学校编码：10384　　分类号____ 密级____
学号：20520091151425　　UDC____

厦门大学

硕士学位论文

锌铝层状双金属氢氧化物及其衍生物对钢筋混凝土的多功能缓蚀作用研究

Study of Multifunctional Corrosion Inhibition of Zn-Al Layered Double Hydroxides and Its Derivatives for Steel in Concrete

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论文提交日期：　2012 年 7 月
论文答辩时间：　2012 年 7 月
学位授予日期：　2012 年　　月

答辩委员会主席：
评　　阅　　人：
2012 年 7 月

Study of Multifunctional Corrosion Inhibition of Zn-Al Layered Double Hydroxides and Its Derivatives for Steel in Concrete

A Dissertation Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of

Master of Science

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July, 2012

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摘 要

钢筋腐蚀是引起钢筋混凝土结构过早失效的主要原因，是当今腐蚀与防护领域研究的热点和难点问题之一。开展钢筋混凝土的腐蚀防护研究具有重要的理论和实际意义。混凝土的碳化和氯离子的侵蚀是导致混凝土中钢筋腐蚀的主要因素。添加钢筋缓蚀剂是一种经济而有效的腐蚀防护措施。针对混凝土中钢筋腐蚀的特点，本论文工作发展了一种层状双金属化合物（及衍生物），多功能钢筋缓蚀剂，利用各种方法对缓蚀剂性能和功能进行评价，并初步研究了缓蚀剂对钢筋的缓蚀机理。主要取得以下研究结果：

1. 在碳酸盐溶液环境下制备了Zn-Al CLDHs，发现NaCl溶液经Zn-Al CLDHs浸泡处理3 h后，钢筋的腐蚀电流密度明显降低。利用Cl^-探针和pH探针测量Zn-Al CLDHs处理前后溶液中Cl^-浓度和pH值，发现Zn-Al CLDHs能够 降低溶液中的Cl^-浓度和提高溶液碱度，改善钢筋的腐蚀环境。这可能因为是Zn-Al CLDHs在结构重组过程中能够载入大量Cl^-，并且释放出OH^-。

2. 发展了在空气气氛和碱性溶液反应环境下合成锌铝氢氧化物焙烧产物的新方法。并应用XRD、SEM和FTIR进行了表征，发现经过350℃焙烧后并在酒石酸盐溶液中处理得到的Zn-Al CLDHs-tar具有一定的层状结构，其颗粒尺度为数百纳米，能够成功将酒石酸根离子载入层间。

3. 利用腐蚀电化学技术考察了Zn-Al CLDHs-tar对NaCl溶液和混凝土中的钢筋的缓蚀作用。发现Zn-Al CLDHs-tar能够释放出缓蚀剂离子酒石酸根，在溶液中浸泡处理7 h后基本达到酒石酸根在Zn-Al CLDHs-tar层间释放和吸附平衡，浸泡处理30 h后，对钢筋的缓蚀效率达到最大（97%）。在混凝土体系中，Zn-Al CLDHs-tar对钢筋具有良好的缓蚀作用，可归因于：(1)微纳米尺寸的Zn-Al CLDHs-tar颗粒填充混凝土微孔隙，阻挡有害物质的入侵；(2)吸收Cl^-、CO_3^{2-}离子，改善腐蚀环境；3）同时能够释放缓蚀剂离子，有效保护钢筋表面钝化膜，使之免遭腐蚀。

关键词：钢筋混凝土；腐蚀；锌铝层状氢氧化物；多功能；缓蚀剂

Abstract

The corrosion of steel is one of the main reasons causing the premature failure of reinforced concrete construction, and it has become a research focus in the field of corrosion and protection in the world. It is significant and urgent to further study the corrosion and protection of steel in concrete from theoretical and practical aspects. The carbonation of concrete and ingress of Cl^- are known to be the two major factors resulting in corrosion of steel in concrete. Corrosion inhibitor, as one of the most convenient and efficient techniques for corrosion protection has been extensively applied in reinforced concrete. Compared with the general corrosion process of steel in an opened system, the corrosion process of reinforcing steel in concrete usually behaves very complicatedly, which often depends on some crucial factors, such as the non-uniform corrosion under the included condition, chemical environment, especially pH and Cl^- concentration at the interface of steel/concrete, and permeability of concrete resulting in the ingress of the harmful species. It is desired and challenged to develop a multifunctional inhibitor to control the corrosion of steel in concrete, which is not only able to efficiently inhibit corrosion at the included condition, but also can absorb and eliminate harmful anions (like Cl^-, CO_3^{2-}) in concrete. Furthermore, the increase of the compactness of concrete for blocking the transportation of corrosive species in concrete is also desirable. Accordingly, the Zn-Al layered double hydroxides (Zn-Al LDHs) and its derivatives were developed as multifunctional corrosion inhibitors for steel in concrete in this thesis work. The main research results and progress are listed as follows:

1. Zn-Al CLDHs was successfully synthesized in the carbonate solutions under a routine air atmosphere. After adding 5 g/L Zn-Al CLDHs in 0.1 mol/L NaCl solution for 3 h, the corrosion current density of steel decreased obviously in the solution. It was found that the Cl^- concentration decreased and the pH value increased in the test solution which might be due to the loading of Cl^- ions and release of OH^- ions onto

and from the Zn-Al CLDHs respectively during the reconstruction process.

2. A new synthesis method of Zn-Al LDHs in the alkaline solution under a routine air atmosphere was developed. The products were characterized by XRD, SEM and FTIR. The final product of Zn-Al CLDHs-tar was of layered structure with hundreds nanometer. It was demonstrated that the tartrate anions could be loaded into the layered structure of Zn-Al CLDHs-tar after a simple tartrate solution treatment.

3. The inhibition of Zn-Al CLDHs-tar for steel was studied in NaCl solution and concrete respectively by electrochemical techniques. It was shown that the synthesized Zn-Al CLDHs-tar was of effective inhibition to steels in 0.1 mol/L NaCl solution, and the inhibition efficiency was up to 90% after 7 h immersion when the absorption and release of tartrate anion might reach a balance. The addition of 5 g/L Zn-Al CLDHs-tar into concrete was able to notably retard the corrosion development of rebar. A concept model was proposed to further understand the corrosion protection mechanism of Zn-Al CLDHs-tar for steel rebar in concrete. Firstly, the tartrate anion is released from the synthesized Zn-Al CLDHs-tar and formed a protective film on the steel surface. Secondly, the Cl^-, CO_3^{2-} or other anions are adsorbed into the layer structure of Zn-Al CLDHs-tar and the corrosion environment is improved. Finally, the concrete becomes more compact and exhibits higher resistance to the mass transport for corrosive species because the micro size of Zn-Al CLDHs-tar can fill up the structural gaps in the concrete.

Keywords: Steel Reinforced Concrete; Corrosion; Zn-Al Layered Double Hydroxides; Multifunctional; Inhibitor