 640 °C, and the transformation of the Al-Si coating to intermetallic phases was also close to 100% (**Figure 5.5H**). The  $\tau_6$  layer transformed to  $\tau_5$ , and  $\text{Fe}_3\text{O}_4$  transformed when the heating temperature increased to 650 °C (**Figure 5.5I**). A new layer of intermetallic phase,  $\eta$ , emerged between the steel and  $\tau_5$  layer during 660 to 670 °C (**Figures 5.5J-5.5K**). The growth of  $\theta$  at the interface between  $\eta$  and  $\tau_5$  was observed at 800 °C (**Figure 5.5L**). A significant degree of  $\eta$  growth was observed at 900 °C, along with the transformation of  $\theta$  and  $\tau_5$  to  $\tau_2$  (**Figure 5.5M**). There were no obvious changes in the iron oxide layer from 650 to 900 °C, with only  $\alpha\text{-Fe}_2\text{O}_3$  persisting (**Figures 5.5I-5.5M**).

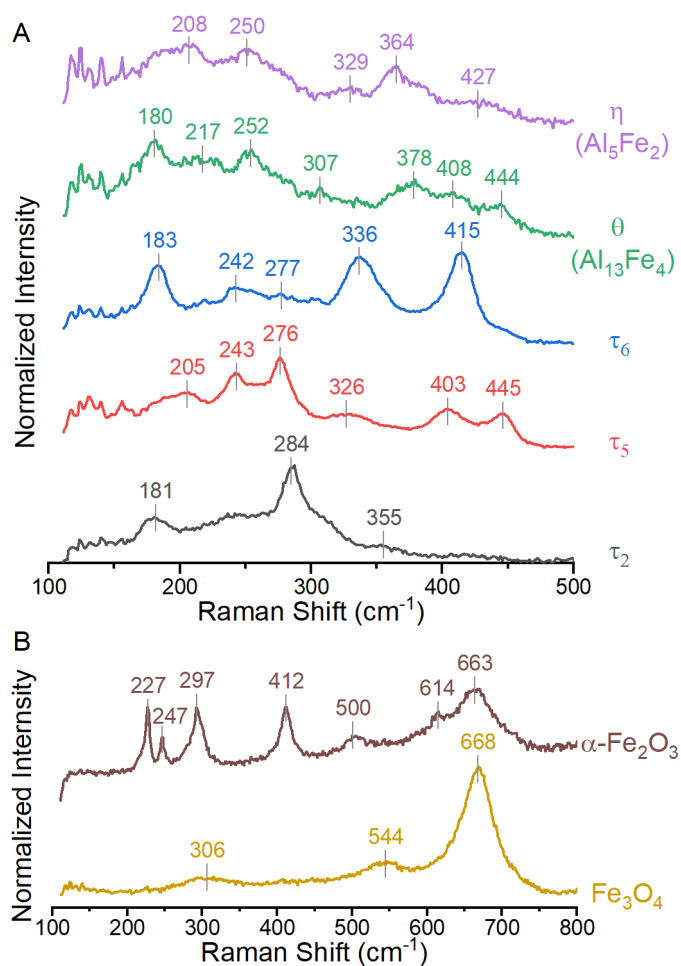


**Figure 5.4** The averaged Raman spectra for Fe coated samples. All unique spectra identified across all 3477 spectra in 13 cross sectional Raman microscopic maps on heating treated samples. **(A)** Raman spectra for intermetallic layers. **(B)** Raman spectra for iron oxides.

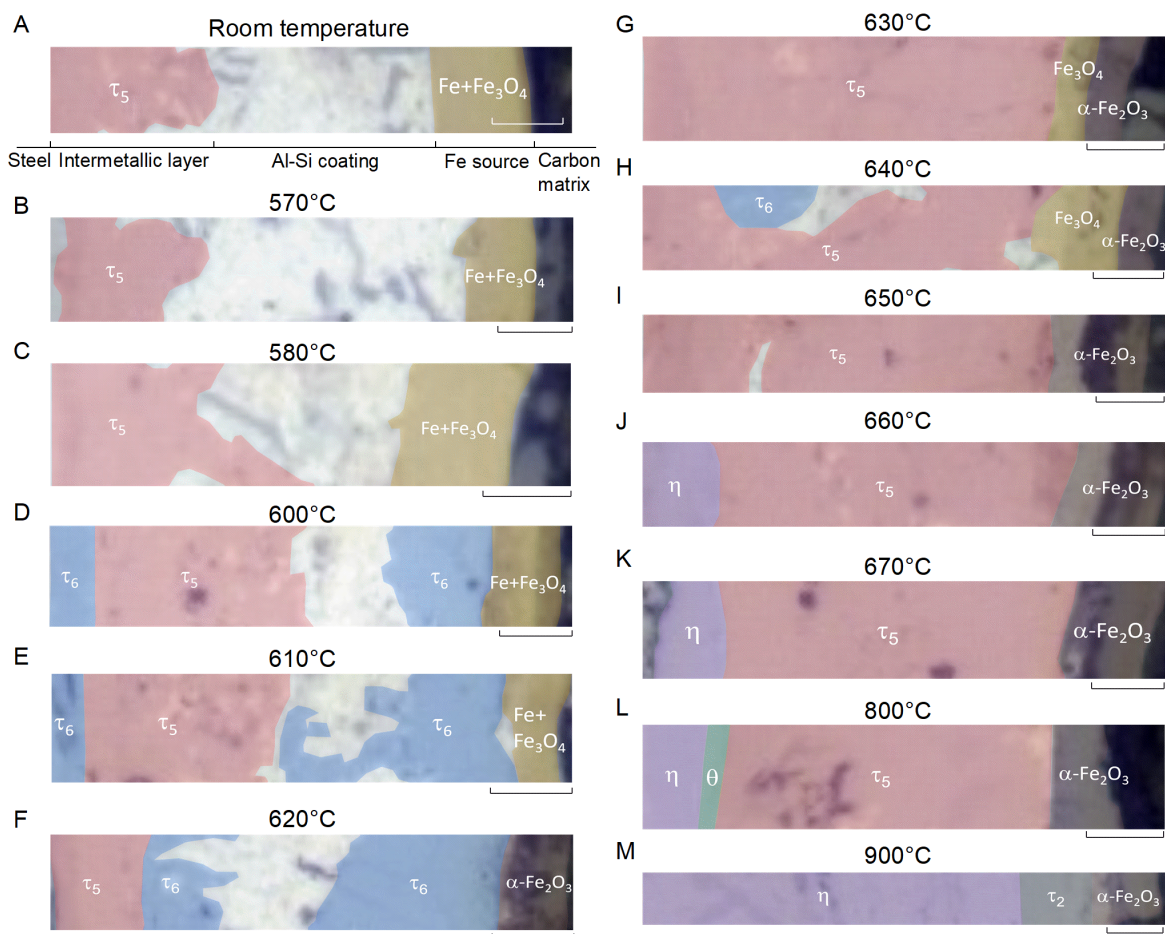


**Figure 5.5** The chemical distribution maps characterized by Raman microscopic mapping for Fe coated 22MnB5 samples. **(A)** A Fe coated sample without heating treatment is labeled with steel, intermetallic layer, Al-Si coating, iron source, and carbon matrix to illustrate the layout of the maps. Additional maps for samples heated for 2 minutes at **(B)** 570, **(C)** 580, **(D)** 600, **(E)** 610, **(F)** 620, **(G)** 630, **(H)** 640, **(I)** 650, **(J)** 660, **(K)** 670, **(L)** 800, and **(M)** 900 °C have a similar layout with no heating treated sample. A 5 µm scale bar is attached in each panel.

## 5.3 Discussion

### 5.3.1 Inferred Reaction Mechanisms

Seven reaction mechanisms can be used to summarize the phase transformation during the heating process of Fe-containing source coated samples, where some of them are consistent with previous

studies.<sup>5,12,107,108</sup> Five of those reactions are the same with previous inferred reactions (1.3, 1.4, 3.1, 3.2, and 3.3), while the other two reactions include: equation (5.1) the generation of  $\tau_6$  from the Fe source side with the Fe from Fe + Fe<sub>3</sub>O<sub>4</sub> layer contacting the Al-Si mixture; and equation (5.2) the transformation between iron oxides in the Fe coated layer:



These two reactions happened from the Fe-containing source coated side. The Fe source from the Fe + Fe<sub>3</sub>O<sub>4</sub> layer interacts with the liquid Al-Si mixture to generate  $\tau_6$ , which is an Al-Si rich ternary phase (equation 5.1). The equation (5.2) is a transformation of Fe<sub>3</sub>O<sub>4</sub> to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, where the  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is a frequently encountered oxidation product that forms at higher temperatures.<sup>107</sup> In our results, this oxidation-reduction reaction starts at 620 °C, and only  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> is found in the iron oxide layer when the heating temperature is higher than 650 °C.

### 5.3.2 Assessment of Fe Coating Effectiveness

To assess the effectiveness of the Fe-containing coating in facilitating intermetallic layer growth, we need to compare the map distribution of Fe-containing coated samples with the uncoated samples. The distribution maps for the Fe-containing coated samples (**Figure 5.5**) can be compared to the map distributions of uncoated samples subjected to the same heating temperature and duration (**Figure 4.2**). The  $\tau_5$  phase is a dominant intermetallic phase during the heating process of uncoated samples, while  $\tau_6$  also plays an important role during intermetallic layer growth in the heating process. In uncoated samples, the growth of the intermetallic layers reaches around 50% at 660 °C and reaches 100% conversion at 900 °C (**Figure 4.2L**). In Fe-coated samples, the growth of intermetallic layers becomes obvious when the heating temperature reaches 600 °C, and 100% growth is reached at 630 °C (**Figures 5.5E and 5.5G**). This strategy therefore enables dramatic acceleration of coating conversion, which also occurs at lower temperatures. This strategy therefore enables dramatic acceleration of coating conversion, which also occurs at lower temperatures.

In addition to comparing coated and uncoated samples under the same heating conditions, we can also explore the heating conditions under which uncoated samples achieve a similar degree of intermetallic layer growth as the Fe coated samples. By comparing the map distributions of the uncoated samples for 1, 2, 4, 6, 8, and 10 minutes of heating with the Fe-coated samples' maps

distribution, we found that the intermetallic layer growth in the Fe-coated samples heated for 2 minutes is similar to the layer growth in the uncoated samples heated for 10 minutes (**Figure 4.4**). For uncoated samples, a significant increase in the intermetallic layer ratio in the coating is observed at 600 °C (**Figure 4.4C**), and complete Al-Si coating transformation into an intermetallic layer is seen at 620 °C (**Figure 4.4E**). This temperature of 620 °C is comparable to the 630 °C required by Fe-coated samples (**Figure 5.4G**). Achieving a similar ratio of intermetallic layer growth in Fe coated samples with shorter heating time reduces the duration of the liquid Al-Si mixture. This Fe addition strategy is expected to decrease the probability of roller contamination in industrial furnaces.

In conclusion, strategically enabling Fe incorporation into Al-Si coating from both the top and bottom directions can dramatically increase the rate of intermetallic layer growth. This strategy has the added benefit of lowering the temperature required for intermetallic phase growth while also reducing the necessary heating time. The lower the temperature and the shorter the duration at which phase growth is completed, the less time the molten Al-Si mixture appears, resulting in a lower probability of pollution to the furnace. This will improve production efficiency and increase profitability.

## 5.4 Conclusions

A Fe-containing source was coated on the top of the Al-Si coated 22MnB5 sample to facilitate the growth of the intermetallic layer for decreasing the melted Al-Si coating quantity and duration during the heating process. The Fe source coated samples were heated for 2 minutes in the temperature range of 570 to 900 °C to capture the reaction mechanisms and structural changes during heating. A total of 13 specimens were characterized with Raman mapping microscopy to obtain the cross-sectional map distributions for those samples. By analyzing the map distributions, two new reactions were inferred to summarize the reaction mechanisms during the heating process that happened on the Fe source coated side. The effectiveness of this Fe-containing source addition method is assessed by comparing the map distributions of Fe-coated samples and uncoated samples. The results indicated that the Fe-coated samples can achieve 100% intermetallic layer growth at a lower heating temperature and for a shorter heating duration. This fast intermetallic layer growth is crucial to alleviate furnace roller contamination by decreasing the quantity and existing time of melted Al-Si coating, which provides a potential method for alleviating roller pollution. Besides, this rapid heating method can enhance production efficiency and increase profitability. By reducing the heating time while achieving the

desired phase growth, production cycles can be shortened, allowing for higher throughput and improved overall productivity.

## Chapter 6

### Conclusions

#### 6.1 Summary

The Al-Si coatings are globally utilized in the hot stamping process to provide high oxidation resistance and decarburization during processing, as well as favorable properties in the final products including corrosion resistance, paintability, and weldability. However, the Al-Si coating melts during the heating process of hot stamping, causing contamination to the furnace rollers. It is crucial to have a clear understanding of the reaction mechanisms of the intermetallic layers' transformation during the hot stamping process, which will provide better guidance for proposing solutions aimed at mitigating contamination issues. Previous research proposed phase transition mechanisms that were temperature-dependent, and the identity of intermetallic phases was characterized by SEM-EDS. More accurate and time-saving characterization methods are needed to study the Al-Si coating reaction with steel during heating.

We first developed a rapid method of using Raman microscopy to study film compositions. The Al-Fe(-Si) intermetallic phase standards were synthesized by arc melting and characterized by XRD and Raman microscopy. The steel samples were heated for 10 minutes under different heating temperatures between 570 – 900 °C. The cross-sectional views of all the samples were characterized by Raman microscopic mapping to confirm the distribution of intermetallic phases by comparing with the Raman spectra for intermetallic standards. Five critical reactions were proposed to describe the reaction mechanisms on the interface of Al-Si coating and steel during heating process, where the Fe and Si were gradually diffused to the top of Al-Si coating and Al towards the inner interface. This simple and rapid analysis method can be applied to build a comprehensive understanding of interfacial reactions.

In the next part, a more comprehensive analysis of interface reactions was conducted using Raman microscopic mapping. To minimize heat loss when opening the furnace door to insert samples, we utilized a tube furnace for heating the samples. A total of 72 steel samples were prepared under different heating temperatures from 570 – 900 °C for different heating dwell times of 1 – 10 minutes. The cross-sectional views of each map were characterized and analyzed to investigate the influence of heating duration and temperature on the reaction mechanism. The results indicated that the degree of

phase transition and the thickness of phase growth increased with the increase in heating time and sample temperature. Fe diffusion is the main driver for the interface reactions.

With the understanding of the phase transition mechanism, we proposed a surface modification method to alleviate the contamination issue. A Fe-containing source was electrodeposited to the surface of the Al-Si coating. The Fe source coated samples were heated at different temperatures from 570 – 900 °C for 2 minutes and the cross-section of the samples were characterized by Raman microscopic mapping. The obtained results were compared with no Fe-coated samples to demonstrate the effectiveness of incorporating Fe on the top of Al-Si coating in the heating process. By facilitating the formation of intermetallic layers, the melted Al-Si coating will reduce and further reduces the transfer to furnace rollers to contaminate the furnace rollers.

In summary, this project provided a more systematic and comprehensive study of phase transition mechanisms, and it also introduced an innovative characterization method, Raman mapping microscopy. In addition, this work proposed a surface modification method for facilitating the formation of intermetallic layers during the heating process to alleviate the contamination of melted Al-Si coating on furnace rollers.

## **6.2 Future work**

The Fe addition approach shows promise and now needs to be optimized. Following lab-based optimization, the strategy must be adapted to an industrial setting.

The method we used to deposit Fe-containing coating on the Al-Si coated steel is the electrodeposition method, which works well on small-scale steels. However, this method may not be efficient or optimal for industrial production. The steel coupons are large in the industrial hot stamping process, which would cost a lot of electrolyte solution and generate a lot of waste, causing environmental issues. While this method demonstrates the production of well-performed coatings, it is worth considering alternative approaches that could potentially achieve comparable coating performance in a more time-efficient manner. Thus, alternative coating methods, such as spray coating and roll coating, will be investigated for a more cost-effective and efficient approach.

Furthermore, the thickness of our coating is approximately 5  $\mu\text{m}$ , and it has been observed to effectively facilitate phase transitions during heating. However, it is possible that such a thickness may not be necessary to achieve similar results in promoting phase transitions. Exploring the optimal

coating thickness could lead to identifying a minimum effective thickness that minimizes both the cost and time required while still promoting the growth of intermetallic layers.

Additionally, as the theory mentioned in Chapter 4, adding a Fe-containing source on top of Al-Si coated steel would facilitate the formation of intermetallic layer growth. In this project, we electrodeposited Fe onto the coating, while the Raman spectroscopy indicates it got oxidized to iron oxide. Thus, we can explore an alternative, more cost-effective, and simpler source of Fe coating.

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## Appendix A

### Supplementary Information for Chapter 3

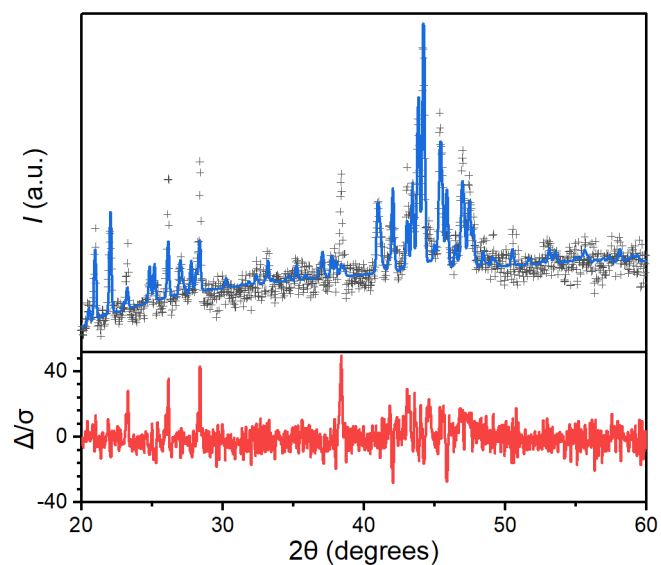


**Figure A. 1** Rietveld refinement for synthesized  $\tau_2$  sample. Refinement performed using  $R\text{-}3$  space group as in ICSD 99169.

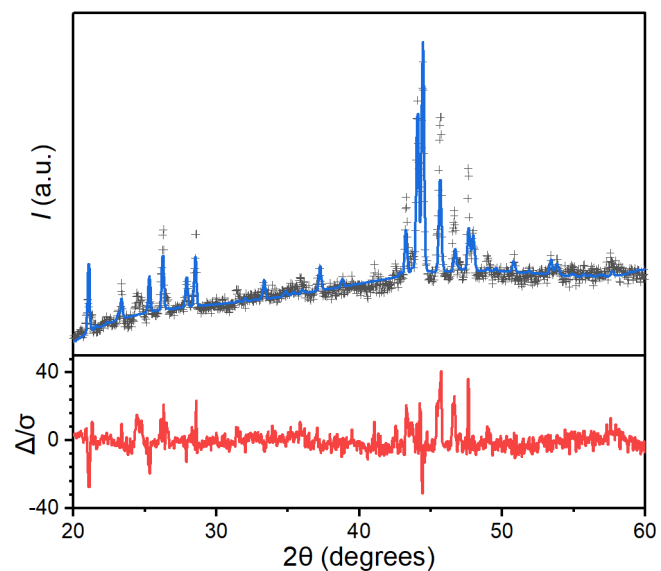


**Figure A. 2** Rietveld refinement for synthesized  $\tau_3$  sample. Refinement performed using  $Cmma$  space group as in ICSD 40317.

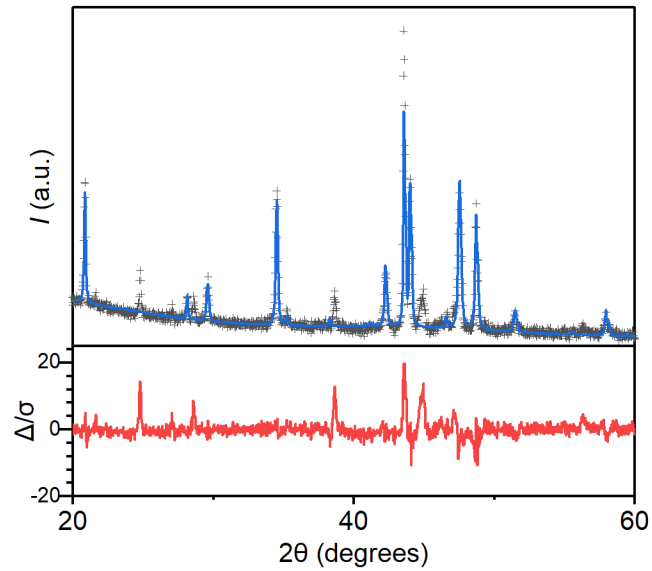


**Figure A. 3** Rietveld refinement for synthesized  $\tau_4$  sample. Refinement performed using  $I4/mcm$  space group as in ICSD 199347.

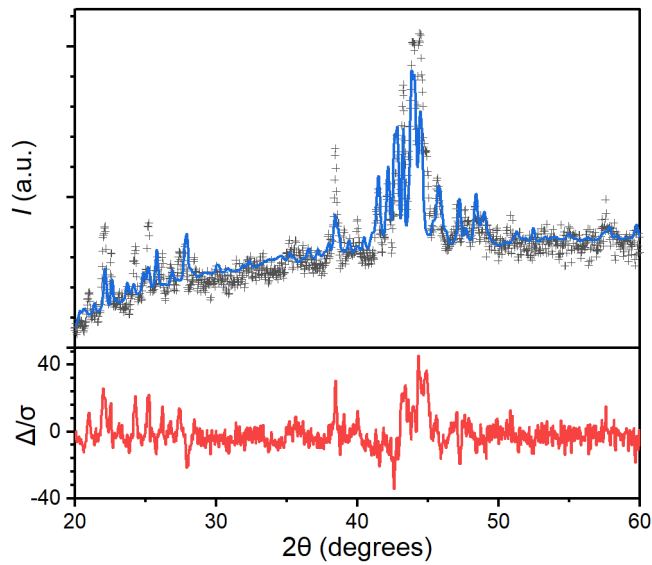


**Figure A. 4** Rietveld refinement for synthesized  $\tau_5$  sample. Refinement performed using  $P63/mmc$  space group as in ICSD 42224.

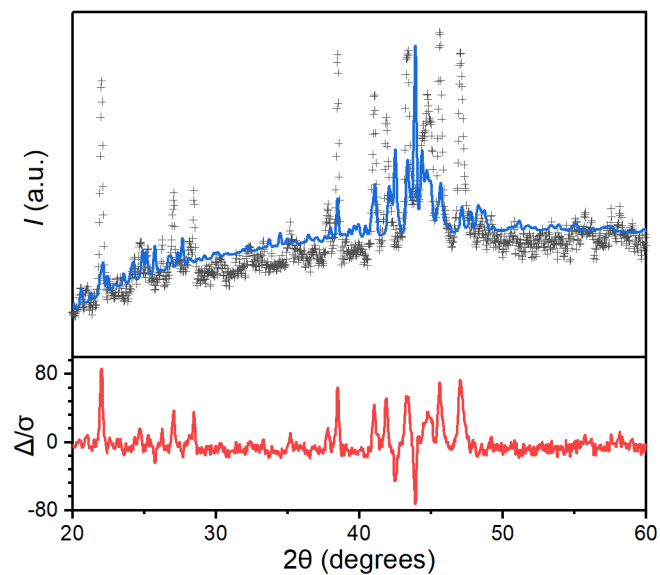


**Figure A. 5** Rietveld refinement for synthesized  $\tau_6$  sample. Refinement performed using  $A2/a$  space group as in ICSD 54050.

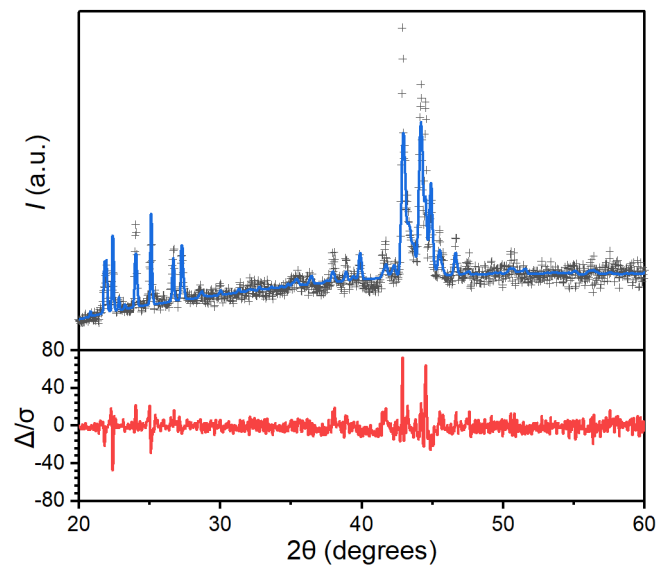


**Figure A. 6** Rietveld refinement for synthesized  $\theta$  sample. Refinement performed using  $C2/m$  space group as in ICSD 57795.

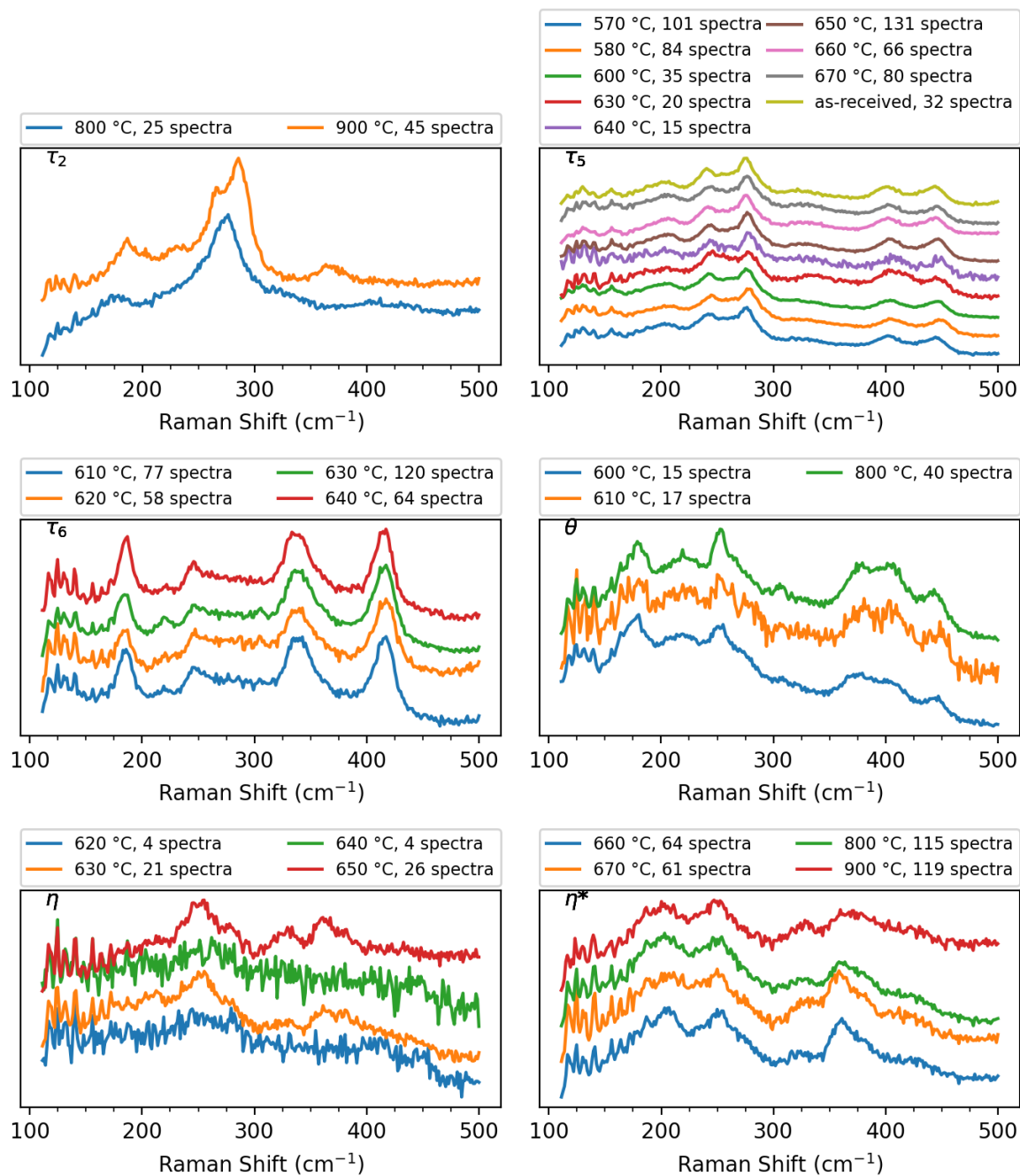


**Figure A. 7** Average Raman spectra observed in 2-D Raman microscopic maps of thin films coatings after heating. The average spectrum for each individual intermetallic phase was calculated on a per-sample basis. The number of samples involved in each calculation are noted.

## Appendix B

### Supplementary Information for Chapter 4

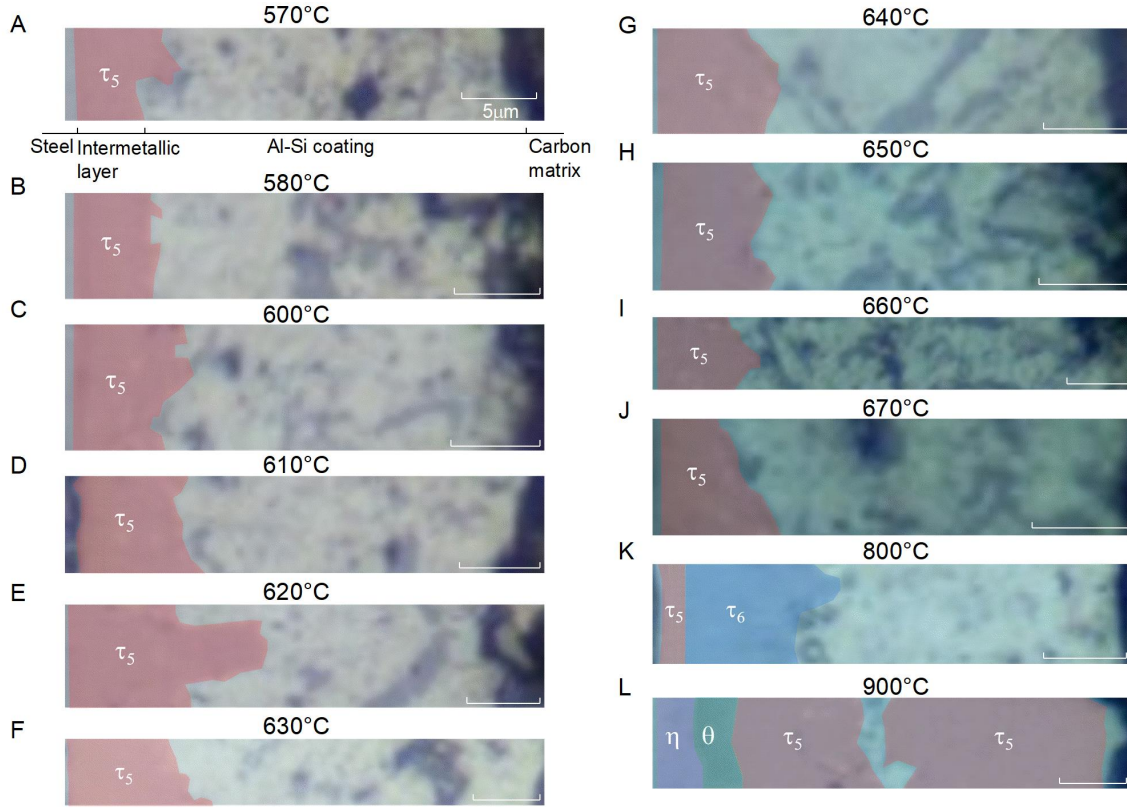


**Figure B. 1** Cross-sectional view of 1 minute heated 22MnB5 steel with phase distribution. (A) The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled with steel, intermetallic layers, Al-Si coating, and carbon matrix to illustrate the layout of the map. Additional maps are from samples heated for 1 minute at (B) 580, (C) 600, (D) 610, (E) 620, (F) 630, (G) 640, (H) 650, (I) 660, (J) 670, (K) 800, and (L) 900 °C, they all have the similar layout with 570 °C sample. A 5 μm scale bar is labeled on each map to show the size of the maps.

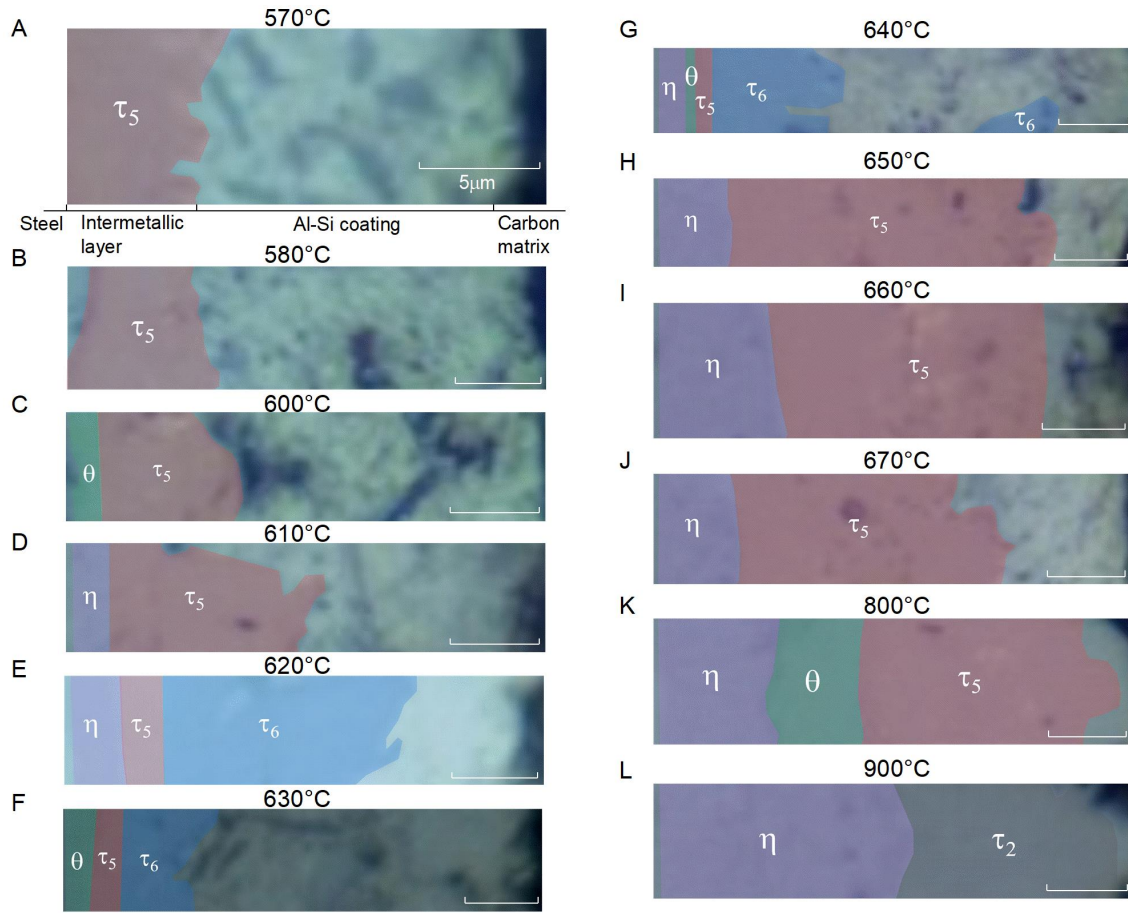


**Figure B. 2** Cross-sectional view of 4 minutes heated 22MnB5 steel with phase distribution. (A) The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled with steel, intermetallic layers, Al-Si coating, and carbon matrix to illustrate the layout of the map. Additional maps are from samples heated for 4 minutes at (B) 580, (C) 600, (D) 610, (E) 620, (F) 630, (G) 640, (H) 650, (I) 660, (J) 670, (K) 800, and (L) 900 °C, they all have the similar layout with 570 °C sample. A 5  $\mu\text{m}$  scale bar is labeled on each map to show the size of the maps.

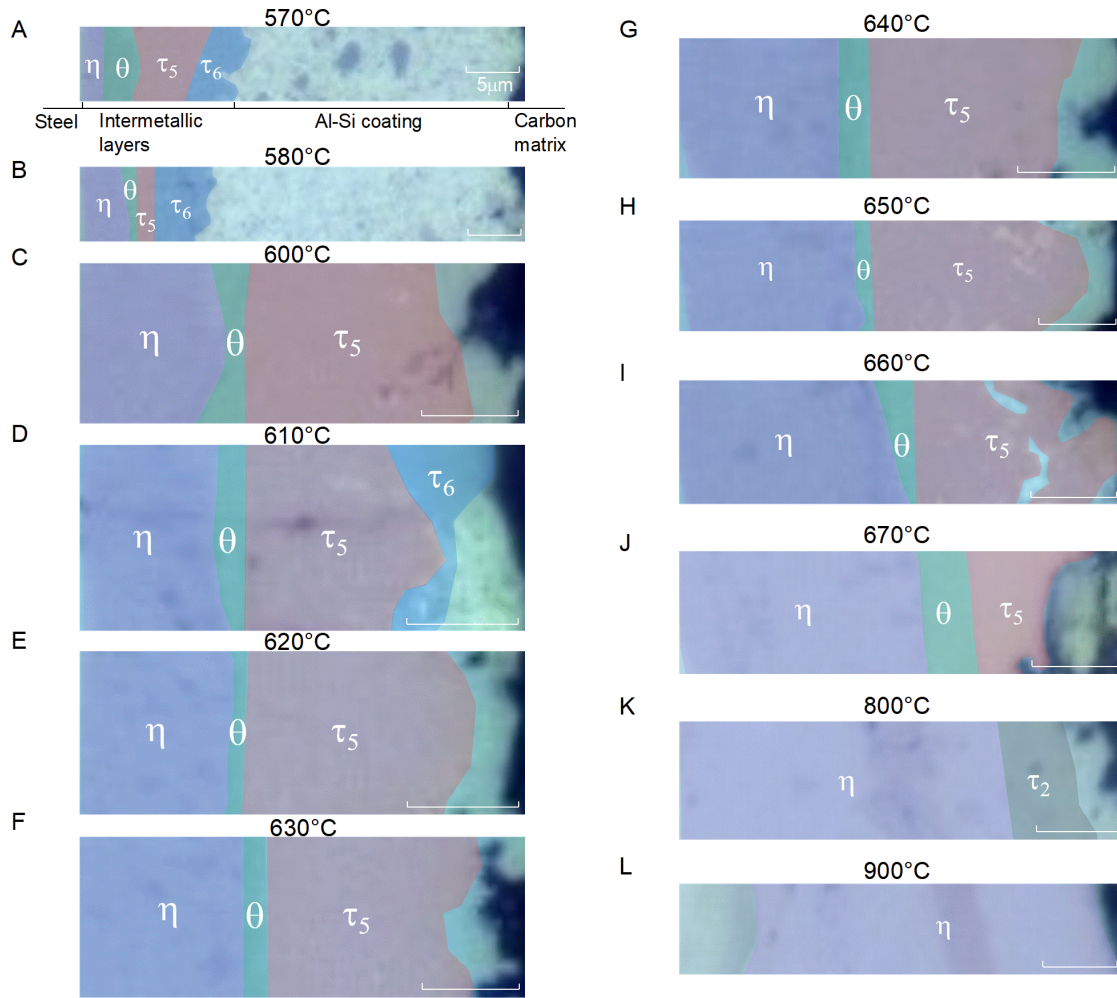


**Figure B. 3** Cross-sectional view of 8 minutes heated 22MnB5 steel with phase distribution. (A) The cross-sectional view of 570 °C heated 22MnB5 steel sample is labeled with steel, intermetallic layers, Al-Si coating, and carbon matrix to illustrate the layout of the map. Additional maps are from samples heated for 8 minutes at (B) 580, (C) 600, (D) 610, (E) 620, (F) 630, (G) 640, (H) 650, (I) 660, (J) 670, (K) 800, and (L) 900 °C, they all have the similar layout with 570 °C sample. A 5  $\mu$ m scale bar is labeled on each map to show the size of the maps.

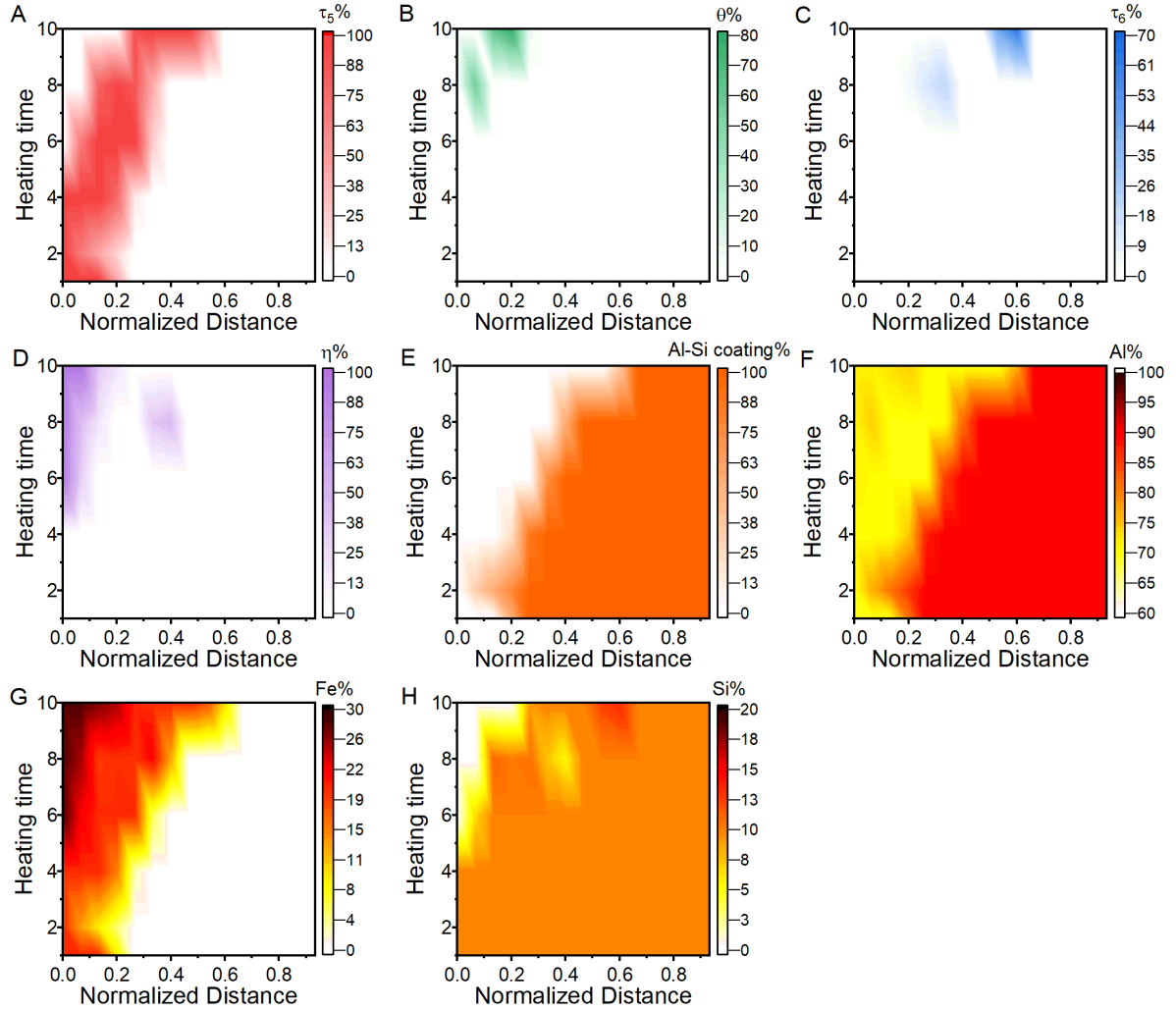


**Figure B. 4** Contour plots of the proportion of individual intermetallic phases for samples heated under 570 °C as a function of normalized location within the coating and heating time. The location within coating is based on the normalized distance to the steel, where a normalized distance of 0 represents the steel surface and a 1 represents the top of the Al-Si coating. The contour plot of **(A)**  $\tau_6$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratio, **(E)** Al-Si coating ratio, **(F)** Al, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 570 °C heating temperature.

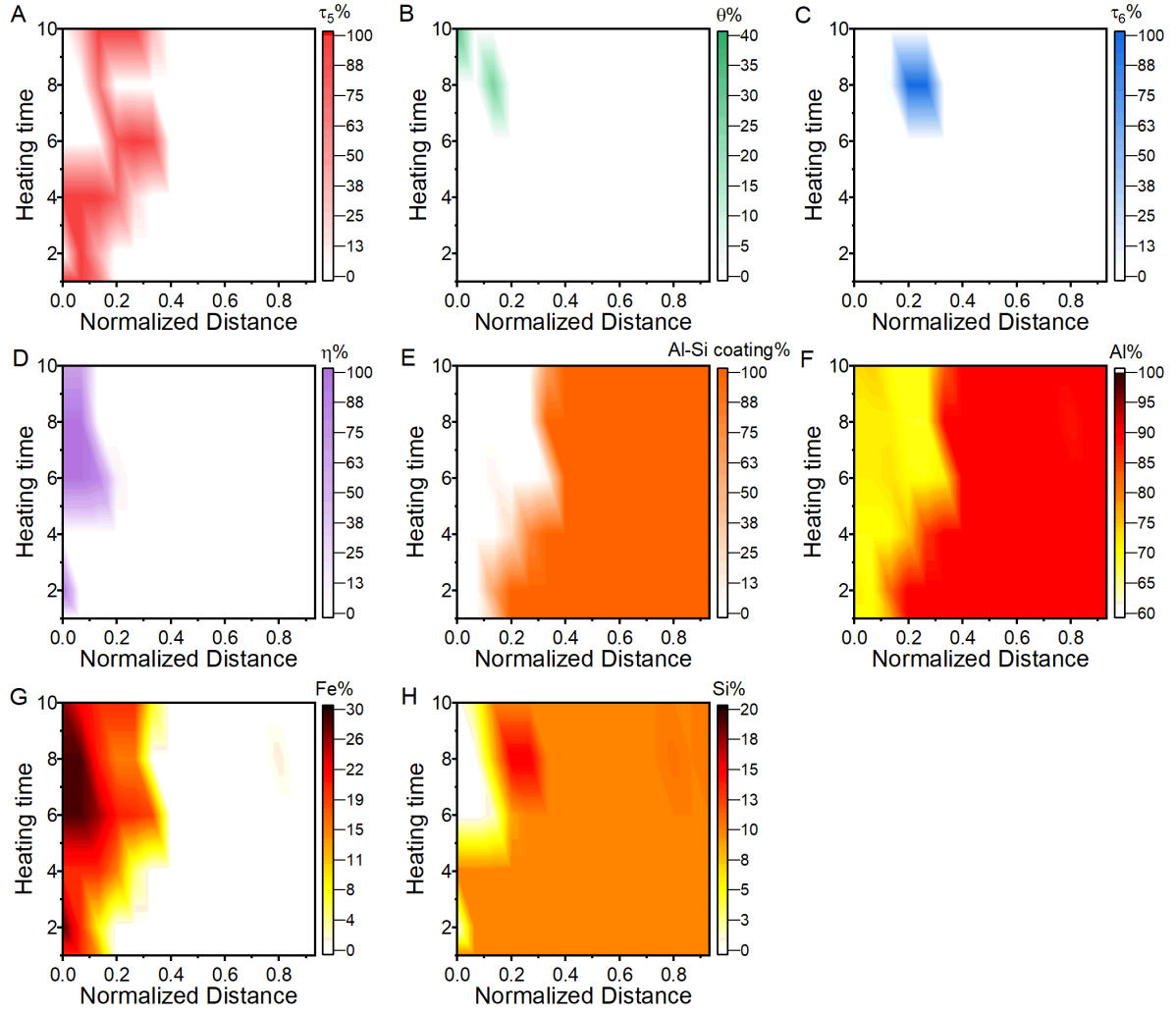


**Figure B. 5** Contour plots of the proportion of individual intermetallic phases for samples heated under 580 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratio, **(E)** Al-Si coating ratio, **(F)** Al, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 580 °C heating temperature.

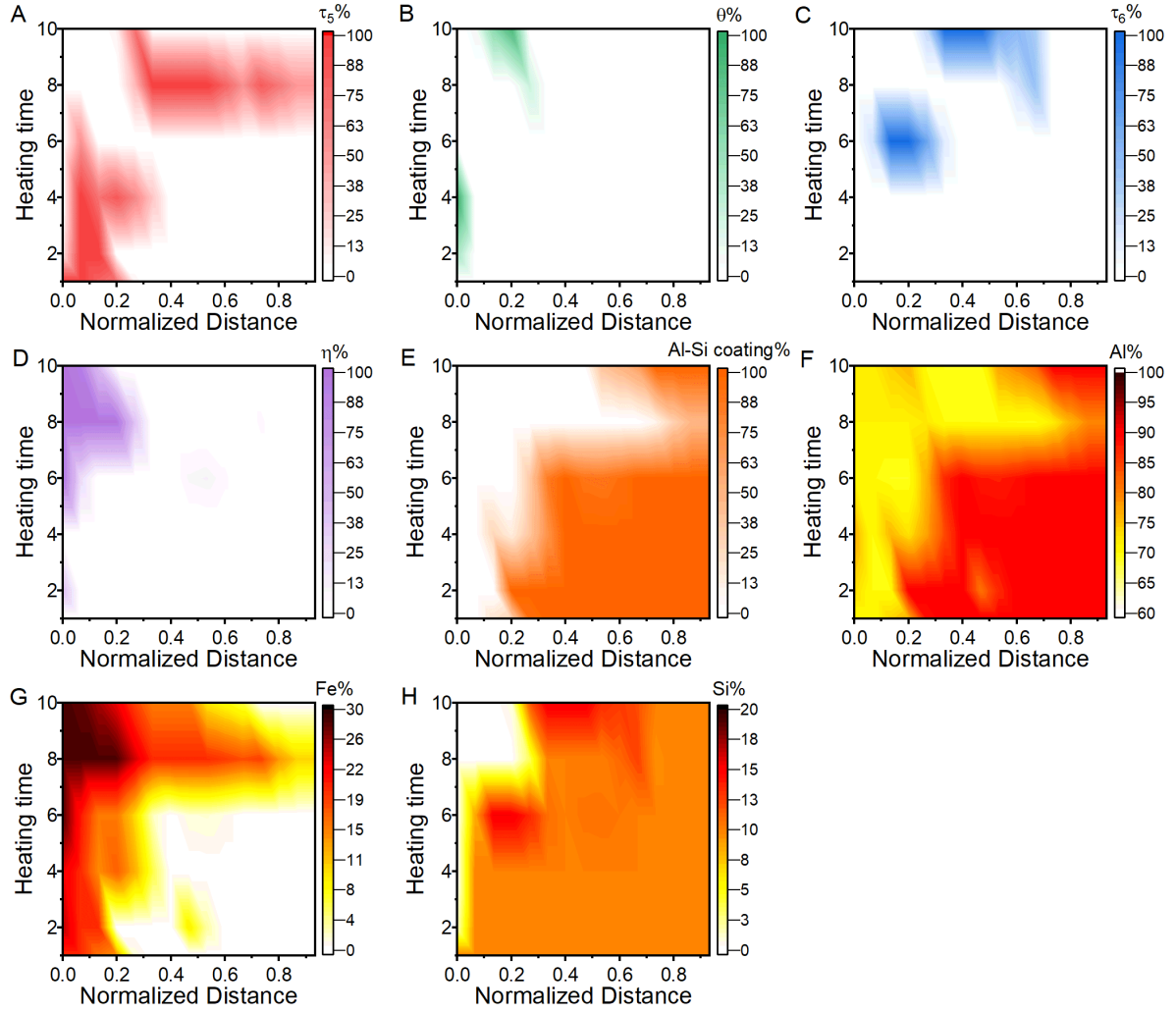


**Figure B. 6** Contour plots of the proportion of individual intermetallic phases for samples heated under 600 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratio, **(E)** Al-Si coating ratio, **(F)** Al, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 600 °C heating temperature.

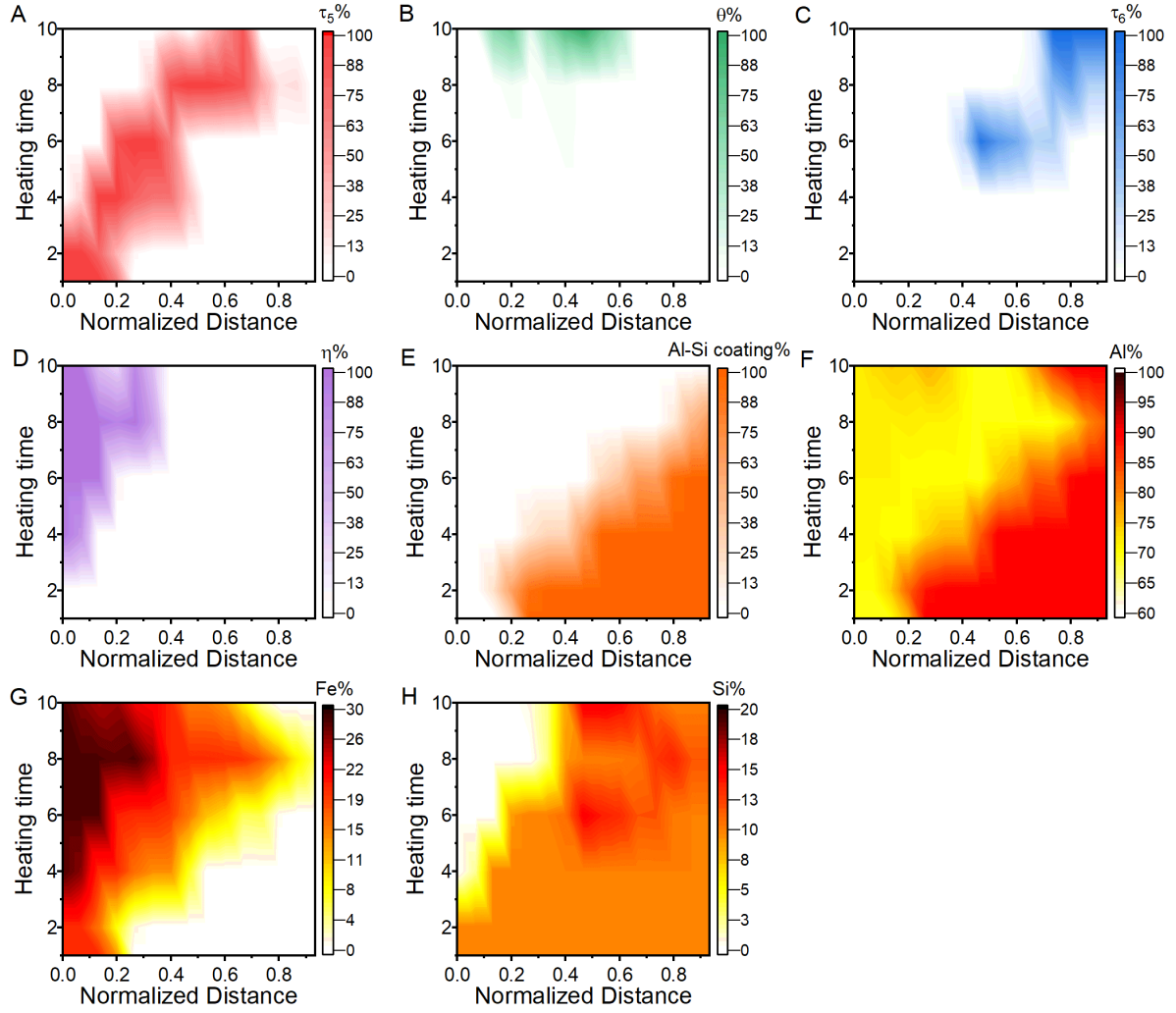


**Figure B. 7** Contour plots of the proportion of individual intermetallic phases for samples heated under 610 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratio, **(E)** Al-Si coating ratio, **(F)** Al, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 610 °C heating temperature.

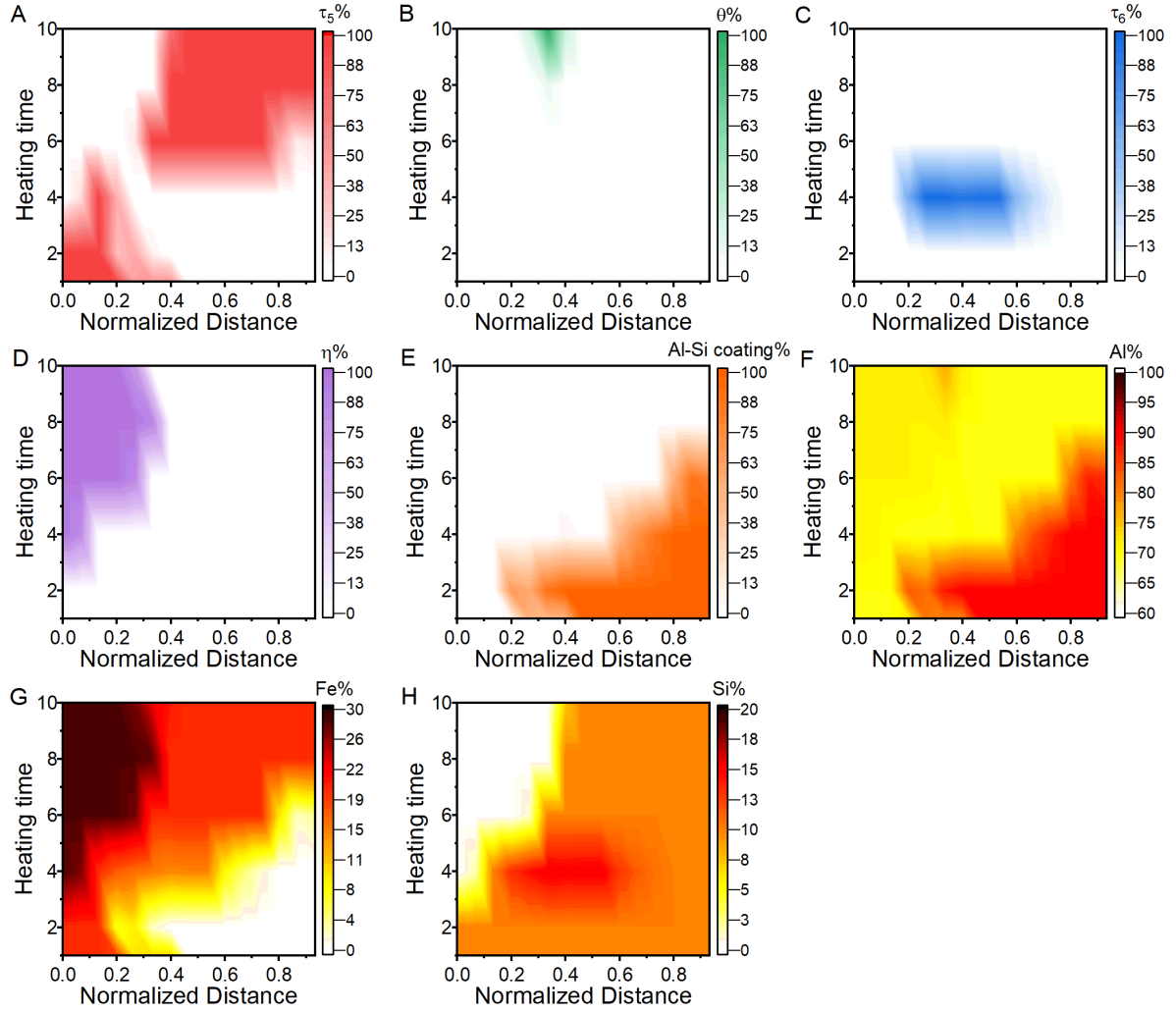


**Figure B. 8** Contour plots of the proportion of individual intermetallic phases for samples heated under 620 °C as a function of normalized location within the coating and heating time. The contour plot of (A)  $\tau_5$  ratio, (B)  $\theta$  ratio, (C)  $\tau_6$  ratio, (D)  $\eta$  ratio, (E) Al-Si coating ratio, (F) Al, (G) Fe, and (H) Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 620 °C heating temperature.

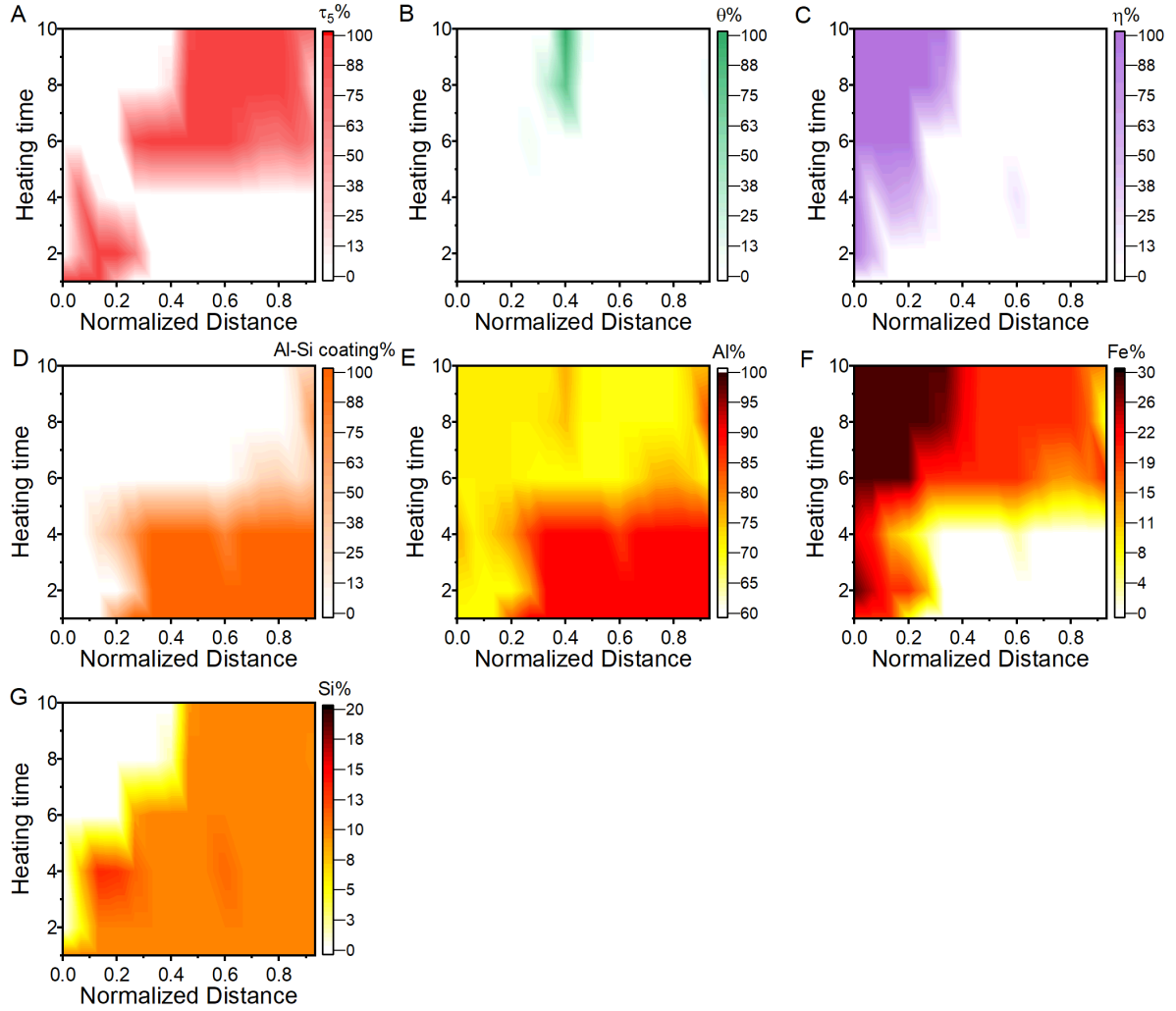


**Figure B. 9** Contour plots of the proportion of individual intermetallic phases for samples heated under 630 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\eta$  ratio, **(D)** Al-Si coating ratio, **(E)** Al, **(F)** Fe, and **(G)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  and  $\tau_6$  ratio changes are shown here since there is no  $\tau_2$  or  $\tau_6$  emerging under 630 °C heating temperature.

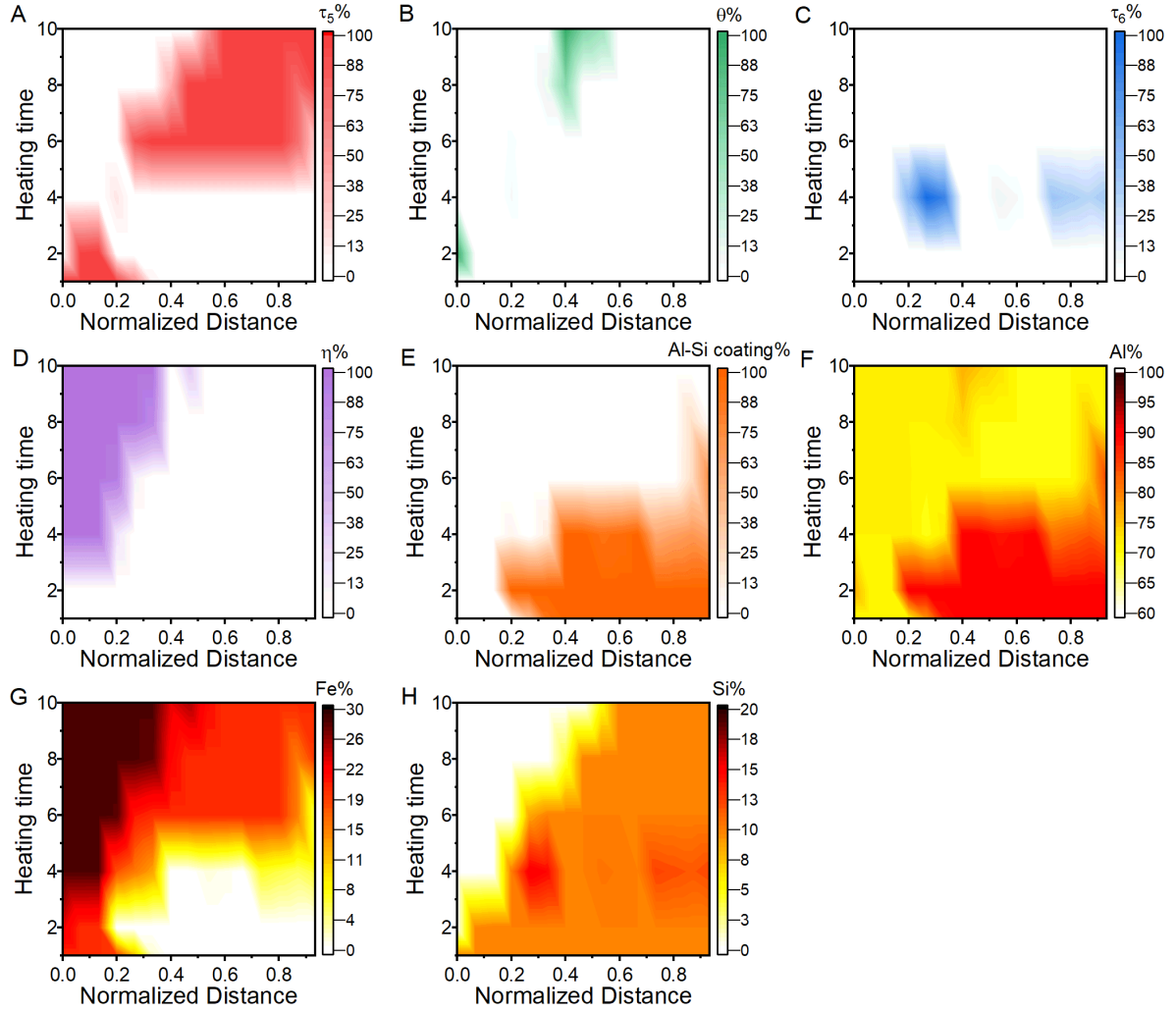


**Figure B. 10** Contour plots of the proportion of individual intermetallic phases for samples heated under 640 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\tau_6$  ratio, **(D)**  $\eta$  ratio, **(E)** Al-Si coating ratio, **(F)** Al, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging under 640 °C heating temperature.

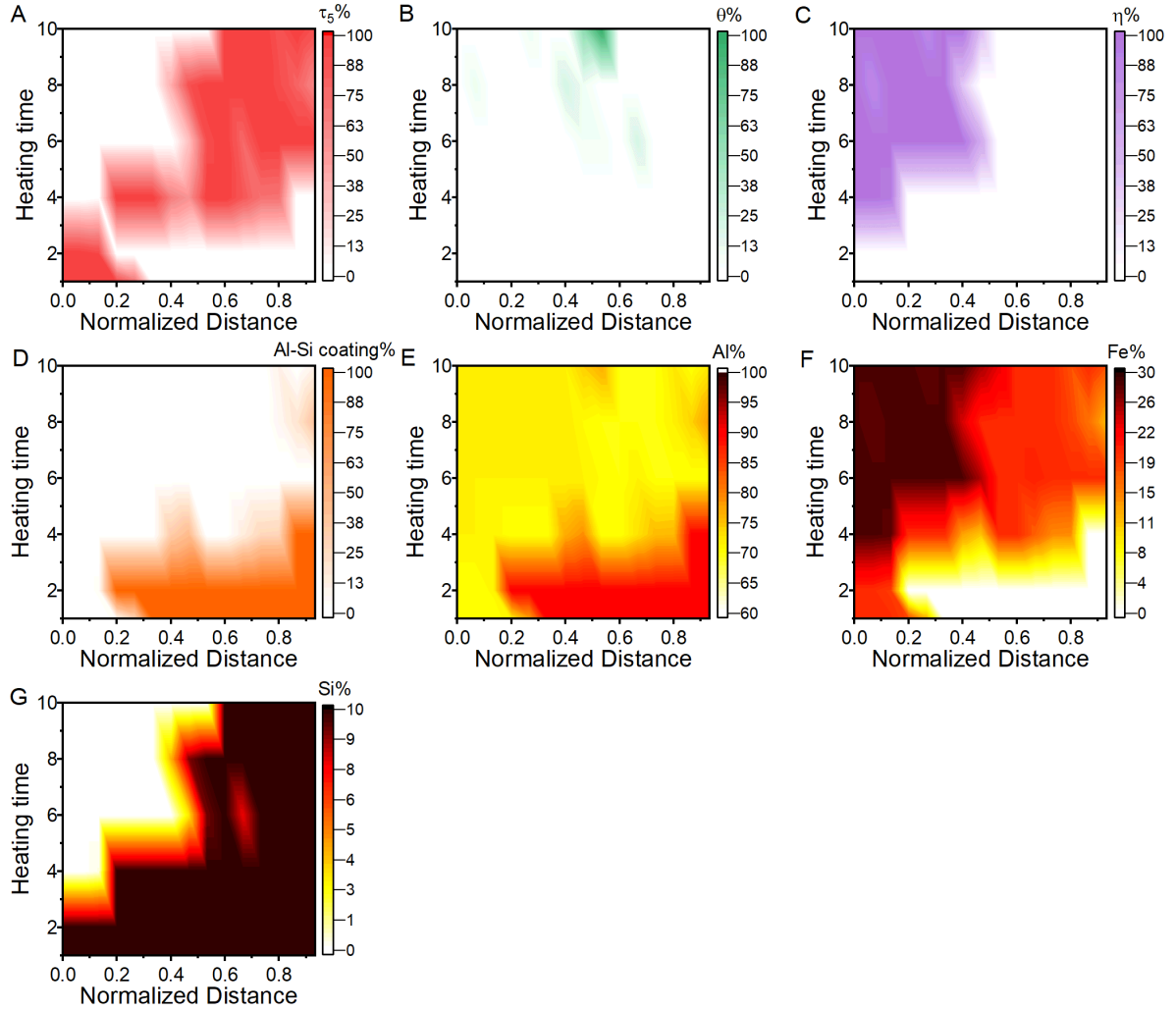


**Figure B. 11** Contour plots of the proportion of individual intermetallic phases for samples heated under 650 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\eta$  ratio, **(D)** Al-Si coating ratio, **(E)** Al, **(F)** Fe, and **(G)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  and  $\tau_6$  ratio changes are shown here since there is no  $\tau_2$  or  $\tau_6$  emerging under 650 °C heating temperature.

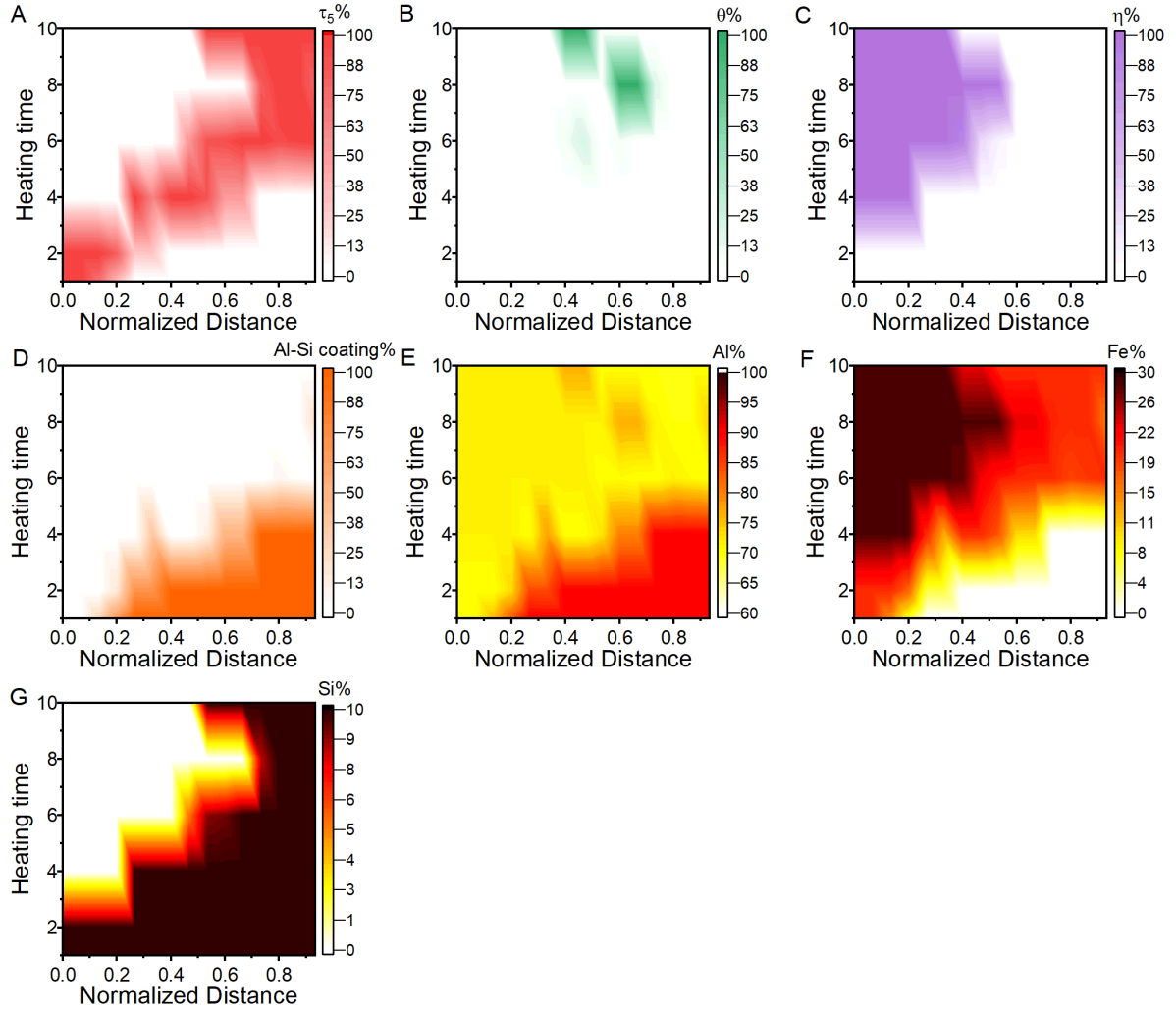


**Figure B. 12** Contour plots of the proportion of individual intermetallic phases for samples heated under 670 °C as a function of normalized location within the coating and heating time. The contour plot of (A)  $\tau_5$  ratio, (B)  $\theta$  ratio, (C)  $\eta$  ratio, (D) Al-Si coating ratio, (E) Al, (F) Fe, and (G) Si element ratio, as a function of heating time and distance from steel. No  $\tau_2$  and  $\tau_6$  ratio changes are shown here since there is no  $\tau_2$  or  $\tau_6$  emerging under 670 °C heating temperature.

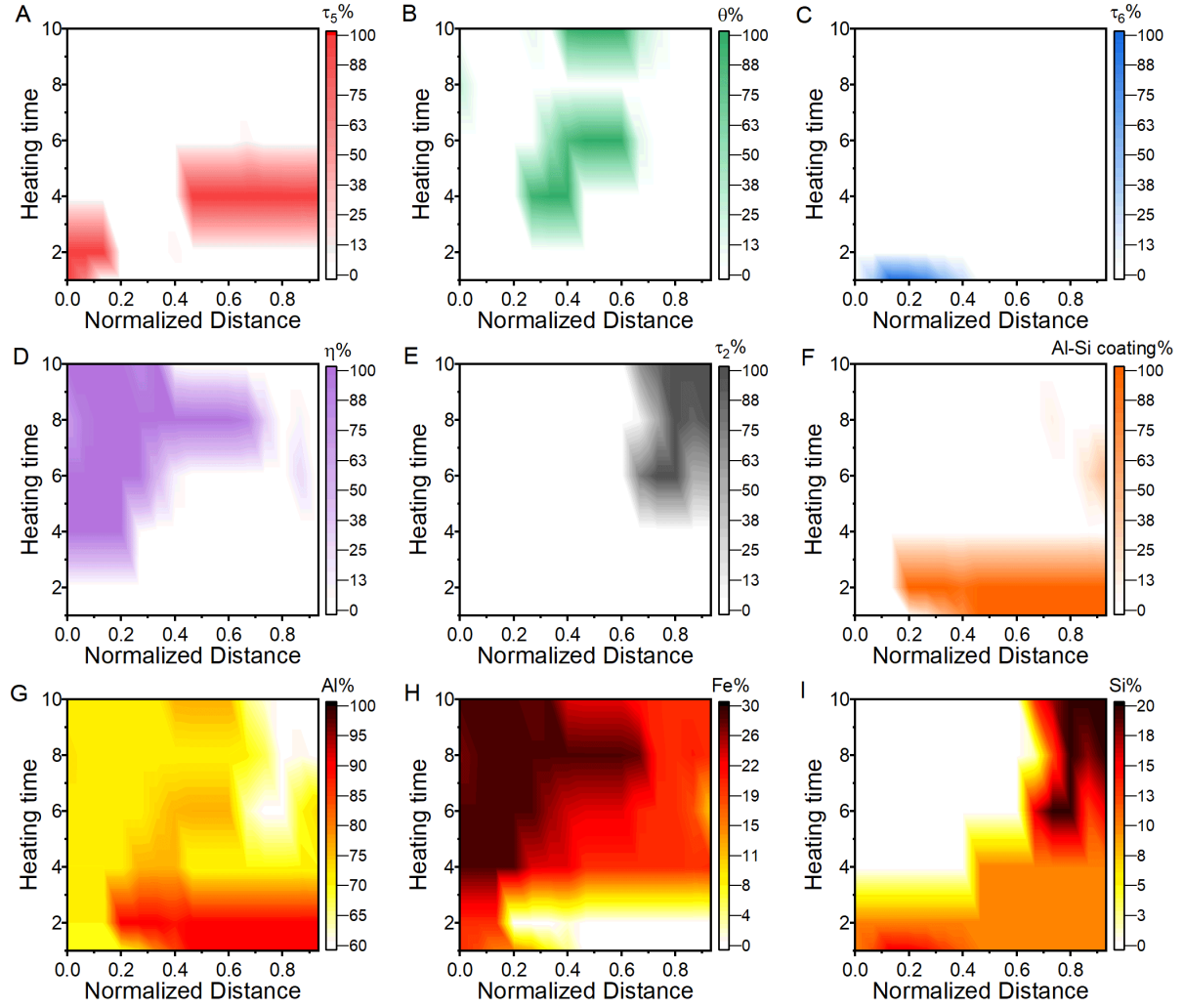


**Figure B. 13** Contour plots of the proportion of individual intermetallic phases for samples heated under 800 °C as a function of normalized location within the coating and heating time. The contour plot of (A)  $\tau_5$  ratio, (B)  $\theta$  ratio, (C)  $\tau_6$  ratio, (D)  $\eta$  ratio, (E)  $\tau_2$  ratio, (F) Al-Si coating ratio, (G) Al, (H) Fe, and (I) Si element ratio, as a function of heating time and distance from steel.

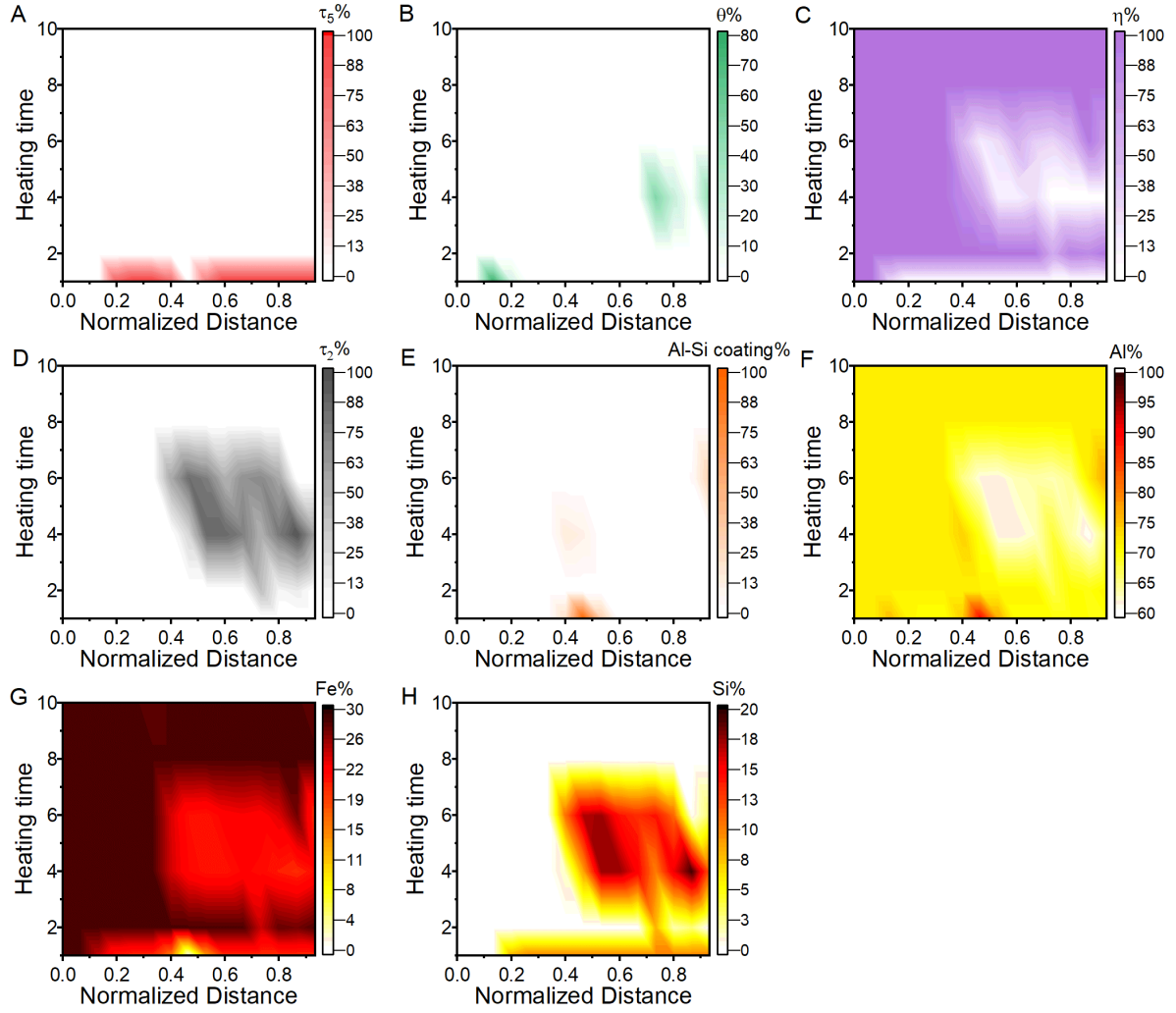


**Figure B. 14** Contour plots of the proportion of individual intermetallic phases for samples heated under 900 °C as a function of normalized location within the coating and heating time. The contour plot of **(A)**  $\tau_5$  ratio, **(B)**  $\theta$  ratio, **(C)**  $\eta$  ratio, **(D)**  $\tau_2$  ratio, **(E)** Al-Si coating ratio, **(F)** Al ratio, **(G)** Fe, and **(H)** Si element ratio, as a function of heating time and distance from steel. No  $\tau_6$  ratio change is shown here since there is no  $\tau_6$  emerging under 900 °C heating temperature.

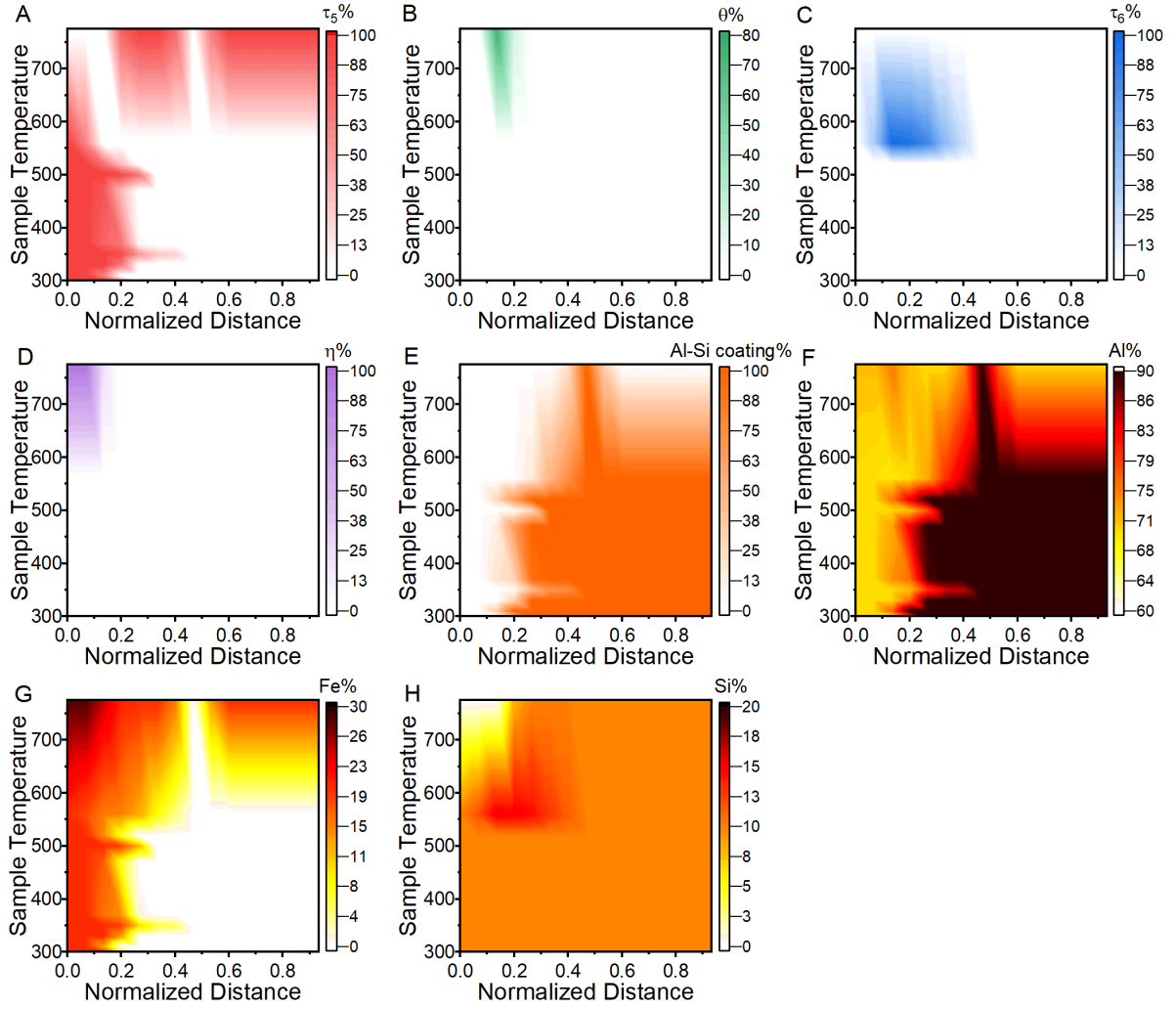


**Figure B. 15** Contour plots of ratio changes for samples heated for 1 minute as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)** Al-Si coating, **(F)** Al element, **(G)** Fe element, and **(H)** Si element, were listed as a function of heating temperature and normalized distance. No  $\tau_2$  ratio change is shown here since there is no  $\tau_2$  emerging for 1 minute heating.

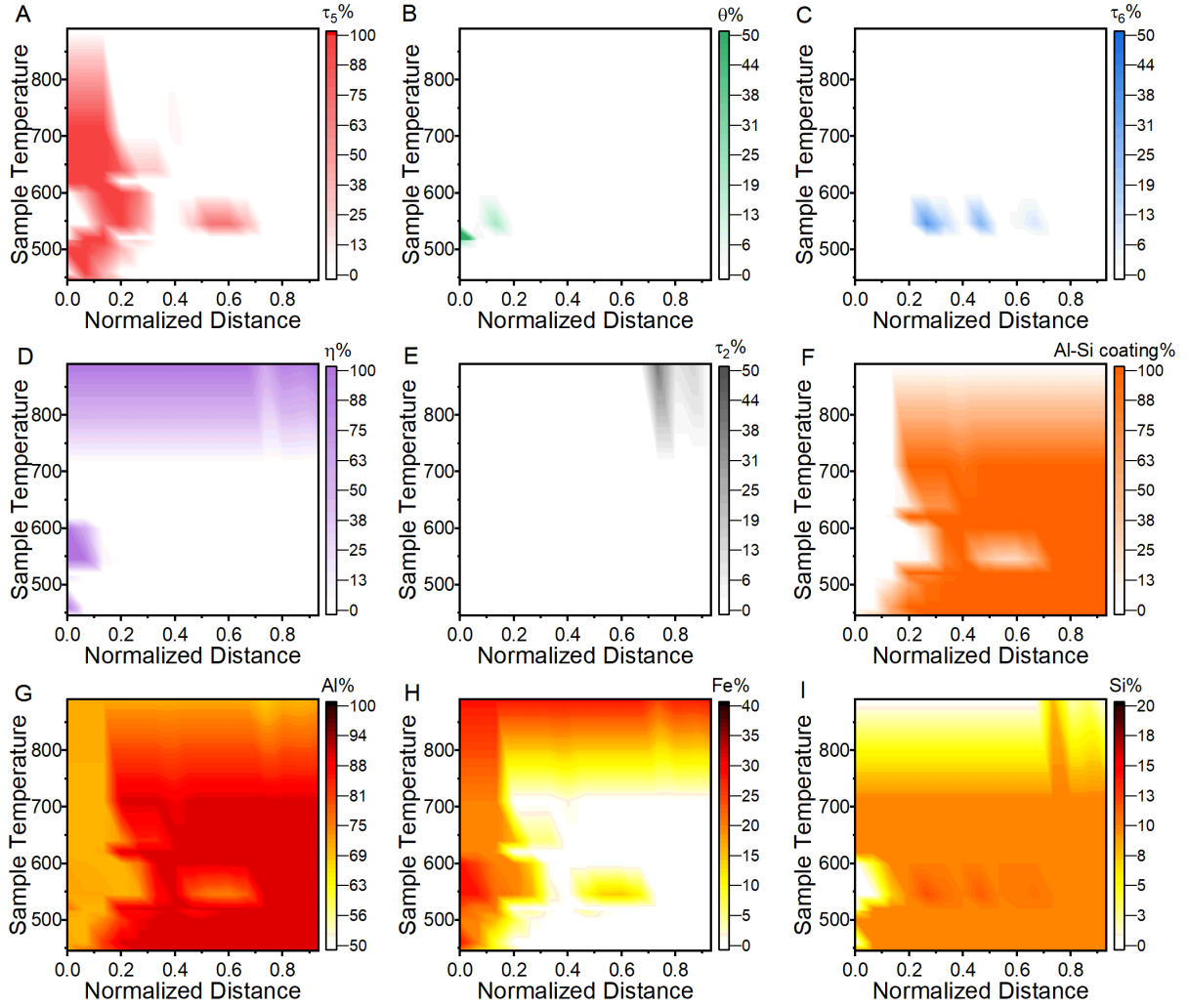


**Figure B. 16** Contour plots of ratio changes for samples heated for 2 minutes as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)**  $\tau_2$ , **(F)** Al-Si coating, **(G)** Al element, **(H)** Fe element, and **(I)** Si element, were listed as a function of heating temperature and normalized distance.

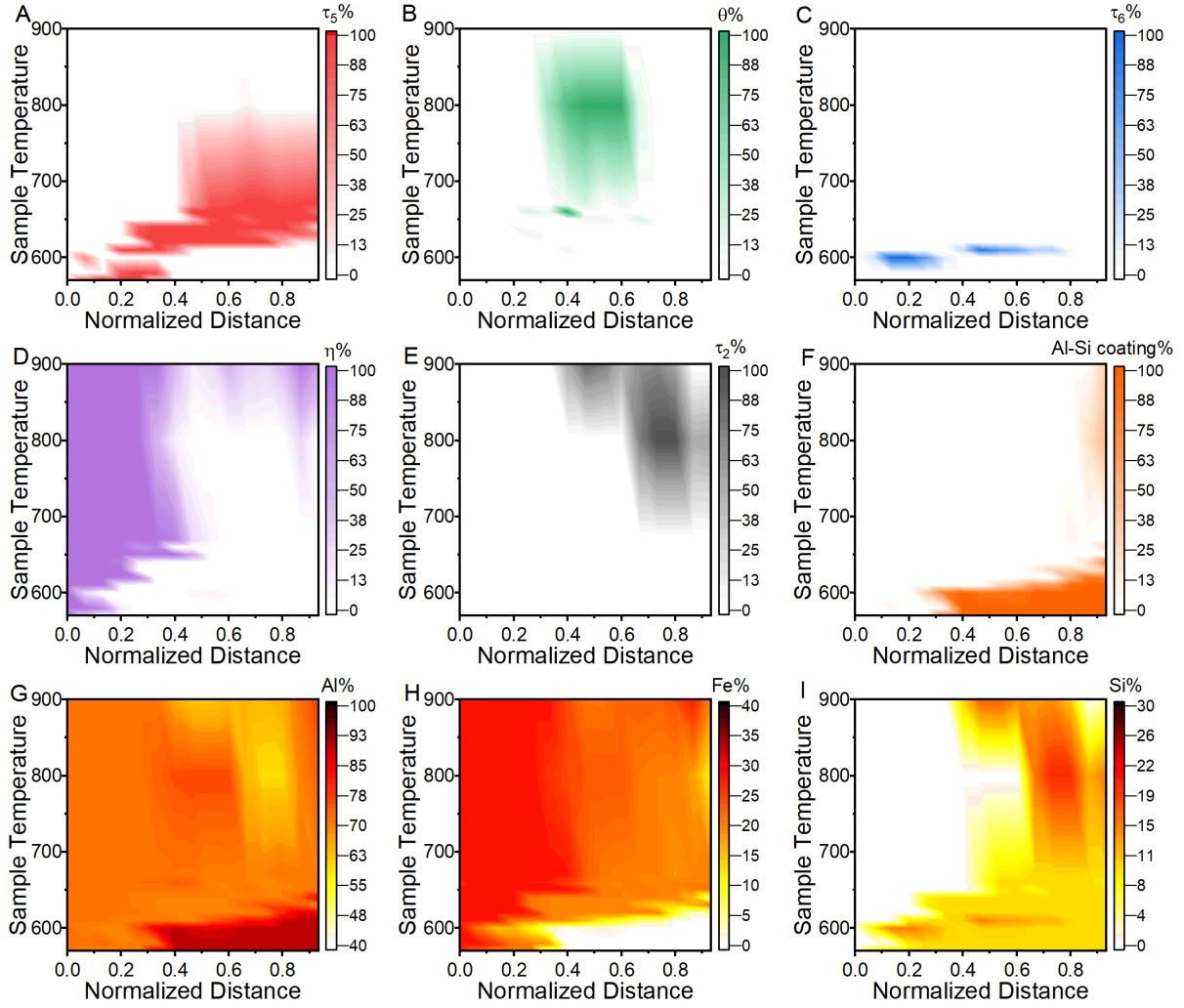


**Figure B. 17** Contour plots of ratio changes for samples heated for 6 minutes as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)**  $\tau_2$ , **(F)** Al-Si coating, **(G)** Al element, **(H)** Fe element, and **(I)** Si element, were listed as a function of heating temperature and normalized distance.

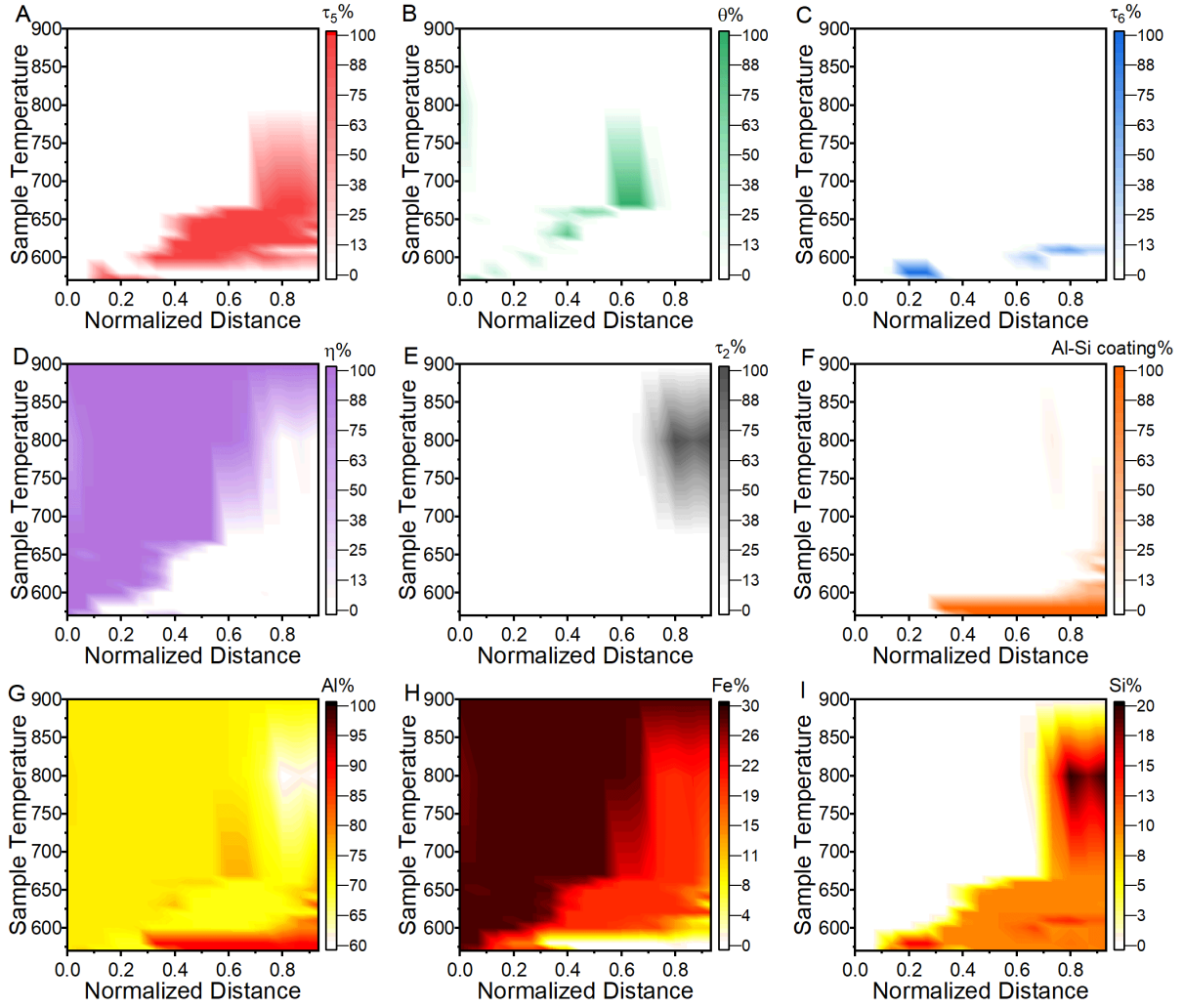


**Figure B. 18** Contour plots of ratio changes for samples heated for 8 minutes as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)**  $\tau_2$ , **(F)** Al-Si coating, **(G)** Al element, **(H)** Fe element, and **(I)** Si element, were listed as a function of heating temperature and normalized distance.

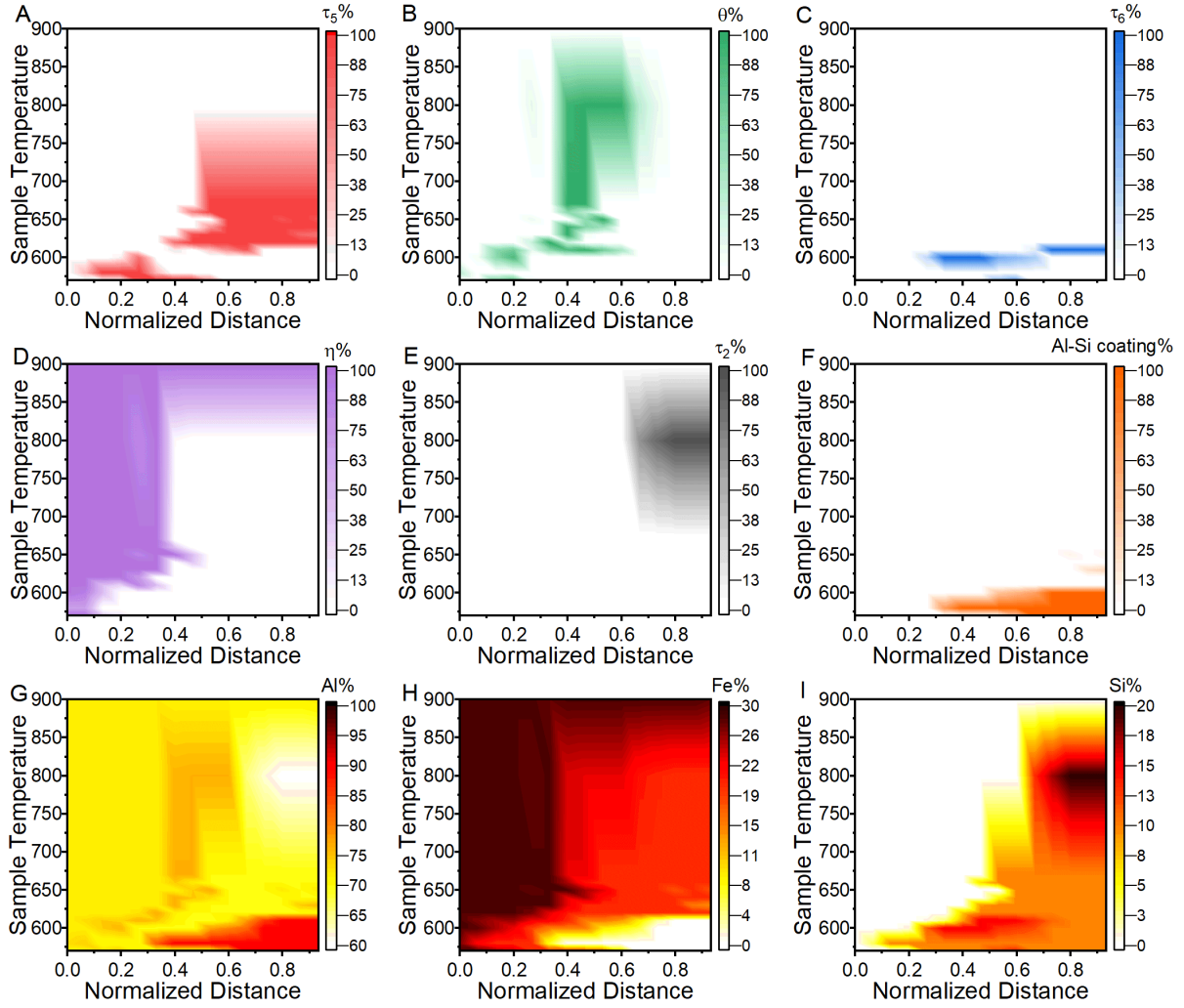


**Figure B. 19** Contour plots of ratio changes for samples heated for 10 minutes as a function of sample temperature and distance from steel. The ratio changes of **(A)**  $\tau_5$ , **(B)**  $\theta$ , **(C)**  $\tau_6$ , **(D)**  $\eta$ , **(E)**  $\tau_2$ , **(F)** Al-Si coating, **(G)** Al element, **(H)** Fe element, and **(I)** Si element, were listed as a function of heating temperature and normalized distance.