Xu, Gaopeng; Wang, Kui; Dong, Xianping; Yang, Lei; Ebrahimi, Mahmoud; Jiang, Haiyan; Wang, Qudong; Ding, Wenjiang

**Review on corrosion resistance of mild steels in liquid aluminum**

*Published in:*
JOURNAL OF MATERIALS SCIENCE AND TECHNOLOGY

*DOI:*
10.1016/j.jmst.2020.08.052

*Published: 30/04/2021*

*Document Version*
Peer reviewed version

*Published under the following license:*
CC BY-NC-ND

*Please cite the original version:*
Invited Review

Review on corrosion resistance of mild steels in liquid aluminum

Gaopeng Xu a, Kui Wang a,*, Xianping Dong b, Lei Yang c.d,*, Muhammad Ebrahimi a, Haiyan Jiang a, Qudong Wang a, Wenjiang Ding a

a National Engineering Research Center of Light Alloy Net Forming and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

b Shanghai Key Laboratory of High Temperature Materials and Precision Forming, Shanghai Jiao Tong University, Shanghai 200240, China

c Nano Life Science Institute (WPI-NanoLSI), Kanazawa University, Kakuma-machi, Kanazawa 920-1192, Japan

d COMP Centre of Excellence, Department of Applied Physics, Aalto University, Helsinki FI-00076, Finland

* Corresponding authors.

E-mail addresses: fateratory@sjtu.edu.cn (K. Wang); l.yang@staff.kanazawa-u.ac.jp (L. Yang).

[Received 26 May 2020; Received in revised form 26 July 2020; Accepted 3 August 2020]

The corrosion of mild steels by liquid aluminum is an intractable issue in aluminum industry. This review aims to provide an overview of the corrosion behavior of mild steels in the static liquid aluminum with an emphasis on the thermodynamic and kinetic aspects. The corrosion mechanisms of mild steels in liquid aluminum are discussed systematically, based on which four corrosion control approaches including alloying, introducing secondary phase, matrix microstructure control and surface treatment are introduced. Currently, a combination of improvement approaches may have a great potential for further enhancement in corrosion resistance.
Keywords: Corrosion resistance; Liquid aluminum; Mild steel; Microstructure control; Surface treatment.

1. Introduction

Mild steels are widely used as the workpieces for the manufacture and processing of aluminum products, thanks to their advantages such as low cost, desirable comprehensive mechanical properties and wear resistance [1]. With the development of aluminum alloy liquid forming technology, corrosion of liquid aluminum has become a major problem in aluminum industry because the corrosive liquid aluminum with high chemical activity has an affinity with almost all metals and metal oxides [2,3]. During the processes of melting [4], liquid forming [5,6], and hot dipping of aluminum alloys [7-9], the crucibles, melting pot sleeves, die-casting molds and sink rolls all suffer to some extent from the corrosion of liquid aluminum. This may trigger a set of problems, including the contamination of liquid aluminum and the corrosion of equipment component, thus compromising the quality of aluminum products and production efficiency with the increase of production costs [2,10,11]. As a result, it is crucial to improve the corrosion resistance of mild steels in liquid aluminum.

In the past few decades, many researchers [5,12-16] have investigated the corrosion behavior of mild steels in liquid aluminum. Previous studies [17-20] have shown that the Fe matrix can react with liquid aluminum to form the Fe-Al intermetallic compounds (IMCs). Due to the difference in diffusion coefficients of Fe and Al atoms in Fe-Al IMCs [21], the growth of Fe-Al IMCs proceeds towards the matrix with the increase of reaction time, leading to the corrosion of the Fe matrix. So far, a number of theories [2,4,8,10,17-22] have been proposed to elucidate the corrosion behavior of mild steels in liquid aluminum, including the reaction mechanism [2,4,22], atom diffusion mechanism [10,19,21], IMCs growth mechanism [8,17,18,20], etc. Nevertheless, there is no consensus on the corrosion mechanisms up to now.

In this paper, based on the previous researches [22-28] on the reactions of mild steels
in liquid aluminum, especially the formation and growth of IMCs during the reaction process, the characteristics, formation and growth mechanisms and Fe-Al IMCs kinetics analysis, as well as the improvement approaches were summarized and discussed systematically. More importantly, the critical factors affecting the corrosion resistance of mild steels in liquid aluminum were unraveled and analyzed, which may provide a guidance for the development of corrosion resistant materials.

2. Corrosion performance and mechanisms of mild steels in liquid aluminum

2.1 Interfacial structure

According to the Fe-Al binary phase diagram \[^{[29]}\] in Fig. 1(a), iron and aluminum react with each other to form intermetallic compounds such as FeAl, FeAl\(_2\), Fe\(_2\)Al\(_5\) and FeAl\(_3\). From the perspective of thermodynamics, the formation sequence of Fe-Al IMCs is mainly determined by the corresponding Gibbs free energy \(\Delta G\) \[^{[30-32]}\]. Xu et al. \[^{[10]}\] calculated the Gibbs free energy of these IMCs at different temperatures, as shown in Fig. 1(b), and inferred that the formation sequence of Fe-Al IMCs was: FeAl\(_3\) → Fe\(_2\)Al\(_5\) → FeAl\(_2\) → FeAl. In fact, for immersion of iron in liquid aluminum, only Fe\(_2\)Al\(_5\) and FeAl\(_3\) phases are observed in the intermetallic compound layer. Bouche et al. \[^{[18]}\] and Cheng et al. \[^{[28]}\] studied the interfacial reactions of mild steel immersed in pure liquid aluminum. The result suggested that the IMCs layer has a two-layer structure composed of two Al-rich IMCs, namely Fe\(_2\)Al\(_5\) and FeAl\(_3\), as shown in Fig. 2(b). Fe\(_2\)Al\(_5\) adjacent to the Fe matrix occupies the IMCs layer dominantly, and extends towards the matrix, leading to the formation of a highly irregular tongue-shaped structure (in Fig. 2(a)). Numerous studies \[^{[3,7,10,19,33-39]}\] indicated that Fe\(_2\)Al\(_5\) grows toward the matrix with a preferential growth orientation of [001]. It is found that Fe\(_2\)Al\(_5\) has an orthogonal structure (a=0.7656 nm, b=0.6415 nm, c=0.4218 nm) with a 30% vacancy along the c-axis direction of [001], which is higher than those along the a-axis and b-axis, and thus it tends to grow along the c-axis. When the c-axis of Fe\(_2\)Al\(_5\) is perpendicular to the incipient iron-aluminum interface, it has the largest growth rate and the crystal growth in other orientations is restricted. Eventually,
the experimentally observed Fe$_2$Al$_5$ often displays an anisotropic tongue-like morphology. The layer adjacent to the aluminum layer consists of FeAl$_3$ with the monoclinic crystal structure (a=1.5489 nm, b=0.8083 nm, c=1.2476nm). Compared with the Fe$_2$Al$_5$ layer, the thickness of FeAl$_3$ layer is almost negligible, as depicted in Fig. 2. Chen et al. [24] stated that, with the reaction temperature increasing, a large number of thin needles and platelets of FeAl$_3$ attach to the FeAl$_3$ layer or even freely distribute in the aluminum layer. Additionally, flocculent Al/FeAl$_3$ eutectic structures can also be found in the aluminum layer far away from the interface. As shown in Fig. 3, the existence of FeAl$_3$ can be divided into three types: FeAl$_3$ adherent to the interface, free FeAl$_3$ away from the interface and the eutectic FeAl$_3$.

2.2 Formation and growth mechanisms of Fe-Al IMCs layer

Although the interfacial IMCs play different roles in the hot dip aluminum plating and the liquid aluminum corrosion: beneficial to the former and detrimental to the latter, their formation and growth mechanisms are essentially the same. Therefore, when studying the corrosion mechanisms of steel in liquid aluminum, theories related to the hot-dip aluminum plating can be used for reference [40,41]. Heumann et al. [36] investigated the formation mechanisms of the interfacial layer during the hot-dip aluminizing of steel. As illustrated in Fig. 4, when the liquid aluminum comes in contact with the solid steel, the interdiffusion of Al and Fe atoms occurs at the interface and the FeAl$_3$ phase begins to form. Due to the concentration fluctuation, a small region with a concentration equivalent to the Fe$_2$Al$_5$ phase is formed in the FeAl$_3$ layer, and the phase recrystallization initiates from the surface of the FeAl$_3$ phase and promotes the growth of Fe$_2$Al$_5$ along the diffusion direction. After nucleation, Fe$_2$Al$_5$ crystals grow rapidly along the c-axis owing to its unique crystal structure, forming a tongue-like morphology with a preferred growth orientation. According to the phase diagram, Adam et al. [42] proposed that the interfacial structure formed by the hot dip aluminum plating can be divided into three layers of Al/FeAl$_3$ flocculent eutectic structures, FeAl$_3$ and Fe$_2$Al$_5$ from the surface to the Fe matrix,
respectively. On this basis, a coating formation mechanism of the coating was proposed in Fig. 5, in which the growth of FeAl₃ with a columnar structure proceeds to the aluminum end.

According to the above discussion, the initial formation process of the Fe-Al interfacial reaction layer can be primarily categorized into four stages, as shown in Fig. 6. Firstly, the iron is immersed in the liquid aluminum until it is completely wetted by the interdiffusion between Fe and Al atoms (Fig. 6(a)). Since the solid solubility of Al in α-Fe is considerable, about 32.6 wt.% at room temperature [29], the Fe(Al) solid solution forms on the iron matrix side (Fig. 6(b)). Studies [10,17,18,24] have shown that the firstly formed phase is FeAl₃ with the most thermodynamic stability. As the interdiffusion proceeds, the FeAl₃ phase forms on the aluminum end (Fig. 6(c)) because the diffusion coefficient of Fe in Al is much larger than that of Al in Fe [17,41]. As Al atoms continue to diffuse into the FeAl₃ and Fe(Al) solid solution, Fe₂Al₅ phases begin to form (Fig. 6(d)). At the final stage, the Fe₂Al₅ layer thickens and gradually becomes a continuous layer, while the thickness of the FeAl₃ layer is almost unchanged (Fig. 6(e)).

It can be seen from Fig. 2 that only a small fraction of FeAl₃ can be observed in the IMCs layer and Fe₂Al₅ is the major component of the IMCs layer. There are several reasons for it. Firstly, the already-formed tenuous FeAl₃ layer may serve as a source of aluminum atoms required for Fe₂Al₅ growth and it is inclined to peel off from the interface and moves into the liquid aluminum. As a result, a discontinuous FeAl₃ phase is often observed at the aluminum end. Secondly, Shin et al. [22] believed that, with the diffusion of interfacial atoms, the Fe₂Al₅ phase can grow rapidly along the direction of the crystallographic c-axis, and the enrichment of aluminum atoms occurs in the Fe₂Al₅ phase, which greatly restricts the further growth of FeAl₃. Thirdly, as pointed out by Balloy et al. [2], Al atoms can easily diffuse into the interface of the Fe matrix to form the Fe₂Al₅ phase. Considering that the diffusion coefficient of Fe in Fe₂Al₅ is more than 10 times higher than that of FeAl₃ [3], the amount of Fe atoms that diffuse into the liquid aluminum through the FeAl₃ layer is greatly reduced, and thus
the growth restriction of FeAl₃ is inevitable to occur.

2.3 Kinetics analysis of IMCs

As is well-known, reaction diffusion law is a classic theory of IMCs growth \[^{[44]}\]. In general, the formation and growth of IMCs are determined by the interdiffusion of Fe and Al atoms. This indicates that the relationship between the thickness of IMCs and reaction time obeys a parabolic law \[^{[17-21,37,45,46]}\]. However, in terms of the two IMCs layers formed via the reaction diffusion between iron and liquid aluminum, their growth kinetics is relatively complicated.

Bouche et al. \[^{[18]}\] experimentally found that the interfacial reaction is the main controlling factor in the initial stage of Fe₂Al₅ formation, and the formed Fe₂Al₅ phase at this stage does not dissolve significantly in the liquid aluminum. After a very short period, the growth of Fe₂Al₅ is determined by the diffusion regime and their dissolution can be observed. Accordingly, the thickness measurement results can only indicate the parabolic stage of its formation. Similarly, Bouayad et al. \[^{[17]}\] and Stergioudis \[^{[47]}\] claimed that, after a period of diffusion incubation, the growth of the Fe₂Al₅ layer follows a parabolic law. However, Yeremenko et al. \[^{[48]}\] and Eggeler et al. \[^{[49]}\] observed negative deviations from the parabolic law after a long period of reaction. Recently, Chen et al. \[^{[24]}\] and Rong et al. \[^{[50]}\] suggested that there is a linear relationship between the average thickness and reaction time when the growth of the Fe₂Al₅ layer is governed by the interfacial reaction, whereas there is a parabolic relationship between them if the growth is controlled by the diffusion process. In addition, the growth obeys a linear law for the Fe₂Al₅ layer with respect to the maximum thickness. The dependence of the average thickness of Fe₂Al₅ on time is plotted in Fig. 7.

On the other hand, the formation and growth mechanisms of the FeAl₃ layer are still controvertible. Bouayad et al. \[^{[17]}\] reported that the growth of FeAl₃ follows a linear law, whereas Bouche et al. \[^{[18]}\] argued that its growth obeys a parabolic law. Rezaei et al. \[^{[51]}\] also concluded that FeAl₃ was formed by dissolution and
precipitation of the IMCs. The research by Chen et al. [24] revealed that, the formation of FeAl₃ adjacent to Fe₂Al₅ layer depends not only on the reaction diffusion but also on the precipitation at relatively low temperatures (<900 °C), while precipitation is the only formation mechanism of FeAl₃ at relatively high temperatures (>900 °C). Additionally, the disassociated/free FeAl₃ is concluded to be formed by precipitation. When the temperature decreases to the eutectic point of FeAl₃ and Al, eutectic structures are formed.

Although many mechanisms have been proposed to elucidate the formation and growth processes of the FeAl₃ layer, the results of the above studies are inconsistent and so far, no theory has been generally accepted. It is possibly because only reaction diffusion is considered during the growth of IMCs. As a matter of fact, the dissolution of the IMCs layer is another important factor affecting its growth [10,17]. Chen et al. [24] showed that the dissolution rate of IMCs in contact with liquid aluminum is nearly constant during the interfacial reaction, while the growth rate of IMCs declines with increasing the reaction time. Hence, the solid/liquid interface migrates inward when the dissolution rate exceeds the growth rate of IMCs after a long reaction period. In addition, the dissolution of IMCs was determined by the dissolution of FeAl₃ at relatively low temperatures (<900 °C) and Fe₂Al₅ at high temperatures (>900 °C). In summary, the growth rate of Fe-Al IMCs layer depends on the migration of two interfacial layers, i.e. the forward migration of the interface between the Fe-Al IMCs layer and the Fe matrix (interface Ⅰ in Fig. 9) and the backward migration of the interface between the Fe-Al IMCs layer and the liquid aluminum (interface Ⅱ in Fig. 9). The former is the reaction diffusion process, while the latter is the dissolution process. Therefore, the growth of Fe-Al IMCs layer essentially depends on both the diffusion rate at the interface Ⅰ and the dissolution rate at the interface Ⅱ.

2.4 Analytical modelling

The corrosion of mild steels in liquid aluminum is mainly divided into three steps: (1) the diffusion inside the mild steel matrix, whose driving force is that the chemical
potential of each element between different phases needs to be balanced and controlled by diffusion; (II) mass transfer at the solid/liquid interface, controlled by dissolution-chemical reaction; (III) the transport of IMCs in liquid aluminum is controlled by convection and diffusion in the liquid aluminum. Based on the work of Yeremenko et al. [48], Tang et al. [52] proposed a modified model for the homogeneous interfacial reactions of solid metal with liquid metal. Wang [53] and Wang [54] qualitatively explained the corrosion behavior of Fe-B alloy in liquid aluminum and liquid zinc based on this model. Experimental work by Xu et al. [10] demonstrated that this model is also suitable for quantitatively accounting for the corrosion behavior of ferrous alloys in liquid aluminum by making the following assumptions: (i) the interdiffusion coefficient is independent of the composition; (ii) the concentration gradient of Al in IMCs layer is independent of the location. The modeling results suggest that the thickness (L) of the IMCs layer is dominated by its growth and dissolution, while the consumption of the Fe matrix is controlled by the diffusion. The diffusion flux perpendicular to the interface can be expressed by Fick’s law [55]

\[ J = D \frac{C_{\|} - C_{\perp}}{L} \]  

where J is the diffusion flux of the Al atoms, \( C_{\perp} \) and \( C_{\|} \) are the concentration of Al at the interface I and II, respectively, \( D \) is the interdiffusion coefficient of the IMCs, and \( L \) is the thickness of the IMCs.

For the static corrosion of ferrous alloy in liquid aluminum, if the thickness of the newly-formed IMCs at the interface I is defined as \( dL_g \) in a duration of \( dt \), then the growth rate of the IMCs can be given by

\[ \frac{dL_g}{dt} = \frac{DW_{\text{IMC}}(C_{\|} - C_{\perp})}{b \rho_{\text{IMC}} L} \]  

where \( b \) is the stoichiometric ratio of Al in the IMCs (Fe\(_a\)Al\(_b\)), \( \rho_{\text{IMC}} \) is the density of the IMCs, \( L_g \) is the thickness of the IMCs, and \( W_{\text{IMC}} \) is the molar mass of the IMCs.

At interface II, the dissolution of IMCs into liquid aluminum can be described by the Nernst-Shchukarev equation [48]. Then, the dissolution rate of the IMCs is determined by
\[
\frac{dL_d}{dt} = \frac{W_{IMC} \rho_{IMC} a S}{V} K \left( C_1 - C_2 \right) = \frac{c_{sK} W_{IMC}}{\rho_{IMC}} \frac{e^{-KS}}{V} \tag{3}
\]

where \( C \) is the concentration of Fe in the aluminum melts, \( K \) is the dissolution rate constant, \( S \) is the area of the IMCs in contact with the aluminum melts, \( V \) is the volume of the aluminum melts, and \( C_s \) is the saturated concentration of Fe in the aluminum melts. During the time \( dt \), the thickness \( dL_d \) of the IMCs dissolves, and \( a \) is the stoichiometric ratio of Fe in the IMCs \((Fe_aAl_b)\). Given that the volume \( V \) of liquid aluminum is sufficiently large, the value of \( S/V \) is almost close to 0, thus

\[
\frac{dL_d}{dt} = \frac{c_{sK} W_{IMC}}{\rho_{IMC}} \tag{4}
\]

Since the thickness of the IMCs layer is determined by its growth and dissolution, the variation rate of the IMCs layer thickness is given by

\[
\frac{dL}{dt} = \frac{dL_g}{dt} - \frac{dL_d}{dt} = \frac{D W_{IMC} (C_1 - C_2)}{b \rho_{IMC} L} - \frac{c_{sK} W_{IMC}}{\rho_{IMC}} \tag{5}
\]

When \( \frac{dL}{dt} = 0 \), the growth and dissolution of IMCs reach an equilibrium. Then, the thickness of the IMCs layer can reach the maximum \( L_{\text{max}} \),

\[
L_{\text{max}} = \frac{D (C_1 - C_2) a}{c_{sK} b} \tag{6}
\]

In fact, there are two specific periods when the time dependence of the thickness loss can be simply expressed. The first is the initial stage of corrosion. When the thickness of the IMCs layer \( L \) is so small that \( \frac{dL_g}{dt} \gg \frac{dL_d}{dt} \). In this period,

\[
\frac{dt}{dt} = \frac{dL_g}{dt} - \frac{dL_d}{dt} \approx \frac{dL_g}{dt} \tag{7}
\]

For the initial condition, \( L = 0 \) at \( t = 0 \). Thus,

\[
L = \sqrt{\frac{2D W_{IMC} (C_1 - C_2)}{b \rho_{IMC} L} t} \tag{8}
\]

At the time of \( dt \), the thickness of the IMCs layer is increased by \( dL_g \), and the corrosion rate of the matrix \( d(\Delta x)/dt \) can be calculated by

\[
\frac{d(\Delta x)}{dt} = \frac{a W_{Fe} dL_g}{\rho_{Fe} W_{IMC}} = \frac{a W_{Fe} (C_1 - C_2)}{b \rho_{Fe} L} = \frac{a W_{Fe}}{\rho_{Fe}} \sqrt{\frac{2 \rho_{IMC} D (C_1 - C_2)}{b W_{IMC} L} \frac{1}{\sqrt{t}}} \tag{9}
\]

Then
\[
\Delta x = \frac{a W_{Fe}}{\rho_{Fe}} \sqrt{\frac{2 \rho_{IMC} D (C_{II} - C_{I})}{b W_{IMC}}} \sqrt{t}
\]

(10)

where \( \rho_{Fe} \) and \( W_{Fe} \) are the density and molar mass of Fe, respectively.

From Eq. (10), it is evident that the corrosion thickness of the Fe matrix, i.e. \( \Delta x \), has a linear relationship with \( \sqrt{t} \), and the consumption of the Fe matrix obeys a parabolic law. Furthermore, the factor \( D(C_{II} - C_{I}) \) indicates that the loss of Fe matrix thickness during this period is mainly determined by diffusion.

The other special period is after the growth and dissolution of IMCs become balanced and the thickness of the IMCs reaches the maximum value (\( L_{max} = \frac{D(C_{II} - C_{I})a}{c_{s}k b} \)). During this period,

\[
\frac{d(\Delta x)}{dt} = \frac{W_{Fe} c_{s} k}{\rho_{Fe}}
\]

(11)

\[
\Delta x = \frac{W_{Fe} c_{s} k}{\rho_{Fe}} t + A
\]

(12)

where \( A \) is a constant of integration.

This is the linear period of the interfacial reaction, when the rate of thickness loss is related to the dissolution process by the factors \( c_{s} \) and \( k \). This relation indicates that this period is mainly controlled by dissolution.

Xu et al. [10] compared the matrix thickness loss measured by experiments with that calculated by theoretical models at the initial stage of corrosion. The dependency of the thickness loss of ferrous alloys on the corrosion time is plotted in Fig. 10. The variation trend of the measured \( \Delta x \) of the ferrous alloys is consistent with the model prediction. The results indicate that the model can make an accurate prediction on the general variation trend of the thickness loss of ferrous alloys with corrosion time.

3. Improvement approaches of corrosion resistance of mild steels in liquid aluminum

Based on the growth kinetics analysis and analytical modeling, the corrosion of mild steels in the liquid aluminum is essentially a process of interdiffusion of Fe and Al atoms. Hence, the inhibition of diffusion is an advisable strategy for enhancing the corrosion resistance of mild steels in liquid aluminum. Researchers have adopted a
large number of methods to inhibit the diffusion of atoms, which can be classified into four categories: (a) alloying; (b) introducing secondary phase; (c) matrix microstructure control; (d) surface treatment.

3.1 Alloying

In order to control the growth of Fe-Al IMCs, the growth restriction of Fe-Al IMCs by alloying has been extensively investigated in the last few decades. According to the statistico-thermodynamical theory of multicomponent alloys combined with electronic theory in the pseudopotential approximation, Akaeniz et al. \cite{56} classified the alloying elements in ferrous alloys into two groups. One contains Si, Cr, Ti, Ge, Sb, Mg, Cu, Ca, Ag and Cd elements, which compromises the activity coefficient of Al and helps to decrease the thickness of the reaction layer, and the other encompasses Co, Zn, Mn, Ni, Pb and Bi elements, which helps to increase the thickness of the reaction layer.

For instance, silicon plays a prominent role in affecting the morphology and growth of Fe-Al IMCs. When studying the corrosion behavior of ferritic and modified pearlitic cast irons (FCI and PCI, respectively) in liquid aluminum, Balloy et al. \cite{2} found that the surface coating is mainly composed of Al, Fe-Al IMCs and Si-rich layer, and no Fe-Al-Si IMCs are formed. Therefore, it is inferred that the Si-rich layer can effectively inhibit the atomic diffusion. Takata \cite{57} believed that the addition of Si can promote the flattening of irregular tongue-like Fe$_2$Al$_5$ phase and reduce the thickness of the Fe$_2$Al$_5$ layer by restricting the rapid growth of the Fe$_2$Al$_5$ phase along the direction of c-axis. Yin et al. \cite{58} and Dangi et al. \cite{59} further stated that the presence of Si in Fe$_2$Al$_5$ layer can fill up the atomic vacancies in the crystal lattice and block the diffusion path for the migration of Al and Fe atoms. In this way, the growth rate of the Fe-Al IMC is effectively decreased. Lemmens et al. \cite{60} examined the hot-dipped mild steel of Al-Si alloy with different Si contents and found that the Fe$_2$Al$_5$ layer has the smallest thickness when Si content reaches 5%, and the entire IMCs layer has the smallest thickness when it reaches 1%. Similarly, Akdenize et al.
Du et al. [62] and Chen et al. [63] claimed that the addition of Si can lead to the formation of the relatively complex and slow-growing Fe$_x$Al$_y$Si$_z$ phase that can restrict the growth of the Fe-Al IMCs layer, and the thickness of Fe$_x$Al$_y$Si$_z$ phase hardly increases with the hot-dip plating temperature. Hou et al. [64] and Zhang et al. [65] argued that the presence of Si in the Fe-Al-Si system can effectively inhibit the diffusion of Al atoms in the matrix, thus restricting the growth of the IMCs layer.

Similarly, carbon content in the steel also has a great influence on the growth of IMCs. Hwang et al. [66] carried out the hot dip aluminizing of mild steel with different carbon concentrations. They found that the thickness of the reaction layer decreases and the interface between the IMCs layer and the matrix becomes smoother with the increase of carbon content in the steel. They believed that carbon atoms in the IMCs layer can both reduce the diffusion rate of Fe and Al through the interface layer and decrease the dissolution rate of the Fe matrix in the liquid aluminum. During the hot dip aluminizing of carbon steel, Awan et al. [7] observed a carbon-rich zone between the matrix and IMCs layer. Because carbon has an extremely limited solubility in the Fe-Al IMCs, the interdiffusion of atoms can induce the entrapment of carbon at the interface to form the so-called ‘carbon build-up’, as shown in Fig. 11.

Cr is another important alloying element to improve the corrosion resistance of mild steels. Zhang et al. [67] suggested that Cr-rich duplex stainless steel enjoys a better corrosion resistance to liquid aluminum than H13, whose interface between the reaction layer and matrix is much flatter. Its reaction layer is found to consist of outer porous (Fe, Cr)Al$_3$ and inner continuous (Fe, Cr)$_2$Al$_5$. The dense and continuous Al-Fe-Cr IMCs layer acts as an effective diffusion barrier to inhibit the interfacial reaction. Besides, the precipitation phases distributed in the reaction layer can also enhance the corrosion resistance to some extent by blocking the diffusion of atoms. Barbier et al. [68] and Stein-Fechner et al. [69] argued that Cr atoms can substitute Fe atoms in the crystal lattice of Fe-Al IMCs. Although the crystal structure of Fe-Al IMCs remains unchanged, the crystal lattice is distorted and the diffusion of atoms in the Fe-Al IMCs layer is inhibited. Su et al. [70] added 30% Mn to the steel and found
that the growth activation energy of the IMCs is lower than that of the hot-dip mild steel during hot-dip plating. It may be due to the formation of \((\text{Fe, Mn})_2\text{Al}_5\) phase, and the addition of Mn can promote the growth of IMCs. Yousaf et al. \([71]\) studied hot-dip aluminized steel and suggested that after the addition of 11 wt.% Cu to liquid aluminum, \(\text{Al}_2\text{Cu}\) and \(\text{Al}_7\text{Cu}_2\text{Fe}\) are formed at the interface. Their formation can inhibit the diffusion of Al atoms toward the steel matrix, thus restricting the growth of \(\text{Fe}_2\text{Al}_5\) IMCs. Nazari et al. \([4]\) investigated the effects of micro alloying elements (Sr and Ti) on the morphology and growth kinetics of IMCs formed by the interface reactions between H13 and A380 aluminum alloy melts. They concluded that the addition of Sr and Ti can result in the reduction in the thickness, number, and growth kinetics of the IMCs.

In conclusion, the mechanisms of alloying-induced growth restriction of Fe-Al IMCs can be summarized as follows: (a) interfacial enrichment mechanism, i.e. the enrichment of alloy elements such as Si and C at the reaction interface can inhibit the interdiffusion of Fe and Al atoms; (b) vacancy occupation mechanism, i.e. alloying elements restrict the growth of IMCs by occupying the lattice vacancies of IMCs; (c) phase formation mechanism, i.e. the formation of Fe-Al-M (M=Cr, Si, Cu, Mn, etc.) phases can restrict the growth of IMCs.

### 3.2 Introducing secondary phase

Studies \([10,25,44,72-76]\) have shown that secondary phases such as graphite, IMCs, ceramics, etc. possess extremely little solubility in liquid aluminum and hardly react with the liquid aluminum. For this reason, they can be introduced into the mild steels as the diffusion barriers to inhibit atomic diffusion. According to their dimension and size, they can be divided into two categories: macroscopic and microscopic barriers. In this paper, the macroscopic barrier refers to the intermetallics, solid solutions and inclusions at the micro-scale, while the microscopic one relates to the nanoscale of the above items.

Balloy et al. \([2,10,25,76]\) suggested that the presence of C-rich phase \((\text{Al}_4\text{C}_3)\) and
Graphite can effectively enhance the corrosion resistance of ferrous alloys in liquid aluminum because they are able to act as an efficient barrier to the Al diffusion. Fig. 12 exhibits SEM images of graphite and black Al₄C₃ precipitates in cast iron for corrosion resistance to aluminum melt. Xu et al. [10] and Wang et al. [76] indicated that the morphology and size of graphite can play a pivotal role in corrosion resistance. Experimental results demonstrated that the flake graphite in HT150 can diminish the corrosion rate most effectively, followed by spheroidal graphite in QT500. During the investigation of Wang et al. [54] on the corrosion behavior of bulk Fe₂B in liquid aluminum, they found that it has a positive corrosion resistance. Zhang et al. [77-80] managed to prepare the high boron cast steels with superior corrosion resistance against liquid aluminum by adding high content B element to steels, as shown in Fig. 13. The corrosion resistance of high boron cast steel is 5 times higher than that of H13. It is mainly attributed to the formation of Fe₂B borides, in particular the primary Cr-rich Fe₂B borides, which can act as physical barriers against the diffusion of Al atoms, effectively improving the corrosion resistance of high boron cast steels. In addition, after a long incubation time of liquid aluminum attacking the (Cr,Fe)₂B, the IMCs with peculiar periodic layered structures (PLSs) may form in the corrosion layer [81-83], as shown in Fig. 14. They can not only inhibit the diffusion of atoms, but also enhance the bonding strength between the matrix and the IMCs, i.e. the internal strength of the corrosion layer. Therefore, the dissolution and exfoliation of the corrosion layer would be impeded remarkably. Although the macroscopic barriers can be very effective in inhibiting the diffusion of Al atoms, the corrosion of Fe matrix may still occur with Al atoms migrating through the gaps between them. Consequently, further improvement in corrosion resistance necessitates the introduction of microscopic barriers. Taking into consideration the excellent corrosion resistance of ceramics in liquid aluminum, Xu et al. [84] successfully prepared novel FeCrB alloys with a large quantity of ceramic nanoparticles (TiB₂ and TiC). The microstructure of the novel FeCrB alloy is composed of multiscale compounds and inclusions acting as physical barriers, whose sizes range from micron to nano scale, as
shown in Fig. 15. Their synergistic effects lead to enhanced corrosion resistance. The illustration of corrosion behavior of the novel FeCrB alloy is shown in Fig. 16.

3.3 Matrix microstructure control

Balloy et al. [2] discussed the corrosion behavior of cast irons with different matrix microstructures in liquid aluminum. It was shown that a pearlitic matrix has a better corrosion resistance than a ferritic matrix. They believed that the eutectoid lamellar structure of pearlitic matrix can more effectively inhibit the diffusion of Fe and Al atoms. Chen et al. [24] declared that austenitizing of steels can lead to a complete transformation of the tongue-like Fe$_2$Al$_5$ phase to a flat-shaped one and impart to the austenitic matrix more superior corrosion resistance than the ferritic matrix. The research by Yousaf et al. [71] revealed that ferrite, pearlite and austenite have different effects on the growth of the IMCs layer depending on the amount of carbon absorbed by them. Of them, the ferrite absorbs the least amount of carbon and is least effective in restricting the growth of IMCs layer, followed by pearlite and austenite. Furthermore, grain size also has a great influence on the material degradation in liquid aluminum [1,44]. During corrosion, as shown in Fig. 17, grain boundaries would be preferentially corroded and turn into shortcuts for atom diffusion. This means that the larger the grain boundary area, the finer the grain size, and the higher the corrosion rate of matrix. Hence, the control of grain structure is another effective approach to enhancing the corrosion resistance of the matrix.

3.4 Surface treatment

Surface treatment of steel materials with the aim of forming a denser diffusion barrier that has poor wettability with liquid aluminum, can effectively hinder the diffusion of Fe and Al atoms. At present, surface treatments for mild steel to improve the corrosion resistance in liquid aluminum are focused on chemical heat treatment and surface coating. Chemical heat treatment is mainly to form the dense Fe-B, Fe-N, and Fe-O compounds on the surface by boronizing, carburizing, nitriding, oxidation,
etc. \cite{85} to effectively slow down the corrosion of the steel matrix in liquid aluminum. Lou et al. \cite{86} found that the corrosion resistance of H13 increased by 3 times after boronizing treatment, which is attributed to the chemical stability and high density of FeB and Fe$_2$B. With the oxidation treatment, Tunthawiroon et al. \cite{87} suggested that the corrosion resistance of FeCrMo alloy to molten aluminum was effectively enhanced because of the dominant coverage of Cr$_2$O$_3$ film formed on the alloy surface. Chen et al. \cite{88,89} investigated that the corrosion resistance of H13 to liquid aluminum can be improved by the low-temperature liquid nitrocarburizing treatment, based on which post-oxidation can further enhance the corrosion resistance of liquid-nitriding H13. In terms of surface coatings, ceramic, cermet composite, and enamel coatings possess excellent corrosion resistance to liquid aluminum. Vourlias et al. \cite{90} prepared a yttria stabilized zirconia (YSZ) coating on the surface of H13 steel by plasma spraying. Immersion tests indicated that the coating has remarkable resistance to molten aluminum erosion, and almost no mass loss occurs after immersion in aluminum melt at 700 °C for 144 h. Wang et al. \cite{91} synthesized a dense, adherent and homogeneous ZrB$_2$ coating on 210 stainless steel by electrodeposition, which can remain complete and unattacked after 72 h immersion. However, for all ceramic coatings, considerable difference in the coefficients of thermal expansion exists with the steel matrix. In this case, cermet composite coating emerges \cite{92}. Khan et al. \cite{93} found that the MoB/NiCr coating displayed the superior soldering resistance during the die casting process, and no phase transition occurred or intermetallic compounds formed, which can act as a strong diffusion barrier to liquid aluminium. WC-Co coating has also been proven to have good corrosion resistance to molten aluminum \cite{94}. Nevertheless, the corrosion caused by replacement and permeation of Al atoms through the adhesive phase (Co, Ni and Cr) is still serious. Yu et al. \cite{95} considered that enamel coating is an alternative of ceramic coating due to its adjustable coefficient of thermal expansion and lower wettability with liquid aluminum. They suggested that enamel coatings provide high corrosion resistance to 304 stainless steel against molten aluminum.
4. Summary and outlook

This article reviews the recent researches on the corrosion of mild steels in static liquid aluminum and mainly focuses on the corrosion mechanisms and improvement approaches. It is demonstrated that introducing the secondary phases into the Fe matrix is one of the most effective methods to achieve the enhanced corrosion resistance. However, it is noteworthy that the introduced secondary phases should satisfy the following criteria: (a) low solubility in liquid aluminum; (b) high thermal stability at high temperature; (c) easy introduction; (d) innocuousness to other properties of alloys. Since the microstructure of mild steels is inevitably affected by the introduced secondary phases, it is of great significance to procure a proper balance between mechanical properties and corrosion resistance. The introduction of multi-scale compounds can not only inhibit the diffusion of Al atoms towards the matrix both macroscopically and microscopically, giving more effective enhancement in the corrosion resistance, but also improve the mechanical properties of alloys [96]. Additionally, the control of matrix microstructure is another important improvement approach. Austenizing [24] or pearlizing [97] of the matrix by alloying or heat treatment has been proven to improve the corrosion resistance of the matrix. An extensive and in-depth research is still required, however, because of the dearth of relevant research. Given the high solubility of Al in the Fe matrix and its easy reaction with liquid aluminum to form Fe-Al IMCs, suitable surface treatment is of great necessity for the improvement of corrosion resistance of mild steels in liquid aluminum. Finally, understanding of the corrosion behavior of novel and established mild steels in liquid aluminum stands to benefit the further development of corrosion resistant materials.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (Nos. 51804197, 51674166 and U1902220), and the Startup Fund for
Youngman Research at Shanghai Jiao Tong University.

Data Availability Statement
All data included in this study are available upon request by contact with the corresponding author.

References


Fig. 1 (a) Fe-Al binary phase diagram \cite{29}; (b) Variation of $\Delta G^0$ of Fe-Al IMCs with different temperatures \cite{10}.
Fig. 2 (a) Cross-sectional SEM image of as-coated steel; (b) magnified micrograph of dotted rectangular region in (a), adapted from Ref [28].

Fig. 3 Existence forms of FeAl₃ after immersion in liquid aluminum [24].
Fig. 4 Schematic of the formation of hot dip aluminized coating layer on steel \cite{36}.

Fig. 5 Schematic formation of three-layer structures with Al coating on steel \cite{42}. 


Fig. 6 Schematic diagram on growth of Fe-Al interfacial layer

Fig. 7 Dependence of Fe$_2$Al$_5$ thickness on time: (a) average thickness of Fe$_2$Al$_5$ and (b) maximum thickness of Fe$_2$Al$_5$ [24].
Fig. 8 (a) Variation of the FeAl\textsubscript{3} layer thickness with time at 800 °C, adapted from Ref. [17]; (b) variation of the FeAl\textsubscript{3} layer average thickness with $t^{1/2}$ at 800 °C, adapted from Ref. [18].

Fig. 9 Schematic of the interfacial reaction between ferrous alloy and Al melts\textsuperscript{[10]}: (a) $t = 0$, ferrous alloy and Al melts just contacted with each other; (b) $t = t_1$ ($t_1 > 0$), at interface I, ferrous alloy has reacted with Al atoms diffusing through the layer to form Fe\textsubscript{$a$}Al\textsubscript{$b$}; at interface II, Fe\textsubscript{$a$}Al\textsubscript{$b$} has dissolved into the Al melts.
Fig. 10 Matrix thickness loss of ferrous alloys vs. corrosion time \([10]\).

Fig. 11 Microstructure of the interface of hot-dip-aluminized carbon steel, adapted from Ref [7].

Fig. 12 SEM images of the cast iron immersed in the aluminum melts at 750 °C for 24 h, adapted from Ref. [10]: (a) flake graphite in HT150; (b) spheroidal graphite in QT500; (c) black precipitates of Al\(_4\)C\(_3\).
Fig. 13 SEM micrographs of FeCrB alloys \cite{77}.

Fig. 14 Cross-sectional interfacial morphology of Fe-Cr-B cast steel immersed in molten aluminum for 8 h \cite{81}.
Fig. 15 (a) SEM image of corrosion interface formed in the novel ferrous alloy after 0.5 h in the dynamic Al melts at 750 °C\cite{84}; (b) carbides and nano-ceramic particles dispersed in the matrix.

Fig. 16 Schematic of the erosion-corrosion mechanisms of novel FeCrB alloys in Al melts \cite{84}.

Fig. 17 Schematic diagram of corrosion along the grain boundary by molten Al \cite{44}.