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博 士 学 位 论 文

Mg 基阳极材料热力学数据库的建立及其合金设计

Development of thermodynamic database of Mg base electrode materials and its applications in alloy Design

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摘要

镁合金具有密度小，理论比容量大，标准电极电位负、电压范围广等优点，因此作为阳极材料被广泛应用于化学电源中。目前，镁基阳极材料还存在极化严重、阳极利用率低、激活时间长等不足。传统镁基阳极材料的开发以“尝试法”为主，研发周期长，浪费了大量人力和物力，严重阻碍了镁基阳极材料的发展。2011 年，随着“材料基因组”计划的的提出，研究者希望通过材料的设计来开发新型镁基材料。相图作为“材料基因组”中的重要组成部分，受到越来越多研究者的关注。目前为止，已报道的镁基阳极材料相平衡信息相对匮乏，有必要对其相平衡信息进行完善，并利用 CALPHAD(Calculation of Phase Diagrams)方法，建立 Mg 阳极材料多元系的热力学数据库，对开发新型镁基阳极材料具有重要的理论意义和实际应用价值。

本研究主要通过合金法对部分重要 Mg-(Pb，Zn，Al，Sn)基三元系的相平衡进行了实验测定，并利用 CALPHAD 方法对上述三元系的相图进行了热力学优化与计算，建立了 Mg 基阳极材料多元系的热力学数据库。利用所建立的热力学数据库设计合理的合金成分，并对 Mg 基合金的组织控制与电化学性能等开展了研究工作。本研究的主要内容如下：

(1) 本研究通过合金法对 Mg-Pb-X(X：Zn、Al、Sn)、Al-Pb-X(X：Zn、Sn)和 Al-Sn-Zn 各三元系在 200 ℃、300 ℃和 400 ℃时的等温截面相图进行了实验测定。在上述实验测定的各三元系等温截面相图中均未发现三元化合物的存在。

(2) 本研究系统地收集和整理现有的热力学性质及相图的实验数据，采用合理的热力学模型，对 Pb-X(X：Mg、Eu、Lu)、Mg-Pb-X(X：Zn、Al、Sn)、Al-Pb-X(X：Zn、Sn)和 Al-Sn-Zn 各体系的相平衡进行了热力学优化与计算，计算结果与实验结果取得了良好的一致性。结合本研究所取得热力学数据以及收集文献报道的热力学计算结果，充分考虑模型的兼容性和统一性，建立了 Mg-Pb-Zn-Al-Ga-Sn 多元系的热力学数据库。

(3) 本研究利用 Mg-Pb-Zn-Al-Ga-Sn 多元系的热力学数据库，计算了 Mg-5Pb-Zn、Mg-Pb-Zn-Al、Mg-Pb-Zn-Ga、Mg-Pb-Zn-Al-Sn、Mg-Pb-Zn-Al-Ga

和 Mg-Pb-Zn-Al-Ga-Sn 的纵截面相图和相分数随温度的变化曲线。结合纵截面相图和相分数的计算结果，设计并制备了一系列合金。

(4) 本研究通过不同的热处理工艺实现了对微观组织的控制。铸态合金中的合金元素富集在晶界处，随着热处理时间的延长合金元素逐渐固溶在镁基体中；当 Zn 含量较少时合金为均一的固溶体，当 Zn 含量为 7 wt.%时，合金中 MgZn 的析出量为 0.9 %；在 Mg-5Pb-7Zn 合金中添加微合金化元素 Al 和 Ga，随着微合金化元素含量的增加，合金中分别析出了 $Al_{12}Mg_{17}$ 相和 Mg_5Ga_2 相；合金在 300 ℃保温 72 h 时组织均匀。

(5) 本研究对一系列合金电极在 300 ℃保温 72 h 时的样品进行了线性极化、恒电流放电和交流阻抗测试。研究结果表明 Mg-5Pb-7Zn-2Al-2Ga 合金电极具有较好的电化学性能，该合金中析出了 MgZn 相，其相分数含量约为 2 %。该合金电极的腐蚀电流密度为 0.662 mA/cm^2，在恒电流为 10 mA/cm^2 和 100 mA/cm^2 时的平均放电电位分别为-1.84 V 和-1.71 V，在电流密度为 100 mA/cm^2 时放电 1 h 后电流效率达到了 84.5%。

关键词：Mg 基合金 CALPHAD 阳极材料 电化学行为

Abstract

Magnesium possesses many excellent properties such as low density, high theoretical specific capacity, negative standard electroreduction potential, wide voltage range etc., therefore Mg-based anode materials are most widely used in chemical power source. Currently, magnesium-based anode materials have many drawbacks such as serious polarization, low anode utilization, long activation time etc. The development of Mg-base anode materials were always based on try-and-error method in the past time, resulting in a long development cycle and a great waste of time and money. In 2011, with the proposal of “Materials Genome Initiative (MGI)”, researchers expect to purposefully design and develop new Mg-based anode materials. Phase diagram as an important part of "Materials Genome" receives more and more attention from researchers. So far, there is a lack of information on phase diagrams of Mg-based alloys, thus it is necessary to improve their balanced information and use the CALPHAD (Calculation of Phase Diagrams) method to develop the thermodynamic database of Mg-based anode materials system, since design and development of new Mg-base anode materials is of both academic interest and practical importance.

In the present work, phase equilibria of some important Mg-(Pb, Zn, Al, Sn) base alloy ternary systems were experimentally investigated by using equilibrated alloys, then the thermodynamic assessments of above-mentioned ternary systems were carried out and a thermodynamic database of phase diagrams of Mg-based alloys were developed with the CALPHAD (Calculation of Phase Diagrams) method. Lastly, based on the developed thermodynamic database of Mg-based alloys, a compositional design of Mg-based alloys were performed. The microstructural control and electrochemical property of Mg-base alloys were investigated. The details of the obtained results are described as follows:

(1) The isothermal sections of the Mg-Pb-Zn, Mg-Pb-Al, Mg-Pb-Sn, Al-Pb-Zn,

Al-Pb-Sn and Al-Sn-Zn ternary systems at 200 ℃, 300 ℃ and 400 ℃ were experimentally determined by the equilibrated alloys. There exist no ternary compounds in the isothermal sections of the present work.

(2) In this study, based on the collected and collated thermodynamic properties and phase diagram of the experimental data, the Pb-X(X: Mg, Eu, Lu), Mg-Pb-X(X: Zn, Al, Sn), Al-Pb-X(X: Zn, Sn) and Al-Sn-Zn were thermodynamically calculated by using reasonable thermodynamic model. Good agreements were obtained between the calculated results and experimental data. Based on the experimental data of present work and literature data, the thermodynamic database of Mg-Pb-Zn-Al-Ga-Sn anode materials was established with a campatible and unified thermodynamic model.

(3) Based on the thermodynamic database of Mg-based anode materials, vertical sections phase diagram and phase fractions of each phase as a function of temperature of Mg-5Pb-Zn, Mg-Pb-Zn-Al, Mg-Pb-Zn-Ga, Mg-Pb-Zn-Al-Sn, Mg-Pb-Zn-Al-Ga and Mg-Pb-Zn-Al-Ga-Sn systems were calculated. Combined with the calculated vertical sectional phase diagram and phase fraction, a series of alloys were designed and prepared.

(4) In this study, different heat treatment processes were carried out to control the microstructure. The microstructure, phase composition and crystal structure of as-cast alloys and heat-treatment alloys were examined. The alloying elements partitioned to the grain boundaries in as-cast alloy; with the extension of heat treatment time, alloying elements gradually dissolved in the magnesium matrix; The alloys presented as a homogeneous solid solution when the Zn content was small, and the content of MgZn phase was 0.9 % when the Zn content was 7 wt% in the alloys; the $Al_{12}Mg_{17}$ and Mg_5Ga_2 phases were precipitated when micro-alloying elements Al, Ga in Mg-5Pb-7Zn alloy increased; The uniform microstructure was observed after annealed at 300 ℃for 72 h for the alloys.

(5) The linear polarization, constant current discharge and electrochemical impedance spectroscopy of alloy electrode annealed at 300 ℃ for 72 h were tested in the present research. The results indicated that the electrochemical properties of Mg-5Pb-7Zn-2Al-2Ga is better, with about 2% phase fraction content of MgZn phase

precipitated. The corrosion current density of the alloy electrode was 0.662 mA/cm^2; the discharge potential the alloy electrode were -1.84V and -1.71V when the alloy electrode was discharged at different current densities of 10 mA/cm^2 and 100 mA/cm^2, respectively; the current efficiencies of Mg-5Pb-7Zn-2Al-2Ga alloy with discharge current density of 100 mA / cm^2 for 1h was 84.5 %.

Keywords: Mg-based alloys; CALPHAD; anode materials; electrochemical behavior

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