

A Review of Corrosion Behavior of Structural Steel in Liquid Lead–Bismuth Eutectic

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Abstract: Liquid lead–bismuth eutectic alloy is one of the candidate coolants for fourth-generation nuclear power systems because of its good physical and chemical properties, neutron economic performance, and safety. However, the compatibility between the coolant and structural steel is still the main factor restricting its large-scale industrial application in the nuclear energy field. Structural steel in a liquid lead–bismuth eutectic alloy for a long time would cause severe corrosion. The erosion of structural steel by high-flow-rate liquid lead–bismuth alloy will lead to a more complex corrosion process. This paper mainly reviews the corrosion characteristics of liquid lead–bismuth and the corrosion behavior of structural steel in liquid lead–bismuth eutectic. The main methods of inhibiting liquid lead–bismuth corrosion are summarized, and future research directions are suggested.

Keywords: LBE; corrosion; dissolution; oxidation; corrosion prevention



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1. Introduction

Energy is an important material basis for human existence. With the rapid development of society and mankind's increasing demand for energy, the issue of energy has attracted the attention of countries around the world. At present, traditional fossil fuels are being depleted and are accompanied by pollution problems. Nuclear power is a comparatively mature clean energy industry and has been highly valued by countries around the world. The further development of nuclear energy should improve safety and efficiency in addition to solving problems such as nuclear fuel supply and nuclear waste disposal. Currently, lead-based reactors are considered to be one of the most effective solutions [1–3]. With the development of fourth-generation nuclear power technology, the research of liquid metal as fast reactor coolant is becoming more and more advanced. Liquid lead–bismuth eutectic (LBE) is a cooling agent for lead-cooled fast reactors (LFR) and is one of the candidates for accelerator-driven subcritical (ADS) reactors and mainly has the following advantages [4–7]:

- (1) LBE has very high heat conductivity and can rapidly export the heat generated by nuclear reactions. Additionally, LBE has a low melting temperature and a high boiling point.
- (2) LBE has excellent neutronics properties with a narrow neutron absorption cross section and low neutron-slowing behavior.
- (3) Lead alloy materials have excellent heat transfer and resistance to radiation. The components of lead-based reactor systems can be designed to be simple and more compact, making them easy to manufacture in small modular sizes.
- (4) Lead-based reactors have high nuclear fuel utilization, low waste, long life cycles, high coolant outlet temperature, high energy utilization, and good economic viability.

- (5) The chemical activity of LBE is very low, and it hardly reacts when in contact with air and water. Due to its chemical inertness, it eliminates some safety hazards and increases the safety of the reactor.

However, there are compatibility problems, such as liquid metal corrosion with LBE coolant for the currently promoted international candidate structural materials for reactors, which impede the progress of LFR engineering applications. Liquid metal corrosion is an important material property degradation phenomenon. The factors affecting the corrosion of liquid metals are complex, such as the composition of the material; its structure; and the oxygen concentration, temperature, and flow rate of the LBE. Numerous studies have been conducted on austenitic stainless steels (e.g., 316L, etc.) [8–14], ferritic/martensitic steels (e.g., T91, etc.) [11,13,15–23], ODS steel, etc. [24–29], in LBE corrosion. The experiments were mainly focused on the temperature range of 300 °C–800 °C, the time from 100 h to 15,000 h, the oxygen concentration from 10^{-12} wt% to oxygen saturation, and the flow state—including static and dynamic (0–5 m/s). The large amount of experimental data provides a good basis for the subsequent study. Scientific workers have conducted large amounts of research on the corrosion of structural materials with LBE [5,12,30–43], which provides an important basis for subsequent material optimization and material selection. This paper mainly reviews the basic structure of liquid lead–bismuth corrosion characteristics, and the main methods of inhibiting liquid lead–bismuth corrosion are summarized.

2. Corrosion Characteristics of LBE

For the corrosion characteristics of structural materials in LBE, three main methods are studied: static corrosion experiments, dynamic corrosion experiments, and large loop experiments. Its main manifestations include the following four aspects:

2.1. Dissolution Corrosion

Dissolution in LBE is one of the basic forms of liquid LBE corrosion. When the steel material is in liquid LBE, the metal elements in the steel material will dissolve into the liquid LBE at a low oxygen ($C_O < 5 \times 10^{-7}$ wt%) concentration [9,12,32,38,44,45] (Figure 1) [46]. This is usually characterized by the transfer of material components for example, Ni, Fe, or Cr to the liquid phase, continuing until saturation [14].

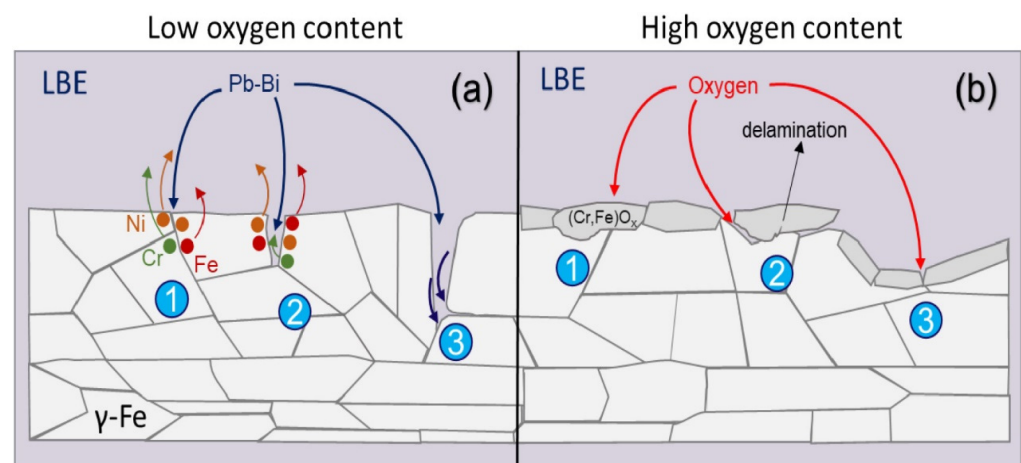


Figure 1. (a) Schematic diagram for corrosion of austenitic steel in LBE with low oxygen concentration. (1) Alloying elements begin to dissolve in the LBE. (2) LBE begins to penetrate and continues to dissolve. (3) Infiltration of Pb–Bi particles deeper into the substrate. (b) Diagram of corrosion in high-oxygen-concentration LBE. (1) A poorly protective oxide layer $(Cr, Fe)O_x$ is formed. (2) The oxide layer is destroyed due to stress. (3) Oxidation continues on the new surface. Reprinted with permission from Ref. [46]. 2022, Serag, E.

In the isothermal liquid metal loops for 316L corrosion experiments, the content of each alloying element in LBE was measured as shown in Table 1 [47]. Due to the different solubility and dissolution rates of different elements in LBE, selective dissolution of steel materials tends to occur in LBE. Dissolution experiments of 316L were conducted in LBE, and preferential dissolution of Ni was observed after temperature control at 500 °C for 3000 h. The analysis concluded that the dissolution kinetics of 316L were controlled by the dissolution reaction rate of Ni [10]. Since the solubility and dissolution rate of metal elements in liquid LBE vary greatly, the degree of corrosion of materials in liquid LBE varies [9,32–34]. As the dissolution speed of Ni in LBE is large, the higher the Ni element content of the material, the more severe the dissolution corrosion will be.

Table 1. The concentration of elemental impurities in LBE and the actual measured composition of 316L stainless steel. Data transferred from Ref. [47].

Loop Temperature	Sampling Time after Startup	Impurity Concentration [mass ppm]			
		Fe	Cr	Ni	Mn
400 °C	1800 h	4	2	14	0.3
450 °C	1300 h	15	2	74	0.4
316L stainless steel composition [%]		64.3	17.4	13.1	1.7

Dissolution is a more serious type of corrosion, and the root cause of its occurrence is the composition of steel elements in the liquid lead–bismuth which have a certain degree of solubility, including Ni, Mn, Fe, Cr, and other significantly dissolved elements [48–51]. Dissolution corrosion does not end on its own, but rather, under certain conditions, it will continue to act until the structural steel fails [4].

2.2. Corrosion by Oxidation

If the oxygen concentration in LBE is more than 10^{-6} wt%, the elemental O in liquid LBE will react chemically with the metal elements (Fe, Cr, etc.) in the steel material, thus causing oxidation corrosion on the surface of the structural steel [8,11,13–16,52–56]. If a continuous and dense oxide film is produced on the surface of the structural steel, then oxidative corrosion will be effectively blocked. On the contrary, the different coefficients of thermal expansion generate strain/stress between the oxide film and the substrate, resulting in the oxide film peeling off [57]. Declining integrity and increasing thickness can also cause the oxide film to peel off [58]. The oxide film tends to break and peel off, which will accelerate further corrosion of the steel material by the liquid LBE.

At high concentrations ($C_O > 10^{-6}$ wt%) [56], the structural steel undergoes an oxidation reaction (Figure 1b). If multiple layers of poorly adherent oxide films are formed, these films can delaminate and oxidize the underlying surface. Even if the thin layer is denser, it still changes the composition and morphology of the material surface, thus changing its mechanical properties [46].

Three materials 316L, SIMP steel, and T91 were selected for the experiments in oxygen-saturated liquid LBE [59]. According to the results, T91 steel has the most serious corrosion, 316L steel has the best corrosion resistance, and SIMP steel is in between the two materials. Austenitic stainless steel 316L can effectively slow down oxidation because it contains more Cr, which forms denser Fe–Cr spinel in oxygen-saturated liquid LBE. SIMP steel has a higher Si content, so it is more resistant to oxidation, and its internal oxide layer is denser than that of T91, protecting against the spread of O and Fe ions [59].

In oxygen-saturated LBE, the film generated by oxidation on T91 steel generally consists of three layers: the inner oxide zone (IOZ), the inner oxide layer (IOL), and the outer oxide layer (OOL) [5,60]. Figure 2 displays the effect of time on the SEM morphology of T91 oxide film [5]. The film thickness increases with time; however, the depth of IOZ does not grow with the experiment's duration. At 2000 h, a fresh oxide film can be clearly observed on the OOL [5]. As the oxygen concentration in LBE decreases, the depth of the

oxide film becomes progressively smaller, and there is an increase in Cr/Fe in Fe–Cr spinel. The three-layer magnetite/spinel/IOZ also becomes two-layer spinel/IOZ [60].

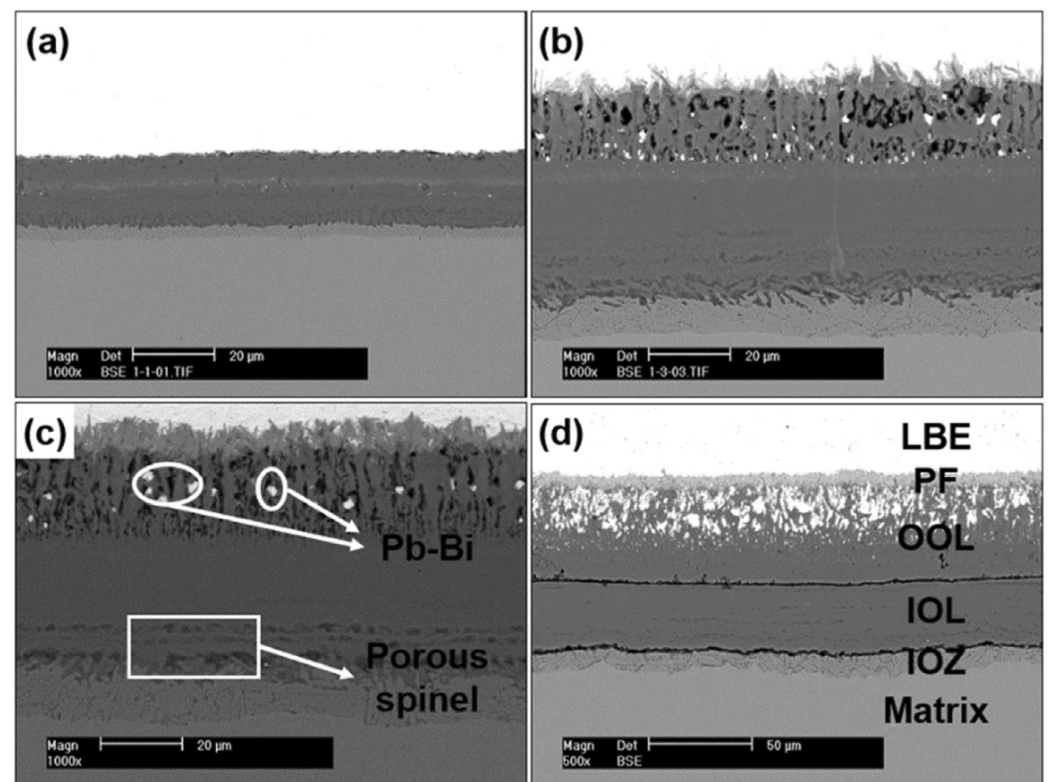


Figure 2. Effect of time on the SEM morphology of T91 oxide film at (a) 200 h, (b) 2000 h, (c) 4000 h, and (d) 8000 h. Reprinted with permission from Ref. [5]. 2022, Zhu, Z.

There is a double effect of the oxide film formed by the structural material in the liquid LBE on the corrosion damage [5]. In other words, as the oxide film thickness increases, the corrosion resistance of structural steel in liquid LBE does not improve because of it. If the oxide film is thicker and easily detached from the substrate, it will accelerate the corrosion of the material in the liquid LBE, thus weakening its corrosion resistance. If the oxide film is thin and dense, it will protect the substrate from further corrosion, which will reduce the oxidation corrosion rate and improve the corrosion resistance of structural material.

2.3. Surface Erosion

When the liquid LBE is in a high-speed flow state, the liquid LBE will produce high-speed motion relative to the surface of the structural steel material, which will cause continuous damage to the surface of the steel material—that is, erosion on the surface of the steel material [28,61–66]. This is caused by wall shear stresses and fluid turbulence. Shear stress at the interface can damage the oxide film or make it thinner. Turbulence can interfere with mass transfer rates and oxide film formation or even destroy the oxide film [41]. The high temperature of the liquid metal and the high flow rate can cause erosion damage due to the scouring friction of the material.

The surface erosion of structural steel is not only related to the flow rate of LBE, but the temperature also has a great influence. T91 was eroded in LBE medium with an oxygen content of 10^{-7} mass% and a flow rate of 2 m/s. The metal decline was about 10 μm after 9000 h at 450 °C. After 2000 h at 550 °C, the metal decline was about 15 μm [15]. A local depth of 100 μm was reached after 20,000 h, when the oxygen content was 2×10^{-7} mass % at 400 °C [67]. The LBE dynamic corrosion test resulted in heavy damage to T91, and the changes in corrosion morphology were remarkable with flow type. The variation in corrosion activity may be interpreted with diffusion or transfer processes and the mechanics

of erosion (Figure 3) [28]. Dissolution experiments of T91 under static and dynamic LBE under low dissolved oxygen concentrations were performed to establish the rate of T91 corrosion in pure dissolution. However, the results can only be used for the pure dissolution case and not for other conditions [68].

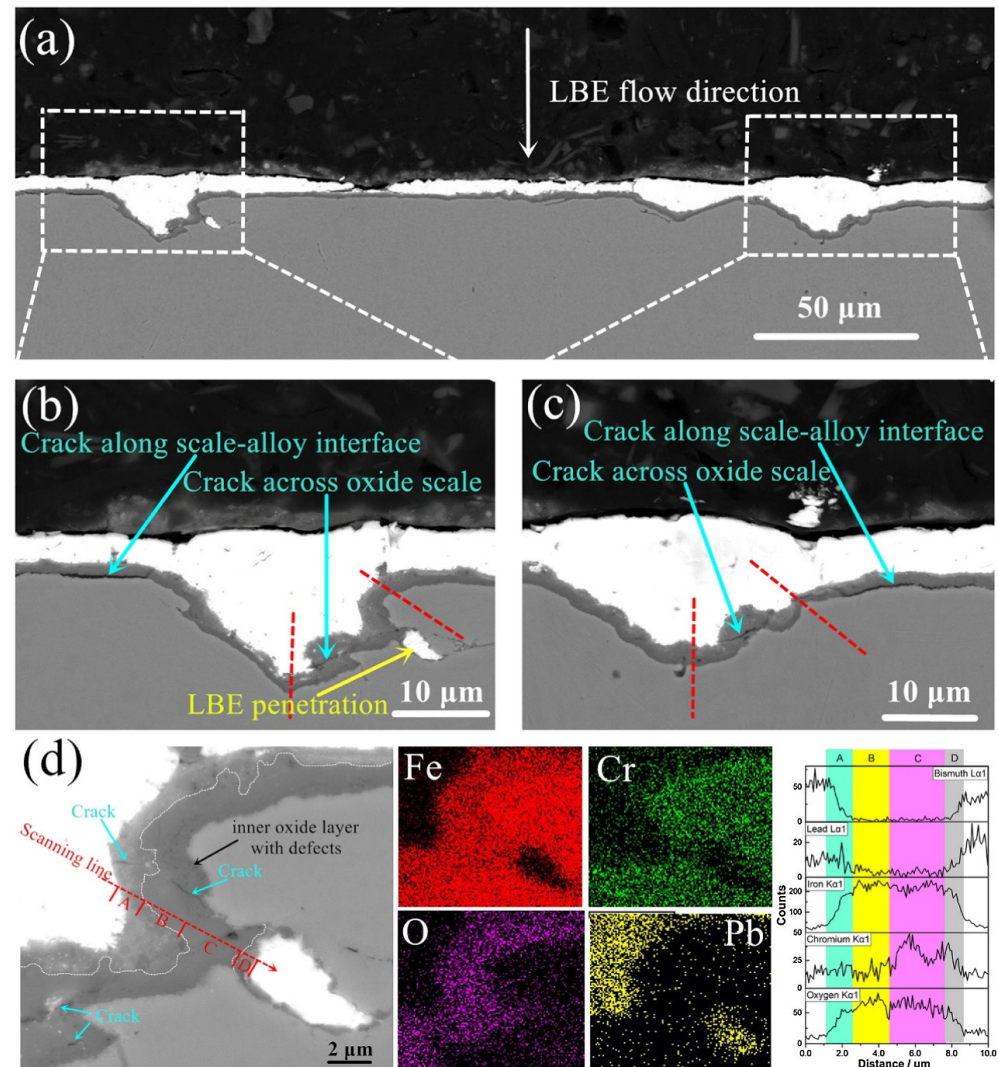


Figure 3. (a–c) BSE images of LBE flowing vertically through T91 at a rate of 5 m/s for 1000 h and (d) BSE images of the enlarged region in (b), with EDS mapping and line scan analysis. Reprinted with permission from Ref. [28]. 2021, Li, C.

It is worth noting that the flow direction, which was previously overlooked, plays a significant role in the corrosion behavior of LBE. When the fluid passes through elbows, valves, welded joints, and changes in pipe cross section, the corrosion damage will be more severe because of the change in flow direction [41,61]. The change in impact angle from 0° to 90° at low fluid velocities also caused significant damage to T91 and resulted in failure. The difference in corrosion behavior can be understood in terms of diffusion or mass transfer processes as well as erosion mechanics [28]. Additionally, 304N austenitic stainless steel is subject to vertical impact from flowing LBE at 400 °C and 1 m / s flow rate. Its corrosion behavior includes oxidation, dissolution, and scouring corrosion [3].

Although in-depth and extensive studies have been conducted on the oxidation and dissolution corrosion of structural steel in lead secrecy, relatively few studies have been conducted on the behavior of washout corrosion, mainly because dynamic corrosion experiments in lead secrecy require higher equipment performance and stability than static

corrosion. For experimental devices, the acceleration of fluid velocity is bound to pose more challenges than the increase in temperature, resulting in few reports in the open literature on strong dynamic corrosion and the complexity of the interaction between environmental corrosion and mechanical loading [28].

2.4. Liquid Metal Embrittlement

The presence of impurities or internal stresses at the grain boundaries of the steel material, as well as the selective dissolution of metallic elements within the steel material in liquid LBE, can cause liquid LBE to penetrate into the matrix tissue. The surface and near-surface will cause further dissolution corrosion and oxidation corrosion of the matrix and embody brittleness under the interaction of stress and corrosion, called liquid metal embrittlement (LME) [69–71]. LME is a very complex phenomenon that is widely present in liquid metals. The LME phenomenon depends on many parameters, including composition, temperature, hardness, stress or strain, and surface condition [72,73].

LME can lead to premature and catastrophic failure of metal components, thus posing a serious threat to the safe operation of nuclear reactors [4]. This material degradation phenomenon involves the sprouting of cracks on the wetted surface of the solid metal and the rapid extension of cracks into the mass [74–76]. It is worth noting that the oxidation structure reduces the wettability of the material surface to the LBE and hinders the direct contact between the LBE and the material matrix, thus retarding the crack sprouting and LME effect [69,77–79]. However, this delay effect seems to be discounted if the LBE lacks oxygen during stretching because not enough oxygen is available to seal the mechanically damaged oxide layer [80]. If the failure of the oxide layer reaches the wetting condition, then regardless of the LBE chemistry, the LME may be in the process of occurring under stress at 300 °C [74].

After tensile testing of T91 in LBE medium, a possible LME degradation mechanism was found by observing the crack morphology (Figure 4) [81]. Complete embrittlement of α -Fe in liquid LBE in the form of grain boundary grooving by Bi and Pb polarization at grain boundaries [52]. Low cycle fatigue behavior of T91 steel with LME was observed on the fracture surface of lead–bismuth eutectic [53]. The LME susceptibilities of Fe14Cr4.5Al-0.5Y2O3 (wt %) and Fe10Cr4Al (wt%) [80] alloys in LBE at 350 °C were obtained in slow-strain tensile tests. The results show that LME has a large impact on both alloys.

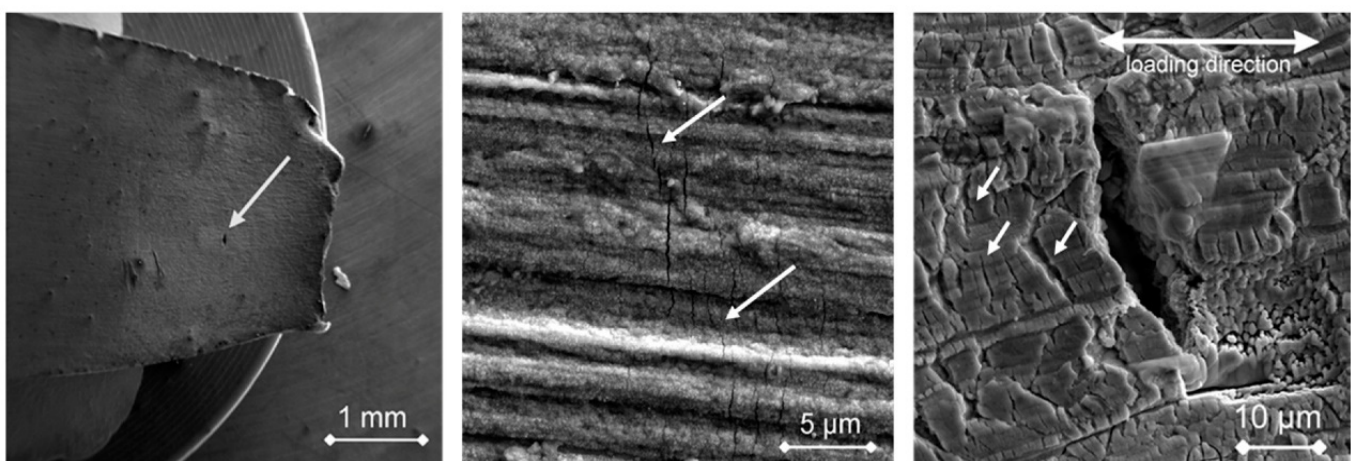


Figure 4. Several cracks in T91 after tensile testing in LBE media. Reprinted with permission from Ref. [81]. 2019, Patricie Halodová.

Structural steel in a liquid LBE environment: the wettability of LBE has a great influence on the performance of structural materials. Structural steel materials with better LBE wettability have a higher probability of LME [69]. Conversely, if the wettability is poor, the reaction between the elements of the structural steel material matrix and the corrosive medium will be weakened. Thus, the corrosion resistance of the material will be enhanced [82–84]. In addition, the surface wettability of the structural material will also have an impact on LME [85].

3. Influencing Factors

By analyzing the corrosion characteristics of structural materials in LBE, it can be seen that the main factors affecting corrosion are as follows: material composition, temperature, flow rate, and oxygen concentration in liquid LBE.

3.1. Material Composition

In dissolution-based liquid LBE corrosion, the degree of corrosion in liquid LBE varies due to the large difference in the solubilities of various metal elements in liquid LBE [9,38,47,48,86]. Elements such as Si, Al, Cr, and Ni have a strong influence on the corrosion of structural materials in liquid LBE. In general, materials with higher Si, Al, and Cr contents have better resistance to LBE corrosion; an increase in their content in steel is beneficial to enhancing its corrosion resistance in LBE. As rapid dissolution occurs in LBE, the higher the Ni element content, the more severe the dissolution corrosion will be. Austenitic stainless steels have a relatively high Ni content, so dissolution corrosion is more severe in LBE with low oxygen concentration. In some nickel-containing alloys, nickel is replaced by manganese elements, and Mn-rich oxides have good stability and high densification [87]. This oxide film reduces the corrosion of LBE and prevents the outward diffusion of Fe elements [88].

Material elements have some influence on LME, and it was found that the order of LME enhancement of pure Fe in low oxygen LBE is $\text{Si} > \text{Al} > \text{Cr}$ [73]. Additionally, 316L material with high Cr content will generate dense Fe–Cr spinel in oxygenated LBE; this layer can play a role in protecting the substrate and preventing the continuation of oxidation, so the resistance to LBE corrosion is stronger. The ferritic/martensitic SIMP steel has a higher Si content, which leads to a denser oxide layer inside the material and can hinder the diffusion of O and Fe. In addition, SIMP contains less Ni, so it is more resistant to LBE corrosion than T91 [89].

The oxide of pure iron consists of an inner layer and an outer layer. The inner layer consists of Fe_3O_4 and FeO at 600 °C, while the outer layer is a finely crystalline oxide. At 800 °C, the inner layer is a FeO grain, while the outer layer is a mixture of Fe_2O_3 and Fe_3O_4 . It was also found that the increase in temperature reduced the number of pores and made the grain size larger [6]. For Al_2O_3 to form on the surface of the material, an elemental Al above 4 wt % is required; Al makes the oxide film denser, but Al promotes the formation of ferrite, so the amount of Al is limited [87]. Cr_2O_3 and SiO_2 will delay the diffusion of Fe atoms while preventing Fe from being oxidized [90].

Adding Zr or Ti to a liquid to form a protective film via reaction with carbon and nitrogen in steel can significantly reduce the corrosion rate of liquid LBE [91,92]. Elements such as Si can enhance the corrosion resistance of materials in liquid LBE. However, Si-rich steel has poor corrosion resistance in LBE flowing at 550 °C, between 10^{-6} mass% oxygen and saturation oxygen [93]. In addition, Si can reduce the material's toughness, increase weld crack sensitivity, and cause liquid metal embrittlement [4]. Therefore, the enhancement of corrosion resistance while ensuring the mechanical properties of the material itself is one of the directions to be studied in the future.

3.2. Temperature

In the isothermal static system, temperature affects the degree of corrosion of steel materials in LBE. When the temperature is lower, the dissolution rate of metal elements decreases, and the degree of dissolution corrosion is weakened. When the system temperature is higher, the solubility of the material components is greater and the dissolution rate is greater, so the corrosion is more severe [11,94]. Table 2 [50] shows the solubility (in at. fraction, T in K, and A_c and B_c are thermodynamic constants) of each element in liquid LBE as a function of temperature. If there is no gradient in the system temperature, then the concentration of each element will eventually reach a uniform distribution [95]. In this case, corrosion will not continue.

Table 2. Fe, Cr, Ni solubilities in LBE. Data transferred from Ref. [50].

Metal	$\text{Log}_{10} S_s (\text{at}\%) = A_c - B_c/T$		Temperature (K)
	A_c	B_c	
Fe	0.5719	4398.6	399–1173
Cr	−0.2757	3056.1	399–1173
Ni	2.8717	2932.9	528–742
	0.2871	1006.3	742–1173

However, for non-isothermal liquid metal systems, due to the temperature difference in each section of the circuit, the elements will dissolve in the high-temperature section, then flow to the low-temperature section and deposit [95]. The greater the temperature difference in the system, the greater the diffusion migration drive of the metal elements dissolved in the LBE and the more severe the corrosion. With the gradient created by the temperature change, the elements in the material will dissolve, be transported to a lower temperature, and precipitate out. The component element concentration will always fluctuate, and dissolution will continue.

The solubility of metals in the liquid metal phase decreases with temperature, so that mass transfer, whether convective or diffusive, can lead to solute reprecipitation and deposition in the colder parts of the system under non-isothermal conditions [14]. The corrosion resistance of austenitic steels was studied by varying the temperature under controlled conditions of oxygen concentration in LBE. At 550 °C, an oxide layer was produced on the surface of the material, and no dissolution was observed; at 600 °C, there was significant penetration [96]. Even if the liquid metal is saturated with oxygen, if the temperature is above 550 °C, dissolution will occur [4].

The corrosion of structural materials in high-temperature liquid metals has been studied in many ways [78–81]. Alloys with higher Si, Cr, or Al contents at high temperatures can generate more stable oxide films and will be more resistant to corrosion. The generation of oxide films during the corrosion process has a dual role. If the oxide film is thick and easy to detach from the substrate, breaking it will accelerate the corrosion of the liquid metal on the structural material; if the oxide film has a thin, uniform texture and good density, the substrate will play a protective role, thus preventing further oxidation corrosion [6].

Combined with the previous analysis, we can conclude that the temperature directly affects the diffusion coefficient, dissolution rate, and solubility of steel components in liquid LBE. In general, these material performance parameters are positively correlated with temperature, and high temperatures accelerate the corrosion rate of structural materials. On the contrary, for some alloying elements, a dense oxide film is formed at a certain temperatures, which in turn improves corrosion resistance.

3.3. Flow Rate

When the liquid LBE flows over the surface of the structural steel, it will produce frictional wear, and since the LBE itself is corrosive, it will cause erosion damage to the surface of the structural steel [28,61–66]. In a flowing system, the oxide film will be destroyed by LBE. Generally, the higher the flow rate of liquid LBE, the more severe the corrosion of steel material will be; that is, the flow rate will accelerate the corrosion of steel material.

To study the effect of flow rate on the behavior of austenitic stainless steels, the steels were subjected to corrosion in flowing liquid LBE for 1000 h [97]. The results show that when the relative flow rate is less than 0.92 m/s, the destruction of the oxide film leads to diffusion oxidation of the steel; as the relative flow rate continues to accelerate, the alloying elements are promptly removed at higher relative flow rates.

The corrosion of T91 varies at different flow rates of LBE. When the flow rate is 1 m/s, the outer layer of magnetite on the steel material surface is still intact, while it is largely invisible when the velocity rises to 2 m/s until it disappears completely at 3 m/s. However, at a flow rate of 3 m/s, the Fe–Cr spinel oxide layer is still intact [4]. The stainless steel 316L specimen was mounted on a rotating disc submerged in molten LBE, and the sensitivity of the thickness of the affected zone to the flow rate decreased as the reaction rate was controlled when the linear velocity of the disc was greater than 2 m/s. At speeds faster than 3 m/s, scouring corrosion begins to occur [98].

It can be seen that at low flow rates, the corrosion rate is generally controlled by mass transfer. At this time, the flow will make the thickness of the mass transfer layer thinner, and corrosion damage will be aggravated [95]. If the flow rate continues to rise and reaches a certain value, then the rate of mass transfer will also be accelerated, thus transporting the corrosion products. The dissolution rate in this case will have a decisive influence on the corrosion rate. When the flow rate is very high, the fluid will generate a large shear stress, which will destroy the protective film. The new surface will continue to be corroded and washed; the interaction between the two makes the damage more serious [4,99].

3.4. Oxygen Concentration

At low levels of oxygen in the LBE ($C_O < 5 \times 10^{-7}$ wt%), dissolution corrosion occurs mainly in structural steel. On the contrary, if the oxygen content in LBE is high ($C_O > 10^{-6}$ wt%), oxidative corrosion will increase and Pb–O compounds will be formed, contaminating the liquid LBE and clogging the pipeline [56]. When the LBE's oxygen content is in this range, which can produce a stable Fe_3O_4 that is not formed between Pb–O compounds, then a double-structured oxide layer will be formed. This oxide layer will prevent the corrosion of steel materials in LBE [4,67,100].

Exposure of 316L steel to liquid LBE with low oxygen concentration results in selective dissolution of some elements. At moderate LBE oxygen concentrations, Cr-based oxide films or Fe–Cr spinel are still formed despite the fact that the oxide films formed lose their protective properties over time, leading to the onset of steel dissolution [101]. In saturated LBE, the corrosion mechanism is oxidation. The critical oxygen concentration associated with dissolution corrosion of 316L in stagnant LBE at 450 °C for 1000 h is between 10^{-6} and 10^{-7} mass % oxygen [102].

Corrosion tests in LBE at 10^{-7} mass % oxygen, 550 °C and 200 MPa creep resulted in solution corrosion of T91. As the concentration of oxygen is increased to 10^{-3} mass %, a double protective film is formed on the steel surface. In the case of stagnant LBE with oxygen concentrations higher than 10^{-7} mass % at 550 °C, T91 is protected from liquid metal erosion in LBE [103].

AISI 316L and T91 were placed in flowing LBE to study the corrosion behavior at two oxygen concentrations. The results show that at low oxygen concentrations, dissolution corrosion occurs, while at high oxygen concentrations, an oxide layer forms on the material surface, protecting the steel from further corrosion by LBE [104].

From the above analysis, we can conclude that the amount of oxygen concentration at different temperatures, materials, and flow rates will change the type of corrosion and even affect the corrosion rate. Therefore, for specific reaction conditions, we must find the correct oxygen concentration to reduce corrosion damage.

4. Corrosion Prevention Measures

In order to achieve the safe use of steel, countries mainly start from two aspects: improving the performance of the material itself and reducing the corrosion of liquid LBE media. Therefore, the future should focus on the design of new materials, reasonable oxygen control technology development, etc. At present, more research is needed on active oxygen control and surface coating.

4.1. Active Oxygen Control

The oxygen content in LBE has a significant impact on the overall system's safety. Studies have shown that oxygen is a reliable corrosion inhibitor in the LBE environment, and oxygen control techniques are used to slow corrosion by forming a protective film on the material surface [95]. When the oxygen content in the liquid LBE is low, it cannot form an effective protective film and actively corrodes the structural material; when the oxygen content increases, the slag accumulation will precipitate and block the loop tube [56,89]. Therefore, it is necessary to adjust the oxygen content in liquid LBE in order to mitigate the dissolution corrosion of structural materials. There are three main techniques for controlling the oxygen content in LBE: solid-state oxygen control, gaseous oxygen control, and oxygen pumping [92,105].

CORRIDA was designed and built by the Karlsruhe Institute of Technology (KIT), as shown in Figure 5. It is a device that controls the oxygen concentration in the flowing LBE by changing the temperature and flow rate [106]. Flow tests were conducted on F/M steel T91 in the CRAFT cycle run by the Belgian Nuclear Research Center SCK·CEN. The results were compared with experiments in CORRIDA under similar test conditions, and their corrosion data were found to corroborate each other [67].

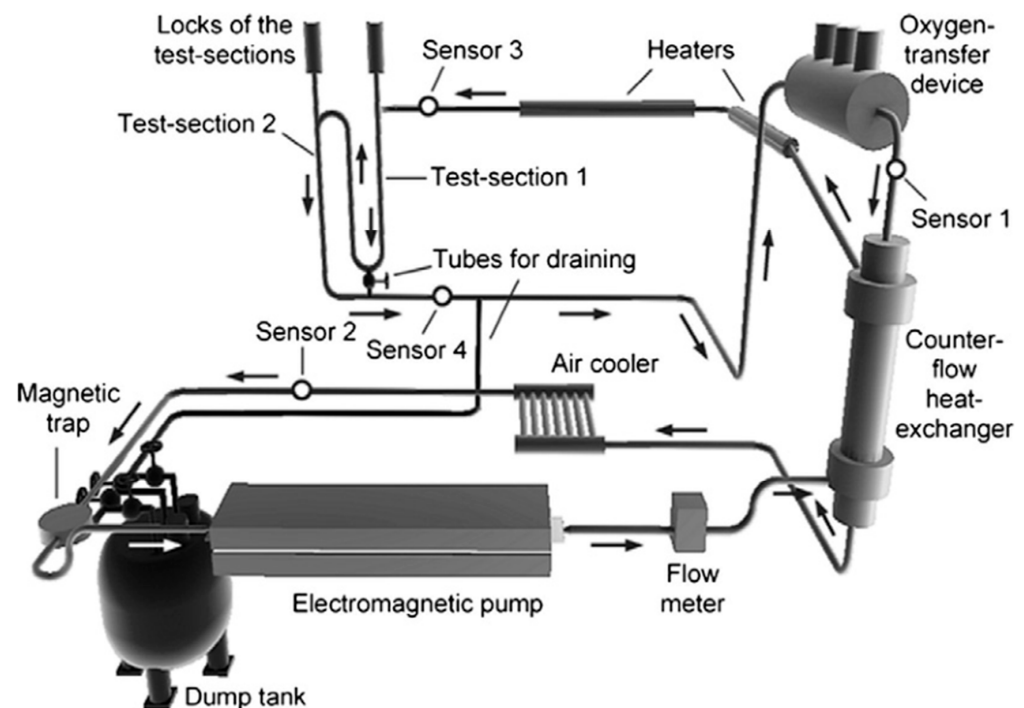


Figure 5. Schematic diagram of the CORRIDA device for testing steel in flowing oxygenated LBE. Reprinted with permission from Ref. [106]. 2011, L. Brissonneau.

In the liquid LBE with low oxygen concentration ($C_O < 10^{-7}$ wt%), the depth of ferritization increased with the degree of cold working. At moderate oxygen concentrations (10^{-7} wt% $< C_O < 10^{-6}$ wt%), Ni dissolution and Pb–Bi penetration caused slight iron seepage. In high oxygen concentrations ($C_O > 10^{-6}$ wt%), only oxidation occurs [56,100].

Currently, active oxygen control technology is developing rapidly, and gas-phase oxygen control has been popularized in industry, but its stability is poor. Solid-phase oxygen control technology has the advantages of fast response and simple design. Oxygen control technology can effectively reduce material corrosion problems [91], but it is still in the laboratory stage in an LBE environment and has not achieved large-scale engineering application. Electrochemical oxygen pumping (EOP) is another simple and clean method of controlling the dissolved oxygen concentration in LBE. EOP is based on the migration of oxygen ions, which can add or reduce oxygen to the medium. If this method operates safely and stably in LBE, it will be a very competitive oxygen control method in the future [107].

Although the control of oxygen concentration in LBE can slow down corrosion to a certain extent, its mechanical properties are not ensured accordingly. Under stress, the formed oxide layer cracks and delaminates, exhibiting poor mechanical properties [46]. In addition, the technique is only applicable for operating conditions below 500 °C. This method is not reliable in high-temperature situations.

4.2. Surface Coatings

Coatings are typically used to protect materials from various types of damage and are often used to protect surfaces from wear and tear, corrosion, heat and oxidation, and chemical attack [46]. The main corrosion-resistant coatings studied at home and abroad are poly coatings, functional gradient composite coatings, ceramic coatings, refractory metal coatings, ODS and high-entropy alloy coatings, and combinations of the above coating forms [31,46,83,108–111]. Coating technology is a method of improving the compatibility of structural steel with liquid LBE, such as powder embedding, physical vapor deposition, pulsed laser deposition/fusion coating, plasma electrolytic oxidation, and cathodic arc ion plating [112]. Although extensive corrosion experiments have been performed on protective coatings, some issues regarding the coating materials are still unclear.

The design idea of corrosion-resistant coatings is mainly achieved by adding some elements. These elements will form a dense oxide film to protect the substrate in liquid LBE with the proper oxygen content. The oxide film prevents the outward dissolution loss of the matrix elements and also blocks the inward diffusion penetration of lead and bismuth.

TiC layers in low-oxygen LBE can effectively prevent LBE corrosion at 600 °C for as long as 2000 h [113]. Carbon-based coatings exhibit outstanding performance in terms of high resistance to corrosion, surface smoothness, and low friction index. The low coefficient of friction and lubrication performance of these coats would have an important function in decreasing friction and reducing wear [46]. The 316SS surface was coated with different contents of Al and placed in LBE at 823 K. It was found that oxidation and corrosion were observed in the unaluminized 316SS, while the aluminized layer prevented further development of corrosion [31]. While in flowing liquid LBE, the aluminized coating on 316L steel was more sensitive because it was eroded during the cyclic test [102].

At present, there are more studies on the corrosion resistance of coatings than on their mechanical properties. Therefore, we can continue to conduct in-depth research on them in terms of coating preparation, such as on coatings in high-speed LBE flow and corrosion-resistant LBE coatings with high interfacial and mechanical properties, simultaneously improving the preparation process.

5. Summary

Although some progress has been made in the research work on LBE, some issues still need to be studied in depth and systematically. In reality, the corrosion process of LBE is very complicated, such as the corrosion process and mechanism when accompanied by the occurrence of wear, scouring, and other mechanical damage.

To ensure reliable nuclear applications of steel, future related research should focus on manufacturing steel adapted to the LBE service environment by adjusting material design and treatment and on reducing the corrosion of steel in the LBE by using active oxygen control technology and adding corrosion inhibitors. Research on solid-phase oxygen control is especially necessary. In addition to the preparation of high-quality coatings, the development of new steel alloys is also an important direction for LBE corrosion resistance. The advantage is that the new alloy as a whole has no interface problem with the coating matrix, and it will not come off due to high temperature stress, etc. Unless a new alloy is found before the development of the alloy coating system, it is still the better choice.

Experimental research has high environmental requirements and a long experimental period, and the experimental results are often limited to a specific set of experimental conditions. More and more comprehensive research must continue to be conducted, such as on the high-speed flow of LBE erosion and corrosion. The rapid development of numerical simulation technology [114–117] and its combination with experimental data will be of great help for the study of lead–bismuth alloys, which are also of great significance for reactor safety design.

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