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Review

Research Progress of Macrocell Corrosion of Steel Rebar in Concrete

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Abstract: Macrocell corrosion of steel rebar in concrete induced by corrosive environments has attracted widespread attention in the engineering community due to its rapid corrosion rate, diverse forms, and multiple incentives. Potential differences between dissimilar coupled rebar or different parts of the same rebar mainly cause macrocell corrosion of steel rebar. The more significant the potential difference, the faster the corrosion rate of the macrocell. Based on the existing research reports on macrocell corrosion of reinforced concrete, this review paper comprehensively discusses the macro- and micro-corrosion behavior of various types of steel rebar, and a variety of induction factors, such as dissimilar metals and concentration differences of the service environment, development rules. and electrochemical mechanisms for corrosion of rebar macrocells are summarized. ZRA (zero-resistance ammeter), micro-area electrochemical testing technology and evaluation techniques commonly used in the laboratory, and electrochemical testing techniques used in engineering testing are listed. Common experimental models for corrosion of rebar macrocells are briefly introduced. Based on the internal characteristics of macrocell corrosion of reinforced concrete, this paper further proposes the control strategy of macrocell corrosion, starting from the improvement of the corrosion resistance of the rebar and regulating the service environment of the reinforced concrete structure (RCS). Meanwhile, the future direction of macrocell corrosion of steel rebar is also preliminarily prospected.

Keywords: reinforced concrete; macrocell corrosion of rebar; corrosion inducement; investigation methods; controlling strategy

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1. Introduction

Reinforced concrete structures (RCSs) are widely used in building structures worldwide. Generally, reinforced concrete has good durability and long-term effectiveness in the common service environment. The hydration of cement in concrete produces a large quantity of OH^- ions, which results in the high alkalinity of the concrete environment with a pH value of around 13 [1–3]. In a highly alkaline concrete environment, the steel rebar's surface can quickly form a protective and dense passive film, ensuring that the steel rebars are in a passivation state for a long time without any corrosion [4–7]. However, due to the defects of materials of RCSs and the impact of the external erosive environment, corrosion of steel rebar and expansion of rebar rust in concrete can easily occur, resulting in cracking of the concrete protective layer, ultimately leading to a decline in structural durability and premature failure [8]. With the acceleration of social development and the deepening of human exploitation of the Earth, reinforced concrete materials have become more widespread, and the service environment has become more diverse and harsher. Corrosion of steel rebar in concrete induced by corrosive environments has become a bottleneck issue in the deterioration of structural durability. Delaying rebar corrosion to improve the durability of RCSs is of great significance to ensure long life and safe service of structures.

There are many forms of corrosion of reinforced concrete induced by corrosive environments, which can be roughly divided into rebar corrosion caused by micro-corrosion cells (referred to as microcell corrosion of steel rebar) and rebar corrosion caused by macro-corrosion cells (referred to as macrocell corrosion of steel rebar) based on the electrochemical mechanism of corrosion. Comparing the two corrosion forms, the macrocell corrosion of steel rebar has more inducing factors and a faster corrosion rate. The cathodic rebar is protected in the macrocell corrosion system, while the anodic rebar acts as the corrosion carrier of the macrocell corrosion system, becoming the main corrosion occurrence area and sacrificial electrode. In addition, the macrocell corrosion of rebar is always accompanied by microcell corrosion, resulting in the apparent complexity of rebar corrosion.

Meanwhile, the anodic and cathodic electrodes of the macrocell corrosion system of rebar are the typical large-area electrodes, and the corrosion current can even reach tens to hundreds of μA [9–11]. In practical engineering, it is difficult to eliminate macrocell corrosion of steel rebar. However, reasonable prevention can effectively interfere with the corrosion process and decrease corrosion damage. In this paper, the corrosion mechanism of RCSs and the inducible factors of macrocell corrosion, as well as the experimental research methods for examining macrocell corrosion of RCSs. are systematically proposed, and the effective protective measures for macrocell corrosion of RCSs in practical application are given. This provides a useful reference for the relevant researchers of macrocell corrosion of RCSs. It is of great significance to improve the durability and service life of RCSs.

2. Corrosion of Reinforced Concrete

Cement is the primary cementitious material in concrete, containing mainly SiO_2, CaO, Al_2O_3, and other substances [12]. The $Ca(OH)_2$ generated by the hydration process of the cement will fill the concrete's pore structure, making the concrete highly alkaline [13]. In this alkaline environment, a stable passive film with a thickness of about 1 to 5 nm will be formed on the steel rebar surface [14–16], which consists of the oxides and hydroxides of alloying elements contained in the rebar matrix [17–19], providing good corrosion protection to the rebar. However, the decrease in alkalinity of the protective layer concrete caused by carbonation, the diffusion of harmful media such as chloride ions in the concrete pore structure, and the insufficient corrosion resistance of the steel rebar itself will cause corrosion of the steel rebar. In the actual service process, the above incentives often coexist, thereby accelerating the rebar corrosion in concrete.

Carbonization of concrete is one of the main factors causing rebar corrosion, which tends to induce overall corrosion of the steel rebar. During the long-term service of RCSs, CO_2 in the atmosphere will diffuse from the concrete surface into the interior of the concrete through the pore structure [20] and react with $Ca(OH)_2$ generated by the cement hydration to create calcium carbonate, leading to carbonation of the concrete and resulting in the decrease in concrete alkalinity liquid, which in turn leads to rebar depassivation and corrosion [21]. Research has shown that when severe carbonation of concrete happens, the pH value of concrete could drop to 8.5–9 [22–24]. In such a low alkaline environment, the steel rebar cannot form a stable passive film, resulting in electrochemical corrosion of the rebar through oxygen cathodic depolarization. The electrochemical reaction process of rebar corrosion induced by concrete carbonization is shown in Figure 1. In carbonated concrete, the rebar loses the protection of its passive film, and many corrosion microcells form on its surface. As an anode, the steel rebar matrix loses electrons and hydrolyzes into Fe^{2+}, while as a cathode, oxygen traps electrons and generates OH^-. Furthermore, the Fe^{2+} produced by the corrosion reaction combines with OH^- to form a primary corrosion product, $Fe(OH)_2$, and further reacts and oxidizes to form $Fe(OH)_3$, continuously consuming the Fe^{2+}, and thereby causing the overall corrosion of the rebar.

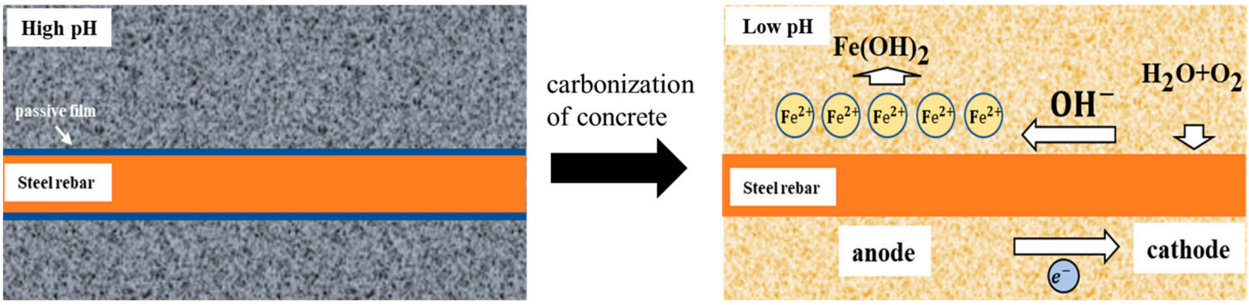

Figure 1. Corrosion mechanism of rebar induce by the carbonization of concrete.

RCSs serving in chloride-containing environments, such as oceans and salt lakes, also face the problem of pitting corrosion of rebar caused by chloride-ion erosion, which is a form of typically localized corrosion. The effect of chloride ions on rebar corrosion is mainly reflected in the localized destruction of the passive film [25]. Chlorine ions have a minimal ion diameter. When they adsorb on the passive film of the rebar surface and accumulate to a specific concentration, they can penetrate the passive film and enter its interior, causing localized dissolution of the passive film and pitting corrosion of the rebar. Therefore, the increase in chloride-ion concentration at the rebar/concrete interface is a crucial factor causing the pitting corrosion of rebar, and the critical chloride-ion concentration that causes the initiation of pitting corrosion is an essential indicator for evaluating the corrosion resistance of the rebar–concrete system. Figure 2 is a schematic diagram of the pitting corrosion of rebar induced by chloride ions. After the partial dissolution of passive film induced by chloride ions, pitting corrosion will be initiated on the rebar surface. Furthermore, chloride ions will further promote the local dissolution of the rebar matrix into Fe^{2+} and form corrosion pits. Then, iron ions react with OH^- to form precipitates of corrosion products that accumulate on the pit's surface. Moreover, the Cl^- ions are continuously used to transfer the Fe^{2+}, which forms large corrosion pits on the rebar matrix, causing rapid corrosion of the steel rebar.

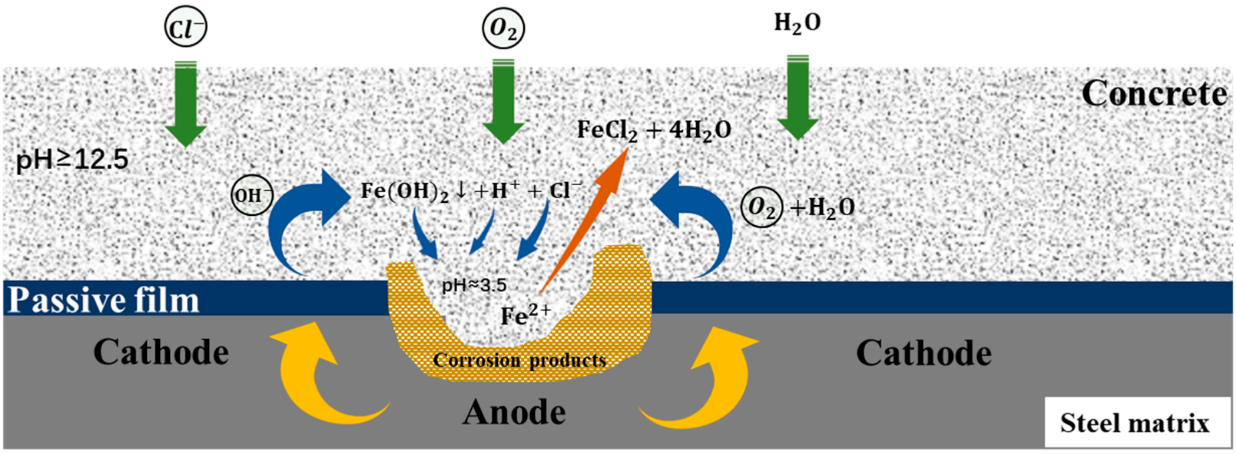

Figure 2. Rebar corrosion mechanism induced by the Cl^- ions erosion.

According to recent research reports, chloride-ion corrosion is the most critical external factor causing rebar corrosion. The synergistic effect of concrete carbonation and chloride-ion erosion will further accelerate rebar corrosion. During the service life of RCSs, due to differences in the degree of concrete carbonation and chloride-ion concentration in different areas of the structure where the rebars are located, there will be significant differences in the corrosion rate of the rebar in different parts of the RCSs. In addition, to meet the economic requirements of the RCSs, it is necessary to use several steel rebars with different corrosion resistance at the same RCS, and coupling between different types of steel rebar can also accelerate the corrosion rate of rebar. The above corrosion phenomenon of an RCS is mainly due to the potential difference of the rebars caused by the environmental differences in different parts of the RCS, as well as the potential difference between different types of rebars, which promotes the formation of macrocell corrosion of the rebar in the concrete. In the macrocell corrosion system of the RCS, the steel rebar (or the part of the rebar) with a lower potential becomes the corrosion anode and is the primary carrier of corrosion. The steel rebar (or the part of the rebar) with a higher potential will act as the cathode, which will be protected against corrosion in the macrocell corrosion system. Macrocell corrosion can accelerate the corrosion of anodic rebar, causing severe corrosion damage to the RCS. Compared to microcell corrosion, the harm of macrocell corrosion in RCS is more severe and harder to control, and thus requires in-depth research and discussion.

3. Macrocell Corrosion of Reinforced Concrete

3.1. Behavior and Mechanism of Macrocell Corrosion of Reinforced Concrete

When a metal is in an electrolyte solution, as water molecules are strongly polar molecules, metal atoms on the metal surface are attracted by water molecules and migrate from the lattice to the surface to become adsorptive atoms. Under the influence of the electric field of the double layer, they become metal ion M^{n+} [26], as shown in Figure 3a. The electrode reactions are as follows in Equations (1) and (2). The former represents the absence of anions in the electrolyte that react with metal ions to form insoluble compounds, while the latter represents the presence of anions that react with metal ions to form insoluble compounds.

$$M \leftrightarrow M^{n+} + ne^- \tag{1}$$

$$mM + nX^{m-} \leftrightarrow M_m X_n + nme^- \tag{2}$$

$$E = E^0 + \frac{RT}{nF} \ln a^{n+} \tag{3}$$

$$E = E^0 + \frac{RT}{nF} \ln a^{m-} \tag{4}$$

In the Nernst Equations (3) and (4), E^0 is the standard electrode potential, E^0 (M^{n+}/M) = $\varphi^0(H^+/H_2) - \varphi^0(M^{n+}/M)$, the standard electrode potential of metal is the potential difference of the galvanic cell composed of the standard hydrogen electrode and metal half-cell under the standard state (T = 298.15 K, p = 101.325 kPa, effective activity of metal ions = 1) with water as solvent, where $\varphi^0(H^+/H_2)$ = 0; any kind of metal standard electrode potential can be measured by experiment in this way. a^{n+} is the activity of metal ions in the solution, and a^{m-} is the anionic activity of forming insoluble compounds with metal ions.

Different types of steel rebar, as well as the different parts of rebar located in different erosion environments, will exhibit different electrode potentials. Generally, the higher the electrode potential, the better the corrosion resistance [27–29]. When the steel rebar is in the same electrolyte solution, the one with a high electrode potential will act as the cathode, and the one with a low electrode potential will act as the anode. At this time, the electrode potential difference constitutes the reaction force for macrocell corrosion of the rebar [30–32]. When two types of steel rebars are connected, electrons move towards the cathode due to the difference in electrode potential, and the anodic reaction equilibrium is destroyed, accelerating the anodic dissolution. The accumulation of electrons in the cathode enhances the cathodic ion reduction reaction, and the cathode is protected, resulting in severe anodic corrosion in the macrocell corrosion system. The electrochemical principle of macrocell corrosion of steel rebar is shown in Figure 3b.

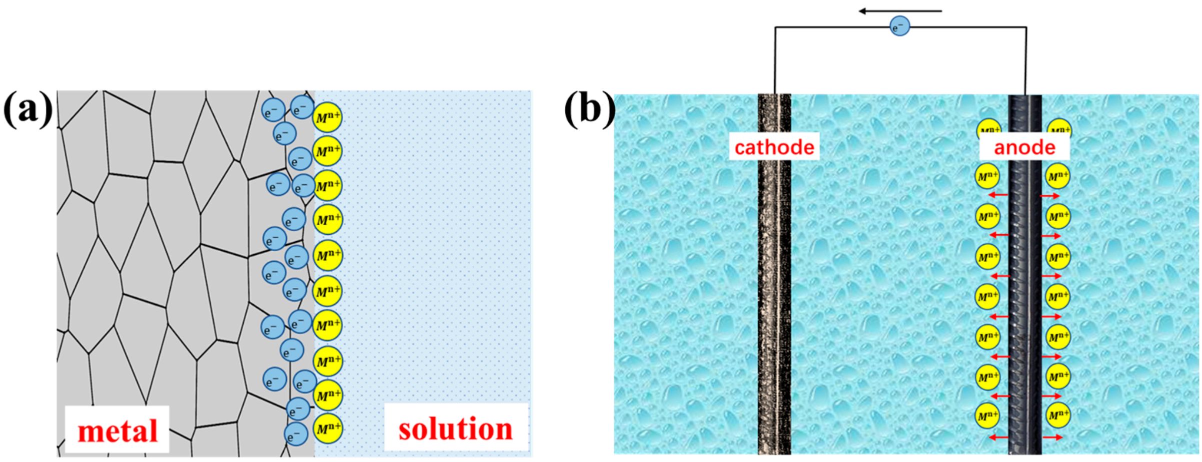

Figure 3. Mechanism of macrocell corrosion of rebar. (**a**) Hydrolysis reaction of rebar, (**b**) charge transfer processing of rebar during the macrocell corrosion.

The existence of the potential difference causes a macro corrosion current to be generated between two rebars, and the calculation equation of the corrosion current is as follows:

$$I = \frac{E_c - E_a}{R_c + R_a + R_s + R_t} \tag{5}$$

where E_c and E_a represent the open circuit potential of the cathodic rebar and the anodic rebar, R_c and R_a represent the polarization resistance of the reaction between the cathodic and anodic rebar electrode, $E_c - E_a$ represents the macrocell corrosion driving force between rebar, R_s represents the resistance of the concrete and pore solutions between the two rebars, and R_t represents the resistance in the corrosion cell circuit. I is the macrocell corrosion current, representing the corrosion rate of the macrocell corrosion system. The larger the value, the faster the corrosion rate. Cao et al. studied the influence of the water–cement ratio on corrosion polarization behavior of embedded reinforced macrocells in cement mortar, and analyzed the relationship between a large cell potential difference and macrocell current density according to Equation (5). It was concluded that a lower water–cement ratio could reduce the macro-current by reducing the potential difference of macrocells and increasing the corrosion polarization resistance of macrocells of the cathode and anode [33]. Based on Equation (5), J. Warkus et al. simulated the calculation method of the macroscopic current value under various geometric effects through laboratory experiments and numerical simulation, and verified that concrete resistivity and water content have a significant influence on the generated macrocell current in experiments [34]. Qian et al. suggests that the corrosion driving force of macrocells cannot completely represent the corrosion rate, but is more influenced by the polarization reaction of cathode reinforcement. Moreover, the resistance of concrete and the ratio of the anode area to cathode area also affect the current density of macrocells to a large extent [32].

3.2. Inducements of the Macrocell Corrosion of Reinforced Concrete

3.2.1. Macrocell Corrosion of Rebar Induced by Coupling of Dissimilar Rebars

Different metals have different electrode potentials due to their different arrangements in the galvanic sequence. Therefore, when steel rebars with different corrosion resistance are coupled in concrete and form a current circuit, the difference in electrode potential between the two rebars constitutes a prerequisite for macrocell corrosion. The rebar with a lower electrode potential is the anode of the macrocell corrosion system, giving priority to the anodic oxidation reaction. The rebar with a higher electrode potential is the cathode, which undergoes a cathodic reaction of oxygen depolarization. The galvanic current increases as the difference between the electrode potentials of the two types of rebars increases, and is inversely proportional to the total resistance of the entire circuit.

In the existing reports, there are relatively more studies of macrocell corrosion caused by the coupling of dissimilar rebars. For example, Jinyang Jiang et al. studied the macrocell corrosion behavior caused by the coupling of alloyed-steel rebar and carbon-steel rebar in the simulated concrete pore solutions (SCPSs) with different alkalinities. They believed that as the pH values of the SCPSs increased, the electrode potential difference between the two rebars gradually decreased, and the driving force of galvanic corrosion decreased, which is beneficial to inhibiting the occurrence of macrocell corrosion of rebars [35]. Y.Y. Li et al. studied the macrocell corrosion of N80 carbon steel and 13Cr stainless steel under supercritical CO_2 conditions. They found that the reduction in the potential difference between the two steels caused the formation of protective corrosion products on the surface of N80 steel [36]. The above research shows that the corrosion environment of the coupled rebars has an essential impact on their macrocell corrosion.

The area ratio of the cathode to the anode and the distance between electrodes in a macrocell corrosion system are also important factors affecting the development of corrosion. C. Arya et al. found that the galvanic current between coupled rebars gradually increases with the increase in the cathode/anode ratio, and is inversely proportional to the electrode spacing [37]. The existence of galvanic corrosion accelerates the corrosion of anodic rebar, but some studies have shown that the cathode and anode of galvanic corrosion are not fixed. Wenhua Zhang et al. found that when weathering steel is coupled to 316L stainless steel, it acts as a corrosion anode due to its lower potential than stainless steel at the initial stage of corrosion. As the corrosion products on the surface of the weathering steel deposit, its electrode potential increases, resulting in a phenomenon of cathode and anode conversion [38]. Macrocell corrosion, as an adverse factor of steel corrosion, can be transformed into a method of protecting steel from corrosion if its intrinsic electrochemical mechanism can be scientifically applied. For example, the cathodic protection method with a sacrificial anode is used via coupling the anodic metal with the rebar, which decreases the rebar corrosion in the concrete and improves the durability of RCS.

3.2.2. Macrocell Corrosion of Rebar Induced by Concentration Difference of Service Environment

Concentration-difference-induced macrocell corrosion is one of the common forms of metal corrosion. The corrosion behavior of the concentration-difference-induced macrocell is significantly related to the environmental factors of the corrosion system, and the concentration of gases and ions in the environment is a crucial factor inducing concentration-difference macrocell corrosion [39,40]. The electrode potential of steel bars is greatly affected by the environmental substances in which they are located, and the changes in environmental substances are uneven. This uneven local change leads to the severity of concentration difference macrocell corrosion.

The concentration difference of chloride ions in concrete is an essential factor causing macrocell corrosion of steel rebar. Due to the difference in chloride-ion concentration of the service environment in which RCSs are located and the concentration gradient formed by chloride-ion diffusion in the concrete protective layer, the electrode potential of rebar in areas with high chloride concentration decreases significantly. The above phenomenon results in potential differences between the rebars located in different areas, which constitutes the driving force for macrocell corrosion of rebar. Chloride concentration-difference-induced macrocell corrosion of rebar mainly occurs in marine RCSs, for which the corrosion principle is shown in Figure 4. Many chloride ions in the marine environment will diffuse from the concrete surface to the interior, forming a concentration gradient of chloride ions. The chloride concentration on the outer side of the concrete is significantly higher than that on the inner side. The rebar located on the outer side of the concrete is preferentially corroded, and acts as the anode in the macrocell corrosion system of rebar induced by the chloride concentration difference, while the rebar located on the inner side of the concrete is protected as the cathode [41]. In addition to the above phenomenon, the difference in chloride concentration in different areas where the same rebar is located can also cause macrocell corrosion between different parts of the rebar.

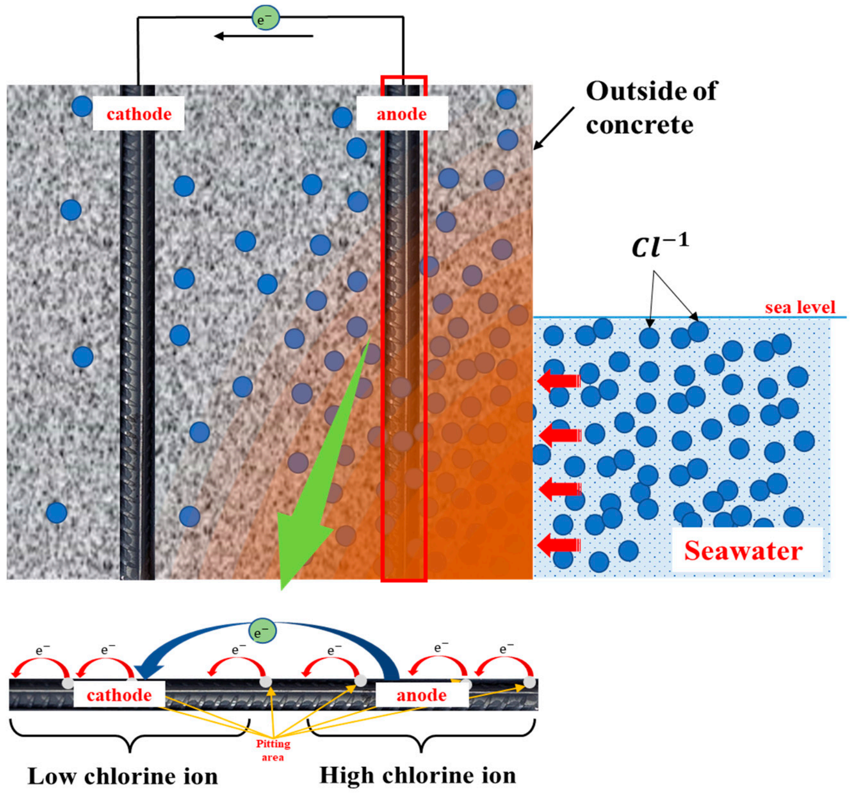

Figure 4. Schematic diagram of macrocell corrosion of rebar induced by chloride-ion concentration difference.

Macrocell corrosion of rebar induced by chloride concentration differences is extraordinarily complex and destructive, and many researchers have conducted in-depth research on it. Karla Hornbostel et al. found that during the galvanic corrosion process of rebar, the transmission of electric current is related to the uniformity of mortar. They believe the transmission of electrons is mostly affected by the resistance near the anode [39]. The complexity of such macrocell corrosion has also been discovered and determined during researchers' experiments. Ominda Nanayakkara et al. placed segmented embedded rebars in uniform and non-uniform chloride-ion environments, and found that uniform chloride-ion environments can also cause macrocell corrosion [42]. As research progressed, researchers found that the type of chloride salts can also have a significant impact on the chloride concentration-difference-induced macrocell corrosion of rebar. A. Poursaee et al. used $CaCl_2$, NaCl, and $MgCl_2$ as chloride-ion donors. When the salt concentration increased to 30%, the rebars in the mortar of the $CaCl_2$ corrosion system suffered the most severe corrosion damage [43].

The different degrees of concrete carbonation are another factor that causes macrocell corrosion of rebar. Carbonization starts from the concrete surface and gradually develops towards the interior, forming the carbonation and alkalinity gradients of the concrete from the surface to the interior [44]. It is generally believed that the passivation state of the rebar is closely related to the alkalinity of the concrete environment in which it is located, and high alkalinity is beneficial to the stability of the rebar passive film. Therefore, when the rebars are in concrete with different carbonization degrees, significant potential differences will be formed, which in turn constitutes macrocell corrosion of the rebars induced by the differences in the concrete carbonization. The principle of the concrete-carbonization-induced macrocell corrosion of the rebar is shown in Figure 5. The rebar located in the severely carbonated zone on the outer side of the concrete suffers accelerated corrosion damage as an anode in the macrocell corrosion system, while the rebar on the inner site is protected as a cathode. A. Nasser et al. studied the effect of concrete carbonization on macrocell corrosion of rebar through accelerated carbonization methods. The results showed that carbonization caused significant macrocell corrosion currents for rebars located in different carbonization regions [45].

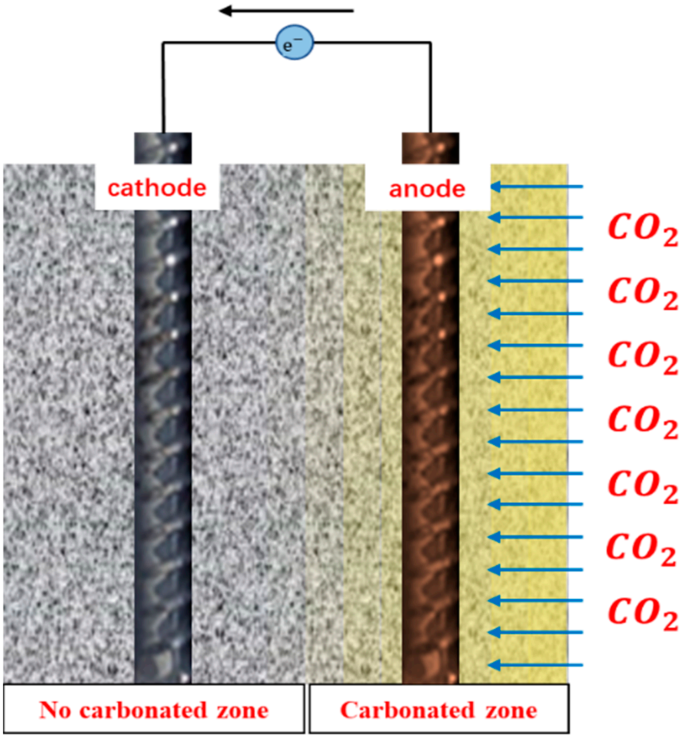

Figure 5. Schematic diagram of macrocell corrosion of rebar induced by concrete carbonization.

Based on the chemical reaction equation of concrete carbonization, it can be inferred that concrete carbonization is accompanied by a decrease in the concentration of conductive ions within the concrete, which can play a particular role in inhibiting macrocell corrosion of rebar. However, M.G. Sohail et al. designed a galvanic corrosion structure of activated and passivated steel rebar in carbonated concrete specimens. They found that despite the proximity of the cathode and anode areas, the macrocell corrosion current of the rebar in carbonated concrete is still strong [46]. Based on this, it can be seen that concrete carbonization plays a leading role in promoting macrocell corrosion of rebar.

The oxygen concentration difference is another essential factor causing macrocell corrosion of rebar. Oxygen is an essential material for cathodic depolarization in electrochemical corrosion systems. The nonuniform oxygen distribution can also lead to macrocell corrosion in certain specific environments. The electrode potential of the metal in an environment with high oxygen concentration is higher, while the metal electrode potential in an environment with low oxygen concentration is lower, constituting a corrosion potential difference condition for macrocells. Macrocell corrosion induced by oxygen concentration differences mainly occurs in environments prone to oxygen concentration differences, such as soil, pipelines, water, and oil wells. For example, the two parts of the rebar-concrete sample above and below the water or soil interface constitute oxygen-concentration-induced macrocell corrosion of rebar, the principle of which is shown in Figure 6. Below the air/soil interface is an anoxic zone, where the rebar is preferentially corroded as an anode in the corrosion system, while the rebar in the air-exposed zone above the interface is protected as a cathode due to sufficient oxygen supply. When the soil where a rebar–concrete sample is located has different oxygen content, it can also cause macrocell corrosion of rebar induced by oxygen concentration differences. Xie JH et al. studied the mechanism of macrocell corrosion of A3 steel induced by oxygen concentration difference by simulating soil environmental differences, and found the accelerated corrosion of the steel during the corrosion process [47].

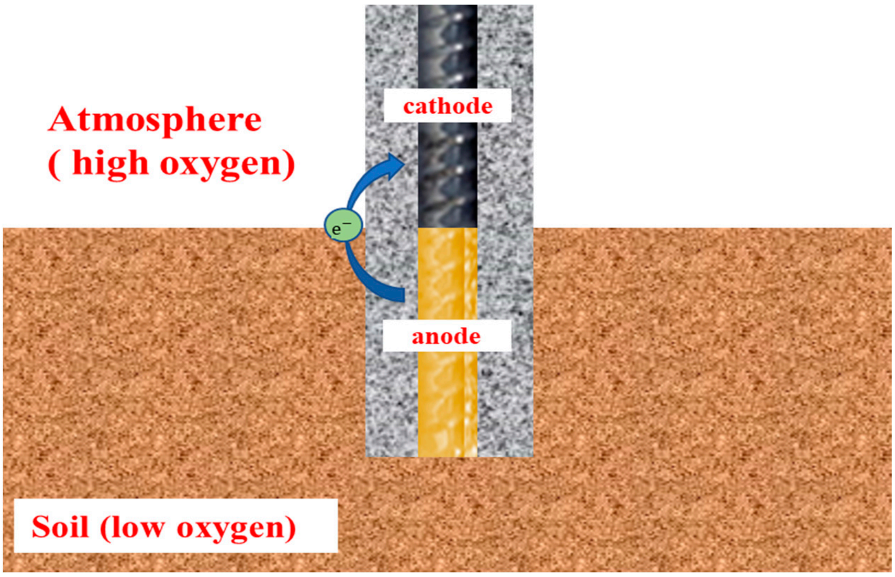

Figure 6. Schematic diagram of macrocell corrosion of the rebar induced by oxygen concentration difference.

3.2.3. Other Inducements of the Macrocell Corrosion of Reinforced Concrete

The difference in the reinforced concrete's temperature field can also cause macrocell corrosion of rebar. Due to the different working environments or application engineering conditions in which RCSs are located, the ambient temperature of different material parts varies, forming a temperature field gradient. It is generally believed that the electrochemical rate of corrosion is significantly affected by ambient temperature. The higher the temperature, the greater the activity of the corrosion system, and the faster the electrochemical reaction rate. The rebar in the low-temperature zone is stable with a high potential, constituting the cathode for macrocell corrosion. The rebar in the high-temperature zone is in an activated state with a low potential, which constitutes the anode of the macrocell corrosion system, leading to the accelerated corrosion of the rebar.

The difference in the areas of anode and cathode in the macrocell corrosion system can also accelerate the corrosion rate of rebar, which is particularly common in epoxy-coated rebar where the coating is partially damaged. Using epoxy coating or other coatings to protect the rebar can effectively isolate the natural erosion of external environmental media to the rebar matrix, and is an effective method to inhibit rebar corrosion. However, the transportation and use process can cause varying degrees of local damage to the coating. The exposed rebar matrix at the damaged part of the coating will form a macrocell with the coated rebar matrix, thereby accelerating the anode corrosion of the rebar matrix as a macrocell corrosion system. In addition, when rebar with different degrees of coating damage is coupled, macrocell corrosion can also occur due to differences in the exposure area, accelerating the corrosion damage of the RCS [48].

4. Macrocell Corrosion of the Different Types of Rebars

Carbon-steel rebars are the most widely used rebar, but their corrosion resistance is unsuitable for harsh service environments. Therefore, researchers have developed various steel rebars to meet different usage requirements. The strength, toughness, and corrosion resistance of steel rebar can be simultaneously improved through the optimized design of alloying composition of the rebar. For example, it is possible to prepare multi-level high-strength corrosion-resistant alloyed-steel rebar using alloying, such as Cr, Mo, and Ni, and advanced melting, controlled rolling, and cold forming technologies. Via the above methods, several alloyed-steel rebars have been fabricated. The representative ones include MMFX alloyed-steel rebars from the United States [49] and 00Cr10MoV alloyed-steel rebar developed by China Shagang Iron and Steel Group [50]. Research shows that MMFX alloyed-steel rebar has a service life of up to 50 years in marine environments. The corrosion resistance of 00Cr10MoV alloyed-steel rebars in chloride salt environments is ten times that of traditional HRB400 carbon-steel rebar. Regarding surface protection treatment of rebar, it is commonly used to apply corrosion-resistant protective coatings on the surface of carbon-steel rebar to isolate the corrosive media and/or provide cathodic protection. Examples include epoxy-coated steel bars, Zn-coated steel rebar, and composite-coated steel rebar.

4.1. Macrocell Corrosion of the Carbon-Steel Rebar

Carbon-steel rebar has excellent mechanical properties and significant price advantages, making it the most widely used rebar in engineering applications. However, the severe lack of corrosion resistance of the carbon-steel rebar in corrosive environments is particularly prominent. Therefore, the corrosion research of carbon-steel rebars is the most extensive and detailed, and the research about its macrocell corrosion is no exception. C.M. Hansson et al. used different types of concrete as protective layers to conduct macrocell corrosion research on carbon-steel rebar. The results showed that the ion resistance of carbon-steel rebars in ordinary Portland cement concrete is relatively low, while the macrocell corrosion in ultra-high-performance concrete (UHPC) can be ignored. The reason for this is that UHPC provides a good service environment to inhibit steel rebar corrosion [51]. However, the application of UHPC in engineering is relatively limited, and there is wider use of ordinary concrete materials. Moreover, rebar corrosion occurs more often when the concrete is partially damaged. In order to study the macrocell corrosion induced by the coupling of HRB335 and HPB300 carbon-steel rebars in concrete, Jin ZH et al. designed pre-crackings with different positions and widths in the concrete protective layer to accelerate rebar corrosion. The results show that the presence of cracks in the concrete protective layer in chloride environments results in more severe corrosion in carbon-steel rebar, and the macrocell corrosion current density of the two types of steel bars is proportional to the transverse crack width [52].

4.2. Macro-Cell Corrosion of the Coated Rebar

Generally speaking, corrosion originates from the interface between materials and environmental media. If the surface properties of materials can be effectively improved, it is expected to significantly improve their corrosion resistance. Covering the surface of carbon-steel rebar with corrosion-resistant coatings has become an important means to effectively improve their corrosion resistance. Zn-coated steel rebar produce a zinc protective layer on the rebar surface by electroplating to isolate the contact between the steel rebar substrate and the external environment, and the cathodic protection can be conducted to the rebar matrix [53]. Due to the microstructure characteristic and performance of the coating layers, the macrocell corrosion behavior of the coated rebars is also significantly different from that of carbon-steel rebar, and has already been the subject of many studies in recent years.

A.P. Yadav et al. conducted a study on the corrosion of Zn-coated steel rebars in artificial seawater. They pointed out that with the development of corrosion, the zinc coating serves as the anode of the corrosion macrocell while the steel rebar matrix serves as the cathode. The anodic corrosion current of the zinc coating provides cathodic protection for the steel rebar matrix. In addition, the corrosion product coverage of the zinc coating also has a certain protective effect on the rebar matrix, and the local damage of the zinc coating does not affect the protection of the rebar [54]. Mohammed MSHS et al. studied the corrosion resistance of steel rebars with multiple coatings, such as cement–polymer composite coatings with a preset damage area of 1%, cement slurry inhibiting coatings, zinc plating coatings, and cement–polymer anti-corrosion coating, and concluded that a small amount of coating damage did not have a significant impact on the macrocell corrosion of steel rebar [55]. Sylvia Keßler et al. connected two epoxy-coated rebars with different damage degrees and implanted them into concrete, resulting in the occurrence of macrocell corrosion of the rebar. It was concluded that the corrosion current density of the macrocell was closely related to the area of the cathode and anode (i.e., the damage degree of the rebar coating) [47]. Vedalakshmi et al. studied the corrosion resistance of macrocells in the case of damage to different types of coated steel rebar, and found that cement slurry coatings perform better than epoxy coatings in the case of pre-damage [9].

4.3. Macrocell Corrosion of the Alloyed-Steel Rebar

Alloyed-steel rebar has significantly better corrosion resistance than carbon-steel rebar [56]. The different types of alloyed-steel rebar with different content of alloying elements can provide different levels of corrosion resistance, which can be adapted to different corrosion environments and designed service life requirements. Compared to carbon-steel rebars, the cost of alloyed-steel rebar is relatively higher. In engineering applications, alloyed-steel and carbon-steel rebars are often used to achieve optimized structural durability and economic configuration. The potential difference between alloyed-steel and carbon-steel rebars, which poses a potential risk of inducing macrocell corrosion when both are used simultaneously, has also attracted attention from researchers and the industry. At this stage, researchers have studied the macrocell corrosion behavior of alloyed-steel rebars from the aspects of alloying content and microstructure characteristics of the rebar matrix, as well as the service environment. Zhang WH found that low-alloying steel rebar containing a small amount of Cr is prone to macrocell corrosion in simulated marine atmospheric environments after being coupled to 316L stainless steel. Further research indicates that the Cr element has an inhibitory effect on macrocell corrosion of rebar and improves the resistance to macrocell corrosion. The positive effect of Cr becomes more outstanding as its content increases [38]. In the study of the intrinsic relationship between the microstructure and the macrocell corrosion of the alloyed-steel rebar, Bright O. Okonkwo et al. found that microstructure changes in alloyed steel caused by welding heat effects can cause non-uniform corrosion in the welding-heat affected zone of the low-alloying steel rebar. The corrosion driving force comes from the heat-affected zone's macrocell and the rebar matrix [57]. Wang PJ et al. found that ultrafine grains have an excellent inhibitory effect on macrocell corrosion between different types of grains in the alloyed-steel rebar [58].

Stainless-steel rebar is a special alloyed-steel rebar with a large number of alloy elements such as Cr, Ni, and Mo. It has higher corrosion resistance and can be used in critical structural parts serving in extremely severe corrosive environments such as inland salt lakes and tropical seas. Due to the superior corrosion resistance of stainless-steel rebar, there is a huge electrode potential difference between stainless-steel and carbon-steel rebars. There is also a significant potential advantage compared to ordinary alloyed-steel rebar. Therefore, when stainless-steel rebar is used in conjunction with other steel rebars, there is often a potential risk of causing macrocell corrosion on other steel rebars. Konkwo et al. studied the galvanic corrosion between dissimilar metals of A508 alloyed steel and 309/308L stainless steel, and found that the galvanic current density increased with coupling time [59]. Regarding macrocell corrosion inhibition, G.Y. Zhu et al. studied macrocell corrosion between X65 carbon steel and 316 stainless steel in a crevice environment and found that 316 stainless steel inhibits macrocell corrosion of the galvanic pair under crevice conditions [60].

5. Experimental Methods and Testing Technologies of the Macrocell Corrosion of Reinforced Concrete

5.1. Experimental Research Methods

Due to the diversity of inducing factors for macrocell corrosion of reinforced concrete, such as different rebar coupling, environmental concentration differences, and concrete carbonization, the research focus of the macrocell corrosion of reinforced concrete is to establish corresponding experimental devices for different inducing factors, and design scientific experimental procedures to achieve the expected experimental research results.

5.1.1. Basic Model for Microcell-Corrosion Experiment of Rebar

The galvanic macrocell corrosion experimental device is relatively simple. After coupling two types of rebar samples through wires, place them in an aggressive medium, maintain a certain distance between them, and test the macrocell corrosion of the rebar through an electrochemical workstation. Figure 7 shows the schematic diagram of the macrocell corrosion test device for the rebar galvanic couple. First, disconnect the coupling of the samples, connect the two types of rebars to the two working electrodes of the electrochemical workstation (there are specific differences in connection methods between different electrochemical workstations), and use the zero-resistance current module of the zero-resistance ammeter (ZRA) to test the macro-current value between the two rebars. The connection of the reference electrode can be used to test the coupling potential. A series of electrochemical tests were conducted on the corrosion of the samples using a three-electrode test system by connecting the counter electrode.

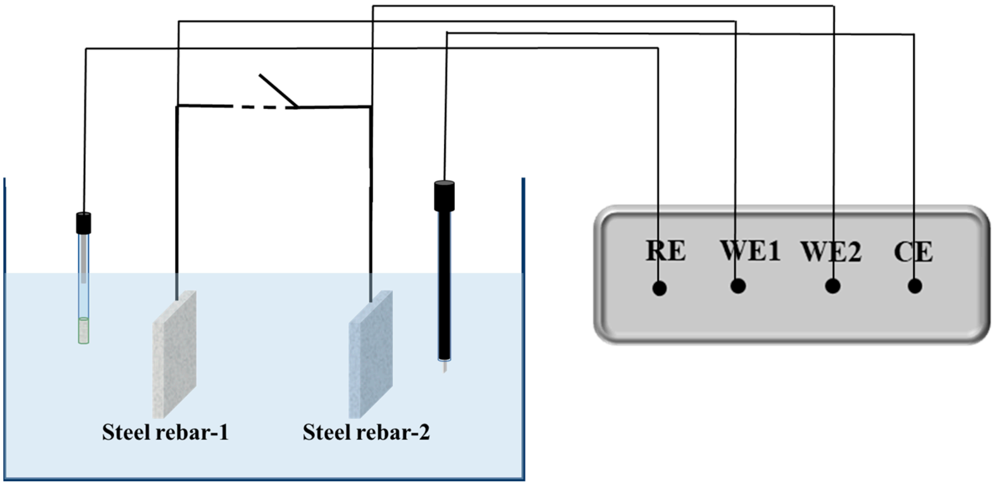

Figure 7. Schematic diagram of macrocell corrosion test device for rebar galvanic couple.

5.1.2. Experimental Model of Concentration-Difference-Induced Macrocell Corrosion of Rebars

The experimental design of the macrocell corrosion induced by the environmental concentration difference can be divided into two forms. One is the fixed concentration difference, and the other is the free diffusion resulting in continuous concentration difference. The former requires isolation of the two corrosive environments to achieve concentration corrosion conditions.

Two common isolation methods for macrocell corrosion experiments are induced by the fixed concentration difference, namely, the salt bridge connection and semi-permeable membrane connection. The schematic diagram of the experimental device is shown in Figure 8. The connection ensures an electronic circuit, while ions or gases cannot migrate, forming a macrocell circuit and a fixed concentration difference. Electrolytes with different ion concentrations are installed on both sides of the experimental device for macrocell corrosion induced by ion concentration differences, while gases with different concentrations are introduced on both sides of the experimental device for macrocell corrosion induced by gas concentration differences. Corresponding electrochemical tests can be conducted simultaneously during the macrocell corrosion test process. Generally, a three-electrode system is used for electrochemical testing. The reference electrode and the counter electrode are placed together in the area on the sample side to be tested to avoid testing errors caused by concentration differences.

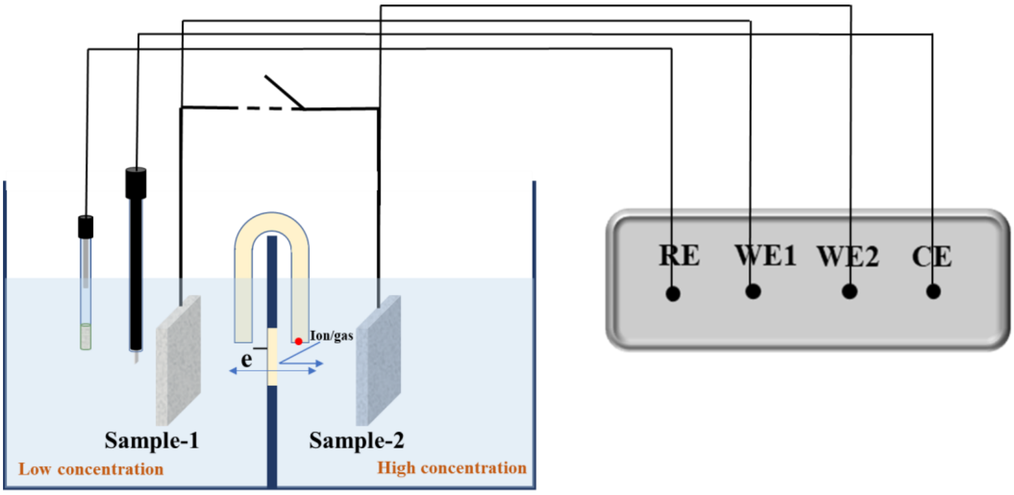

Figure 8. Experimental device for the macrocell corrosion induced by fixed concentration difference.

The concentration difference formed by the free diffusion of corrosive media is generally used for reinforced concrete samples or cement–mortar samples, and the schematic diagram of this testing device is shown in Figure 9. The procedure is to place rebar samples in concrete or mortar at a certain distance, connect them to the conductor, and expose the outside of the protective layer for coupling. A solution tank containing the corrosive medium is fixed on the upper side of the protective layer, and the corrosive medium diffuses freely into the substrate of the concrete, creating the macrocell corrosion of the rebar induced by the ion concentration difference. Via this device, the influencing factors on the ion concentration-difference-induced macrocell corrosion can be systematically investigated, such as the distance between reinforcing bars, solution concentration, and thickness of the concrete protective layer. Hansson CM and other researchers have used this method to study the macrocell corrosion of reinforced concrete induced by the free-diffusion concentration difference [43,51].

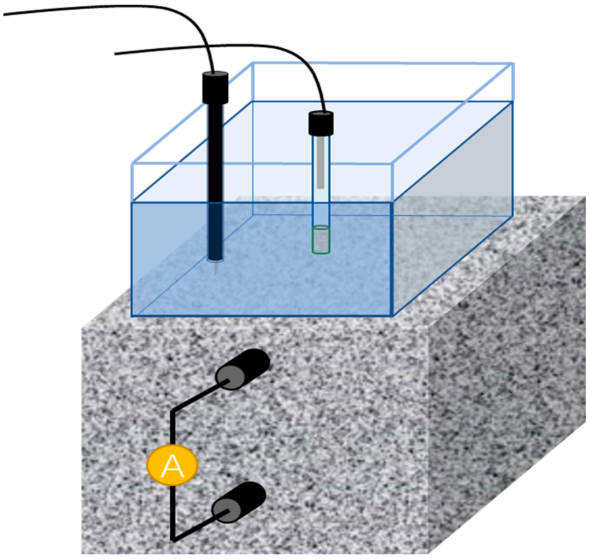

Figure 9. Testing device for the macrocell corrosion of reinforced concrete induced by the ion concentration difference resulting from free diffusion.

5.1.3. Experimental Model for Macrocell Corrosion of Rebar Induced by Concrete Carbonization

It is generally believed that the speed of natural carbonation of concrete is relatively slow, and artificial accelerated carbonation is required to establish experimental conditions for macrocell corrosion of rebar induced by concrete carbonation, of which the experimental principle is shown in Figure 10. After specifying the location parameters, the rebars are set in the concrete, exposing the preset carbonization development surface, and sealing the remaining surfaces with epoxy resin to ensure the carbonization proceeds in a set direction. The testing sample is subjected to carbonization tests in an accelerated carbonization sealed chamber with a 50% CO_2 content and 50% humidity, and the carbonization depth is monitored to meet the experimental carbonization depth requirements. The carbonization of the sample is accelerated to a predetermined degree and corresponding electrochemical tests are then conducted. Nasser A et al. conducted a study on macrocell corrosion of rebar induced by concrete carbonization using the above accelerated carbonization method [40].

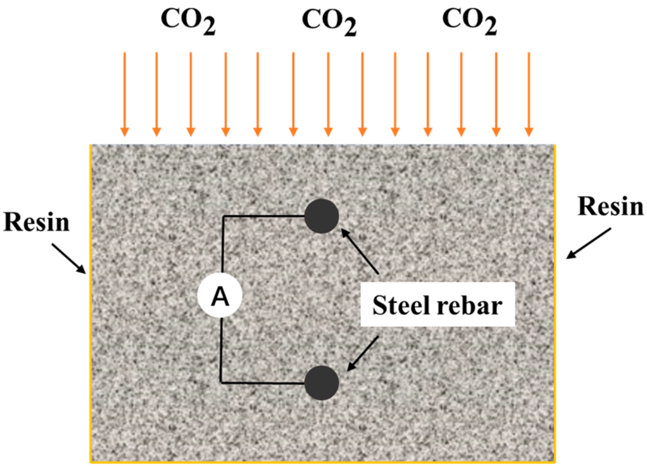

Figure 10. Schematic sample of the macrocell corrosion of rebar induced by accelerated concrete carbonization.

5.2. Electrochemical Corrosion Test Technologies

Corrosion current density is an important parameter and evaluation index for macrocell corrosion systems. Generally, macro-current testing is measured using an ammeter, and the values of the macro-corrosion current are often in the hundreds of microamps [30,61,62]. Such higher-accuracy measurement tools are required to test the macro-corrosion current. A zero-resistance ammeter (ZRA) can solve the internal resistance problem and achieve accurate current measurement. It is widely used in the corrosion current measurement of macrocell corrosion. The simple circuit diagram of ZRA is shown in Figure 11. By adjusting the resistance and voltage, the potential difference between the anode and cathode is zero, representing a short circuit between the two electrodes. At this time, the measured current is the zero-resistance current. C.M. Abreu et al. used the ZRA module in the ACM electrochemical workstation to test the electrical current of carbon-steel and stainless-steel pairs [63].

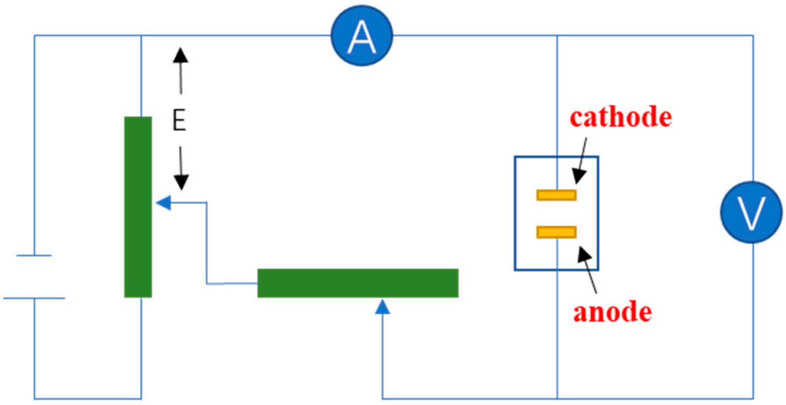

Figure 11. Circuit structure of the zero-resistance ammeter (ZRA).

Conventional electrochemical testing techniques are widely used in the laboratory to study the macrocell corrosion of rebar, including open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), polarization resistance (Rp), and potentiodynamic polarization (PDP). These technologies are generally used to study the critical characteristic parameters of macrocell corrosion. Micro-area electrochemical testing technology is mainly used to reveal the electrochemical mechanism of macrocell corrosion, which mainly includes array electrode technology (WBE), scanning electrochemical microscopy (SECM), scanning Kelvin probe technology (SKP), and scanning vibration reference electrode technology (SVET). WBE testing technology makes multiple small electrode rods from the tested material, forms an electrode sample of an electrode cluster in an array manner, and presents the electrode reaction state on the metal surface in the form of calculus. This technology can clarify the distribution of the corrosion cathode and anode regions [64,65]. SECM technology reflects the micromorphology and electrochemical state of the test electrode surface by establishing a functional relationship between the current between the ultra-microelectrode and the counter electrode. SKP technology tests the work function of a metal or semiconductor surface to determine the surface microzone corrosion state of a material. SVET scans each micro-region through a probe to form potential differences in different micro-regions, thereby obtaining micro-current distribution on the material surface.

The electrochemical testing techniques used for engineering detection of macrocell corrosion of reinforced concrete include the resistance probe method (ER), concrete resistance/Winner configuration method, and half-cell potential method (HCP). The ER method is mainly used for testing by installing a resistance probe element in reinforced concrete that is the same material as the rebar. When the probe is corroded, the diameter of the resistance wire will decrease, and the resistance will increase. The diameter loss of the resistance wire can be calculated through the change in resistance. The corrosion rate of the resistance probe represents the corrosion rate of the rebar in the reinforced concrete, and the corrosion situation of the rebar in different areas can be obtained. The concrete resistance detection method uses the inverse relationship between the current between the cathode and anode of the reinforcement and the resistance of the concrete for testing. When the concrete resistance is high, the smaller the micro-current value, the lower the corrosion rate of the rebar. Generally, the four-probe method is used to test the resistivity of concrete. The resistivity of the concrete to be tested is calculated by applying current and measuring voltage, and the rebar’s corrosion degree is qualitatively estimated. The HCP method consists of a reinforced-concrete half-cell and a copper-copper sulfate half-cell. It can be used to measure the natural potential of the rebar in the concrete at the project site and preliminarily determine the corrosion status of the rebar. The more positive the measured natural potential, the better the condition of the rebar. Conversely, the more negative the potential, the more serious the corrosion of the rebar.

6. Controlling Method of the Macrocell Corrosion of Reinforced Concrete

Macrocell corrosion has a relatively large area of both the anode and cathode. In RCSs in which macrocell corrosion occurs, the anodic corrosion of rebars often occurs in several pieces or a large region, and the corrosion rate of macrocells is also relatively fast, posing a significant threat to the safety of the RCS. The macrocell corrosion of reinforced concrete requires comprehensive and systematic control and protection. According to the characteristics of the macrocell corrosion system of reinforced concrete, it can be effectively controlled based on aspects such as the material properties of the rebar itself, the improvement in the collocation and binding method of the rebar, as well as the optimization of the service environment and the performance of the concrete protective layer.

6.1. Corrosion Protection and Improving Corrosion Resistance of Rebar

According to the RCS’s environmental corrosiveness and designed durability, selecting the reasonable corrosion-resistance grades of steel rebars and optimizing the design of dissimilar rebar combinations are essential prerequisites for preventing macro-battery corrosion of steel bars. Steel bars with different corrosion-resistance grades can easily induce macro-cell corrosion risks. Steel rebars with the same or similar corrosion-resistance grades should be selected first when designing RCSs. Secondly, by considering the risk of environmental erosion and the economy of engineering costs, rebar should be selected that matches the environmental aggressiveness to ensure that dissimilar rebars have enough corrosion resistance in the environmental aggressiveness gradient, thereby effectively reducing the risk of macrocell corrosion between dissimilar reinforcement. Finally, when using rebar in combination, it is essential to note that the area difference between different types of rebars should not be too large to avoid forming a large cathode and small anode structure.

Surface treatment is a crucial method to inhibit macrocell corrosion of rebar. Corrosion originates from the surface of materials; rebars' corrosion behavior and corrosion resistance are greatly affected by their surface conditions. Therefore, surface anti-corrosion modification of rebar is an effective method to improve the corrosion resistance of rebar and inhibit the macrocell corrosion of RCS. On the one hand, the electrode potential of rebar in concrete can be changed by preparing a metallic coating on the rebar surface, such as Zn-coated rebar. On the other hand, insulating coating, such as epoxy coating, can be used to isolate the rebar from the external environment, ensuring the stable electrode potential of the rebar and achieving efficient protection of the rebar. However, the insulating coating significantly negatively impacts the bonding strength of rebar–concrete surfaces, resulting in potential risks to the stability of RCS. In addition, the insulating coating is prone to be partially damaged during transportation and use, resulting in macrocell corrosion induced by the large cathode and small anode, resulting in severe corrosion damage to the exposed rebar matrix at the damaged coating. In engineering applications, ensuring the integrity of epoxy coatings is particularly important for inhibiting macrocell corrosion of the epoxy-coated rebar.

The insulating connection of rebar is a vital way to inhibit macrocell corrosion of rebar. Iron wire binding is a traditional method of connecting rebars. The resistance of the electrode circuit between the rebar and the binding iron wire is small, making it extremely convenient for the transmission of electrons between the rebars, and large-cathode and small-anode macrocell corrosion can easily occur between the rebar and the binding iron wire. In order to reduce the electronic transmission capacity between rebars, it is suggested that insulating components such as insulating ties and clips are used.

Cathodic protection of rebar is an important way to suppress macrocell corrosion of reinforced concrete. According to the principle of electrochemical protection, cathodic protection can be divided into cathodic protection with applied current and cathodic protection with the sacrificial anode, and the latter requires no special equipment and is more economical. It is possible to preset a metal (typically magnesium alloy, zinc alloy, aluminum alloy, etc.) with a lower electrode potential than the rebar as the anode before pouring the RCS. When macrocell corrosion occurs in the rebar, the anodic rebar can form a second macro-corrosion cell with the low-potential metal coupled to it. At this point, the low-potential metal becomes the second anode, and the rebar connected to it receives cathodic protection, thereby achieving the effect of inhibiting macrocell corrosion of rebar in concrete.

6.2. Improving the Performance of the Concrete Protective Layer

The transmission of environmental corrosion media through pore structures and cracks of concrete can be achieved by improving the compactness and impermeability of protective layer concrete, which are essential to prevent rebar corrosion from inducing macrocell corrosion. By optimizing the design of concrete components and using high-grade concrete materials, such as ultra-high-performance concrete (UHPC), the blocking effect on the transmission of corrosive media is strengthened, and the corrosion damage of rebar is reduced. UHPC has good self-compaction, high compressive strength, low shrinkage, low creep, and long durability, which can reduce the inward diffusion of water, oxygen, and corrosive ions, and reduce the probability of rebar corrosion. In addition, UHPC can maintain the integrity of the concrete protective layer during long-term service, reduce the risk of concrete cracking, and provide a long-term stable service environment for rebar.

Concrete admixtures have an important impact on the corrosion resistance of RCSs, and corrosion inhibitors of rebar are essential members of concrete admixtures. The macrocell corrosion process of rebar forms a current circuit between the anodic and cathodic rebar. By adding corrosion inhibitors, the resistance in the circuit is enhanced, thereby reducing the corrosion rate of macrocell corrosion. For RCSs serving in harsh corrosive environments, localized corrosion inhibitors can effectively improve the passivation and corrosion resistance of the rebar, maintaining a similar electrode potential to that of the rebar services in other areas, thereby reducing the driving force of macrocell corrosion.

Surface coating on concrete is a crucial method for corrosion protection of RCSs. The corrosion medium gradually migrates from the concrete surface through the concrete pore structure to the rebar–concrete interface, and induces rebar corrosion. In harsh environmental areas, an anti-corrosion coating on the concrete surface can isolate the invasion of corrosive media, such as oxygen, chloride ions, sulfur ions, and moisture. The impact of a corrosive environment and deterioration of rebar can be cut off by the surface coating of concrete; thereby, the high durability and long life of RCS can be ensured. Materials for anti-corrosion coating of concrete include epoxy resin, polyurethane, asphalt, and polyurea.

7. Conclusions and Prospects

This paper systematically reviews the causes and mechanisms of macrocell corrosion of reinforced concrete, such as dissimilar rebar coupling, concentration difference of corrosive media, and temperature difference. The current research status of macrocell corrosion of different types of rebars was surveyed, including carbon-steel rebar, alloyed-steel rebar, and coated rebar. Given the inducement of macrocell corrosion, the experimental models and electrochemical testing techniques for macrocell corrosion of rebars were summarized. Further, based on the corrosion characteristics, methods for controlling the macrocell corrosion of reinforced concrete were proposed, such as optimization of rebar selection and collocation, anti-corrosion treatment of rebar surface, insulation and connection of rebar, and improvement of concrete performance. Specific protective measures are: (1) In terms of reinforcement materials: the same corrosion-resistance grade or similar corrosion-resistance grade of reinforcement is selected as a construction material; (2) To optimize the use of steel reinforcement types: reinforcement with strong corrosion resistance is used for harsh service environments, reinforcement with poor corrosion resistance is used for relatively friendly service environments; (3) Insulation binding between reinforcing bars; (4) Using high-performance coated steel bar; (5) The use of high-performance concrete: concrete with high resistivity is conducive to reducing the macroscopic current value, reducing the corrosion rate of macro-cells, and blocking the invasion of corrosive media. This paper provides valuable references for promoting the research and prevention of macrocell corrosion of RCSs.

With the continuous emergence of RCSs serving in harsh environments, the prevention and control of macrocell corrosion in reinforced concrete will face increased challenges. In the future, there will be an urgent need to build a full-lifecycle-oriented corrosion-protection system against macrocell corrosion of reinforced concrete through the entire process of design, material selection, construction, management, and maintenance, which is significant for further improving the durability and service life of RCSs. Firstly, high-performance rebars with excellent corrosion resistance and economic applicability need to be developed and used. Based on the careful consideration of environmental corrosivity, corrosion-resistance grade of rebars, and engineering cost, it is suggested that the design and construction schemes for using rebars with different grades of corrosion resistance are optimized, thus minimizing the risk of macrocell corrosion of reinforced concrete. Secondly, accurate and efficient monitoring and detection techniques of macrocell corrosion of reinforced concrete are urgently needed. Via the monitoring and detecting, corrosion damage assessment and residual life prediction methods for RCSs can be optimized, and the safety status of structures in service can be comprehensively understood. Thirdly, it is suggested that efficient integrated technologies for corrosion damage repair, corrosion protection, and durability re-improvement are implemented according to the corrosion-damage degree of the structure; thus, long-term life extension of the RCS can be achieved.

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References

1. Natkunarajah, K.; Masilamani, K.; Maheswaran, S.; Lothenbach, B.; Amarasinghe, D.A.S.; Attygalle, D. Analysis of the trend of pH changes of concrete pore solution during the hydration by various analytical methods. *Cem. Concr. Res.* **2022**, *156*, 106780. [CrossRef]
2. Grengg, C.; Müller, B.; Staudinger, C.; Mittermayr, F.; Breininger, J.; Ungerböck, B.; Borisov, S.M.; Mayr, T.; Dietzel, M. High-resolution optical pH imaging of concrete exposed to chemically corrosive environments. *Cem. Concr. Res.* **2019**, *116*, 231–237. [CrossRef]
3. Feng, Y.; Yang, J.; Zhang, P. Effects of carbonation curing regimes on alkalinity of self-compacting concretes for marine artificial reef. *Constr. Build. Mater.* **2023**, *369*, 130614. [CrossRef]
4. Yao, N.; Zhou, X.; Liu, Y.; Shi, J. Synergistic effect of red mud and fly ash on passivation and corrosion resistance of 304 stainless steel in alkaline concrete pore solutions. *Cem. Concr. Comp.* **2022**, *132*, 104637. [CrossRef]
5. Zheng, H.; Dai, J.; Hou, L.; Meng, G.; Poon, C.S.; Li, W. Enhanced passivation of galvanized steel bars in nano-silica modified cement mortars. *Cem. Concr. Comp.* **2020**, *111*, 103626. [CrossRef]
6. Dong, Z.; Amir, P. Corrosion behavior of coupled active and passive reinforcing steels in simulated concrete pore solution. *Constr. Build. Mate.* **2020**, *240*, 117955. [CrossRef]
7. Torbati-Sarraf, H.; Poursaee, A. Study of the passivation of carbon steel in simulated concrete pore solution using scanning electrochemical microscope (SECM). *Materialia* **2018**, *2*, 19–22. [CrossRef]
8. Michele, W.T.M.; Pieter, D.; Janet, M.L. Corrosion-induced cracking and bond strength in reinforced concrete. *Constr. Build. Mater.* **2019**, *208*, 228–241.
9. Vedalakshmi, R.; Kumar, K.; Raju, V.; Rengaswamy, N.S. Effect of prior damage on the performance of cement based coatings on rebar: Macrocell corrosion studies. *Cem. Concr. Comp.* **2000**, *22*, 417–421. [CrossRef]
10. Gu, X.; Dong, Z.; Jin, Z. Macrocell corrosion between crossed steel rebars embedded in concrete under chloride environments. *MATEC Web Conf.* **2018**, *199*, 4005. [CrossRef]
11. Bertolini, L.; Pedeferri, P.; Pastore, T.; Bazzoni, B.; Lazzari, L. Macrocell Effects on Potential Measurements in Concrete Cathodic Protection Systems. *Corrosion* **1996**, *52*, 552–557. [CrossRef]
12. Shehata, M.H.; Thomas, M.D.A.; Bleszynski, R.F. The effects of fly ash composition on the chemistry of pore solution in hydrated cement pastes. *Cem. Concr. Res.* **1999**, *29*, 1915–1920. [CrossRef]
13. Wang, P.; Wu, H.; Ke, L.; Leung, C.K.Y. Mechanical and long-term durability prediction of GFRP rebars with the adoption of low-pH CSA concrete. *Constr. Build. Mater.* **2022**, *346*, 128444. [CrossRef]
14. Ghods, P.; Isgor, B.O.; Brown, J.R.; Bensebaa, F.; Kingston, D. XPS depth profiling study on the passive oxide film of carbon steel in saturated calcium hydroxide solution and the effect of chloride on the film properties. *Appl. Surf. Sci.* **2011**, *257*, 4669–4677. [CrossRef]
15. Ai, Z.; Jiang, J.; Sun, W.; Jiang, X.; Yu, B.; Wang, K.; Zhang, Z.; Song, D.; Ma, H.; Zhang, J. Enhanced passivation of alloy corrosion-resistant steel Cr10Mo1 under carbonation—Passive film formation, the kinetics and mechanism analysis. *Cem. Concr. Comp.* **2018**, *92*, 178–187. [CrossRef]
16. Olsson, C.; Landolt, D. Passive films on stainless steels-chemistry, structure and growth. *Electrochim. Acta* **2003**, *48*, 1093–1104. [CrossRef]

17. Zou, G.; Wang, Q.; Wang, G.; Liu, W.; Zhang, S.; Ai, Z.; Chen, H.; Ma, H.; Song, D. Revealing excellent passivation performance of a novel Cr-alloyed steel rebar in carbonized concrete environment. *J. Mater. Res. Technol.* **2023**, *23*, 1848–1861. [CrossRef]
18. Feng, X.; Zuo, Y.; Tang, Y.; Zhao, X.; Zhao, J. The influence of strain on the passive behavior of carbon steel in cement extract. *Corros. Sci.* **2012**, *65*, 542–548. [CrossRef]
19. Shi, J.; Ming, J.; Wu, M. Passivation and corrosion behavior of 2304 duplex stainless steel in alkali-activated slag materials. *Cem. Concr. Comp.* **2020**, *108*, 103532. [CrossRef]
20. Marques, P.F.; Costa, A. Service life of RC structures: Carbonation induced corrosion. Prescriptive vs. performance-based methodologies. *Constr. Build. Mater.* **2010**, *24*, 258–265. [CrossRef]
21. Houst, Y.F.; Wittmann, F.H. Influence of porosity and water content on the diffusivity of CO_2 and O_2 through hydrated cement paste. *Cem. Concr. Res.* **1994**, *24*, 1165–1176. [CrossRef]
22. Lu, C.; Wang, W.; Li, Q.; Hao, M.; Xu, Y. Effects of micro-environmental climate on the carbonation depth and the pH value in fly ash concrete. *J. Clean. Prod.* **2018**, *181*, 309–317. [CrossRef]
23. Joshi, S.; Ahn, Y.H.; Goyal, S.; Reddy, M.S. Performance of bacterial mediated mineralization in concrete under carbonation and chloride induced corrosion. *J. Build. Eng.* **2023**, *69*, 106234. [CrossRef]
24. Cascudo, O.; Pires, P.; Carasek, H.; Castro, A.; Lopes, A. Evaluation of the pore solution of concretes with mineral additions subjected to 14 years of natural carbonation. *Cem. Concr. Comp.* **2021**, *115*, 103858. [CrossRef]
25. Qiao, Y.; Wang, X.; Yang, L.; Wang, X.; Chen, J.; Wang, Z.; Zhou, H.; Zou, J.; Wang, F. Effect of aging treatment on microstructure and corrosion behavior of a Fe–18Cr–15Mn–0.66N stainless steel. *J. Mater. Sci. Technol.* **2022**, *107*, 197–206. [CrossRef]
26. Jones, D. Principles and Prevention of Corrosion 2nd Edition. *Mater. Design.* **1996**, *14*, 168.
27. Ampadu, K.O.; Torii, K. Chloride ingress and steel corrosion in cement mortars incorporating low-quality fly ashes. *Cem. Concr. Res.* **2002**, *32*, 893–901. [CrossRef]
28. Uthaman, S.; George, R.P.; Vishwakarma, V.; Harilal, M.; Philip, J. Enhanced seawater corrosion resistance of reinforcement in nanophase modified fly ash concrete. *Constr. Build. Mater.* **2019**, *221*, 232–243. [CrossRef]
29. Tsouli, S.; Lekatou, A.G.; Kleftakis, S.; Matikas, T.E.; Dalla, P.T. Corrosion behavior of 304L stainless steel concrete reinforcement in acid rain using fly ash as corrosion inhibitor. *Procedia Struct. Integr.* **2018**, *10*, 41–48. [CrossRef]
30. Ji, Y.; Zhao, W.; Zhou, M.; Ma, H.; Zeng, P. Corrosion current distribution of macrocell and microcell of steel bar in concrete exposed to chloride environments. *Constr. Build. Mater.* **2013**, *47*, 104–110. [CrossRef]
31. Subramaniam, K.V.; Bi, M.D. Investigation of steel corrosion in cracked concrete: Evaluation of macrocell and microcell rates using Tafel polarization response. *Corros. Sci.* **2010**, *52*, 2725–2735. [CrossRef]
32. Qian, S.; Zhang, J.; Qu, D. Theoretical and experimental study of microcell and macrocell corrosion in patch repairs of concrete structures. *Cem. Concr. Comp.* **2006**, *28*, 685–695. [CrossRef]
33. Cao, Z.; Makoto, H.; Hiroki, G. Effect of Water-Cement Ratio on the Macrocell Polarization Behavior of Reinforcing Steel. *J. Eng.* **2014**, *2014*, 925410. [CrossRef]
34. Warkus, J.; Raupach, M. Modelling of reinforcement corrosiongeometrical effects on macrocell corrosion. *Mater. Corros.* **2010**, *61*, 494–504. [CrossRef]
35. Jiang, J.; Chu, H.; Liu, Y.; Wang, D.; Guo, D.; Sun, W. Galvanic corrosion of duplex corrosion-resistant steel rebars under carbonated concrete conditions. *RSC Adv.* **2018**, *8*, 16626–16635. [CrossRef] [PubMed]
36. Li, Y.; Wang, Z.; Guo, X.; Zhang, G. Galvanic corrosion between N80 carbon steel and 13Cr stainless steel under supercritical CO_2 conditions. *Corros. Sci.* **2019**, *147*, 260–272. [CrossRef]
37. Arya, A.; Vassie, P. Influence of cathode-to-anode area ratio and separation distance on galvanic corrosion currents of steel in concrete containing chlorides. *Cem. Concr. Res.* **1995**, *25*, 989–998. [CrossRef]
38. Zhang, W.; Yang, S.; Geng, W.; Hu, Q.; Zhou, L. Corrosion behavior of the low alloy weathering steels coupled with stainless steel in simulated open atmosphere. *Mater. Chem. Phys.* **2022**, *288*, 126409. [CrossRef]
39. Hornbostel, K.; Angst, U.M.; Elsener, B.; Larsen, C.K.; Geiker, M.R. Influence of mortar resistivity on the rate-limiting step of chloride-induced macro-cell corrosion of reinforcing steel. *Corros. Sci.* **2016**, *110*, 46–56. [CrossRef]
40. Shi, L.; Song, W.; Dong, K.; Wang, H.; Shan, D.; Han, E. The change of cathode/anode roles and corrosion forms in 2024/Q235/304 tri-metallic couple with the variation of oxygen concentrations and area ratios. *Corro. Sci.* **2021**, *184*, 109400. [CrossRef]
41. Christodoulou, C.; Goodier, C.; Austin, S.; Webb, J.; Glass, G.K. Diagnosing the cause of incipient anodes in repaired reinforced concrete structures. *Corro. Sci.* **2013**, *69*, 123–129. [CrossRef]
42. Ominda, N.; Yoshitaka, K. Macro-cell Corrosion in Reinforcement of Concrete under Non-homogeneous Chloride Environment. *J. Adv. Concr. Technol.* **2009**, *7*, 31–40.
43. Poursaee, A.; Laurent, A.; Hansson, C.M. Corrosion of steel bars in OPC mortar exposed to NaCl, $MgCl_2$ and $CaCl_2$: Macro- and micro-cell corrosion perspective. *Cem. Concr. Res.* **2010**, *40*, 426–430. [CrossRef]
44. Bosque, I.F.S.; Heede, P.N.; Belie, N.D.; Rojas, M.I.S.; Medina, C. Carbonation of concrete with construction and demolition waste based recycled aggregates and cement with recycled content. *Constr. Build. Mater.* **2020**, *234*, 117336. [CrossRef]
45. Nasser, A.; Clément, A.; Laurens, S.; Castel, A. Influence of steel–concrete interface condition on galvanic corrosion currents in carbonated concrete. *Corros. Sci.* **2010**, *52*, 2878–2890. [CrossRef]
46. Sohail, M.G.; Laurens, S.; Deby, F.; Balayssac, J.P. Significance of macrocell corrosion of reinforcing steel in partially carbonated concrete: Numerical and experimental investigation. *Mater. Struct.* **2015**, *48*, 217–233. [CrossRef]

47. Xie, J.; He, J.; Wu, Y. Investigation on oxygen concentration difference macrocell corrosion for steel A3. *J. Univ. Sci. Technol. Beijing* **1994**, *16*, 59–63.
48. Sylvia, K.; Ueli, A.; Marc, Z.; Christoph, G. Defects in epoxy-coated reinforcement and their impact on the service life of a concrete structure. *Struct. Concr.* **2015**, *16*, 398–405.
49. Hwang, J.P.; Jung, M.S.; Kim, M.; Ann, K.Y. Corrosion risk of steel fibre in concrete. *Constr. Build. Mater.* **2015**, *101*, 239–245. [CrossRef]
50. Song, D.; Wang, G.; Yang, F.; Chen, H.; Liang, N.; Ma, H.; Jiang, J.; Ma, X. Microstructure and deformation behavior of a novel steel rebar: Effect of the heterogeneous microstructure of soft ferrite and Hard bainite. *J. Mater. Res. Technol.* **2020**, *9*, 12281–12292. [CrossRef]
51. Hansson, C.M.; Poursaee, A.; Laurent, A. Macrocell and microcell corrosion of steel in ordinary Portland cement and high performance concretes. *Cem. Concr. Res.* **2006**, *36*, 2098–2102. [CrossRef]
52. Jin, Z.; Jiang, C.; Gu, X.; Dong, Z. Macro-cell corrosion between crossed steel bars in cracked concrete. *Constr. Build. Mater.* **2022**, *350*, 128867. [CrossRef]
53. Cheng, A.; Huang, R.; Wu, J.; Chen, C. Effect of rebar coating on corrosion resistance and bond strength of reinforced concrete. *Constr. Build. Mater.* **2005**, *19*, 404–412. [CrossRef]
54. Yadav, A.P.; Katayama, H.; Noda, K.; Masuda, H.; Nishikata, A.; Tsuru, T. Surface potential distribution over a zinc/steel galvanic couple corroding under thin layer of electrolyte. *Electrochim. Acta* **2007**, *52*, 3121–3129. [CrossRef]
55. Mohammed, M.S.H.S.; Raghavan, R.S.; Knight, G.M.S.; Murugesan, V. Macrocell Corrosion Studies of Coated Rebars. Arab. *J. Sci. Eng.* **2014**, *39*, 3535–3543.
56. Okonkwo, B.O.; Ming, H.; Wang, J.; Han, E.; Rahimi, E.; Davoodi, A.; Hosseinpour, S. A new method to determine the synergistic effects of area ratio and microstructure on the galvanic corrosion of LAS A508/309 L/308 L SS dissimilar metals weld. *J. Mater. Sci. Technol.* **2020**, *78*, 38–50. [CrossRef]
57. Li, L.; Qiao, Y.; Zhang, L.; Ma, A.; Daniel, E.; Ma, R.; Chen, J.; Zheng, Y. Effect of cavitation erosion induced surface damage on pitting and passive behaviors of 304L stainless steel. *Int. J. Miner. Metall. Mater.* **2023**, *26*, 1551–1558.
58. Wang, P.; Cai, J.; Cheng, X.; Ma, L.; Li, X. Inhibition of galvanic corrosion between crystallographic orientations in low alloy steel by grain ultra-refinement. *Mater. Today Commun.* **2022**, *31*, 103742. [CrossRef]
59. Okonkwo, B.O.; Ming, H.; Meng, F.; Wang, J.; Xu, X.; Han, E. Galvanic corrosion study between low alloy steel A508 and 309/308L stainless steel dissimilar metals: A case study of the effects of oxide film and exposure time. *J. Nucl. Mater.* **2021**, *548*, 152853. [CrossRef]
60. Zhu, G.; Li, Y.; Zhang, G. Interaction between crevice and galvanic corrosion of X65 carbon steel in the CO_2-saturated NaCl solution under the coupling of crevice and galvanic effects. *J. Electroanal. Chem.* **2022**, *918*, 116482. [CrossRef]
61. Shevtsov, D.S.; Zartsyn, I.D.; Komarova, E.S. Relation between resistivity of concrete and corrosion rate of reinforcing bars caused by galvanic cells in the presence of chlorid. *Cem. Concr. Comp.* **2021**, *119*, 104026. [CrossRef]
62. Caglar, E.; Geoffrey, S. The effect of macro-galvanic cells on corrosion and impressed current cathodic protection for offshore monopile steel structures. *Ocean Eng.* **2022**, *265*, 112575.
63. Abreu, C.M.; Cristóbal, M.J.; Montemor, M.F.; Nóvoa, X.R.; Pena, G.; Pérez, M.C. Galvanic coupling between carbon steel and austenitic stainless steel in alkaline media. *Electrochim. Acta* **2002**, *47*, 2271–2279. [CrossRef]
64. Jin, Z.; Feng, G.Y.; Jiang, Y. Corrosion Behavior of Reinforcement Concrete with Cracks in Marine Environment Using Wire Beam Electrode technique. *J. Chin. Ceram. Soc.* **2020**, *48*, 1791–1800.
65. Shi, L.; Song, Y.; Zhao, P.; Wang, H.; Dong, K.; Shan, D.; Han, E. Variations of galvanic currents and corrosion forms of 2024/Q235/304 tri-metallic couple with multivariable cathode/anode area ratios: Experiments and modeling. *Electrochim. Acta* **2020**, *359*, 136947. [CrossRef]