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厦门大学

硕　士　学　位　论　文

镁合金化学镀 Ni-B 工艺及原理研究

Technical and Mechanistic Investigation for Electroless Nickel-Boron Plating on Magnesium Alloy

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摘 要

镁合金具有诸多优良性能，且自然储量丰富，在人们的生产和生活领域具有广阔的应用前景。但镁的电极电位较负，易于发生腐蚀，合金中的第二相或杂质相也会加速镁合金的腐蚀，加之镁合金较弱的力学性能，至今未能工业化应用。镁合金有多种强化手段，化学镀镍作为一种较为成熟的表面处理技术，可以显著提高镁合金的性能。但镁合金因其物理化学性质的特殊性，属于难于化学镀的金属。现阶段镁合金化学镀镍的研究大多致力于化学镀 Ni-P 技术，而作为性能上不亚于 Ni-P 镀层的 Ni-B 合金却少见报道。本论文在大量文献的基础上，经过不断尝试，寻求出一种适合镁合金的化学镀 Ni-B 工艺，并采用多种测试方法对工艺及原理方面进行研究，主要内容如下：

一、基于前人已报道的以及实验室课题组已取得的成果的基础上，对原有工艺进行改进，加入化学抛光和浸锌的前处理步骤，工艺稳定且重复性好。制备的 Ni-B 镀层呈致密均匀的非晶状态，结合力良好。相对于镁合金基体，镀层的硬度提高了十倍以上，达 570.5 HV，Tafel 曲线测试表明耐蚀性能也有较大程度的改善。

二、采用线性扫描伏安法研究了镀液成分及工艺条件对化学镀阴、阳极过程的影响。结果表明：乙酸镍和硼氢化钠含量的提高分别促进了 Ni^{2+} 的还原反应和 BH_4^-的氧化反应；乙二胺、氢氧化钠以及添加剂硫脲、糖精钠对阴、阳极反应均有不同程度的抑制作用；升高温度有利于阴、阳极反应的进行。值得注意的是，添加剂硫脲和糖精钠在工艺上对镀层的整平作用分别是通过对阳极过程和阴极过程的抑制来实现的，并且可能由于镀液中硫元素含量的提高，造成镍溶解反应的峰电流显著增大。硫脲和氢氧化钠的使用可以降低 BH_4^-的水解，但必须控制在适宜的范围内，过量则抑制正常的氧化还原反应。

三、从工艺角度研究了镀液中稳定剂硫脲及光亮剂糖精钠对化学镀层及镀液性能的影响。实验发现少量添加剂就可以明显改善镀层的形貌，镀层颗粒由松散分布变得致密均匀。随着添加剂含量的提高，镀层胞状颗粒尺寸减小，趋于平整；镀层的腐蚀失重大大减小，耐蚀性提高；镀液的稳定时间延长；以上三种情况硫脲的效果更加明显。但过量的添加剂导致沉积速率减慢甚至不再起镀。硫脲降低

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镀层中的硼含量，因此显微硬度有所下降；糖精钠可以减小镀层中的拉应力，甚至向压应力转变，对显微硬度的提高具有促进作用。综合工艺及电化学实验结果，将添加剂含量定于硫脲 0.5 $mg \cdot L^{-1}$，糖精钠 2.0 $g \cdot L^{-1}$。

四、采用电子扫描显微镜、能量散射光谱等多种技术对化学镀工艺过程中各个步骤处理得到的镁合金样品进行表征，初步推测浸锌过程的反应原理以及 Ni-B 镀层的沉积机理。通过除油、整平、酸蚀等步骤可以获得一适合于浸锌的“清洁”的镁合金基体表面，表面适量的粗糙度用于增加后续镀层的结合力。浸锌过程以置换反应为主，获得的锌层主要是以单质锌的形式存在，同时夹杂少量氟化物和磷酸盐等。镁合金表面浸锌层合适的 Zn 含量对施镀成功尤为关键，纯镁合金及纯锌对 Ni-B 化学镀反应均表现出较低的活性。浸锌层在后续的化学镀过程中真正起到中间层的作用，开路电位-时间曲线表明浸锌后的镁合金表面化学镀分为以溶解析氢为主的“诱导期”、以置换反应为主的“形核期”和以氧化还原反应为主的“化学镀反应期”三个过程。

五、对化学镀后的镁合金样品进行惰性气体气氛下的热处理，研究了不同热处理温度对镀层性能的影响。随热处理温度的提高，镀层由非晶态向晶态转变，300 ℃左右为转变温度，相继有面心立方 Ni、Ni_3B 及 Ni_2B 相出现。热处理会导致镀层与基体元素的相互扩散，镀层的显微硬度随温度逐渐提高，但过高的温度会对镀层的耐蚀性能造成不利影响。综合实验结果，将镁合金化学镀 Ni-B 的热处理温度选定在 300 ℃左右。

关键字：镁合金；化学镀镍硼；浸锌；添加剂；热处理

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Abstract

Magnesium alloys have great potential in various industrial fields due to their excellent capabilities and abundant supply. Nevertheless, a number of undesirable properties including poor corrosion resistance and mechanical properties have restricted magnesium alloys to be widespread applied hitherto. Magnesium alloys are susceptible to corrosion even in an atmospheric environment, because of their extremely low electrode potential, second phase and impurity phase co-existing in the materials. As one of the developed surface treatment technologies, electroless nickel plating can improve the defects of magnesium alloys significantly. Unfortunately, it is not easy to fabricate qualified coatings on magnesium alloys. Unlike Ni-P plating, electroless Ni-B plating on magnesium alloys has been rarely investigated recently. The main work of this paper was devoted to obtaining a kind of electroless Ni-B plating suitable for magnesium alloys, basing on massive references and continuous attempts, and several characterization techniques were employed to study this process and principles. The main researches involved in this work are summarized below.

Firstly, pretreatment steps of chemical polishing and zinc immersion were applied to the previous technical flow to improve the Ni-B plating, and the modified technique was stable with well repeatability. The Ni-B coating prepared was amorphous, uniform and compact with good adhesion to the substrate. Compared with magnesium alloys, the microhardness of Ni-B coating was enhanced more than ten times, up to 570.5 HV. Potentiodynamic polarization curves indicated the excellent corrosion resistance of the coating.

The effects of composition of plating solution and operating conditions on the processes of cathodic reduction and anodic oxidation were studied by linear sweep voltammetry. Experiment results indicated that the increases in concentrations of nickel acetate and sodium borohydride accelerated the reduction of Ni^{2+} and the oxidation of BH_4^-, respectively. Ethylenediamine, sodium hydroxide, thiourea and saccharin sodium had inhibitions on cathodic and anodic reactions in varying degrees.

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High temperature was benificial to both cathodic reduction and anodic oxidation. It is worth noting that the leveling effect on coatings from the additives of thiourea and saccharin sodium was performed through inhibitions on cathodic and anodic processes, respectively. The obviously increasing peak current density of nickel oxidation was possibly due to the increasing sulfur content in the plating solution. The usage of thiourea and sodium hydroxide was able to decrease hydrolysis of borohydride in appropriate concentration ranges, or else would hinder the redox reaction of electroless plating.

The influences of thiourea as the stabilizer and saccharin sodium as the brightener on performances of Ni-B coatings and plating solutions were studied in technical aspect. By adding small amounts of additives, coatings with enhanced surface appearance can be obtained due to finer, more uniform and compact nodular particles. With the increases of additives concentrations, the dimensions of nodular particles decreased to form more smooth coatings; the reduced mass losses of coatings in 3.5% NaCl solution indicated better corrosion resistance; the stabilities of solutions were enhanced due to the longer stable time in $PdCl_2$ experiment; thiourea had more obvious effects than saccharin sodium in above results. Additives in excess amounts would decrease the plating rate or even to stop the reaction entirely. Boron content and microhardness of Ni-B coatings dropped because of the increasing concentrations of thiourea; saccharin sodium promoted the formation of coatings with high hardness due to the reduction of tensile stress and the transformation to compressive stress. 0.5 $mg \cdot L^{-1}$ thiourea and 2.0 $g \cdot L^{-1}$ saccharin sodium were determined considering the results of both technical and electrochemical experiments.

Magnesium alloy specimens after every treatment step were characterized, and the primary principles of zinc immersion and electroless plating were deduced. Clean surface of magnesium alloys suitable for zinc immersion was obtained through degreasing, polishing and pickling. Adequate roughness was helpful to form good binding force. The main reaction during zinc immersion process was replacement, and the zinc layer obtained was composed of simple substance of zinc, trace amounts of fluorides and phosphates. Pure magnesium alloys and pure zinc electrodes performed

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poor catalytic activity to Ni-B plating, and therefore the control of zinc content on the alloy surface was the key to successful Ni-B coating. A successful zinc layer was proved to be the interlayer between magnesium alloy and Ni-B coating. Open circuit potential-time curves indicated that there were three sections in electroless plating process on the zinc layer: “induction period” dominated by metal dissolution and hydrogen evolution; “nucleation period” dominated by replacement reaction; “electroless plating reaction period” dominated by redox reaction.

Finally, heat treatment experiment of Ni-B coatings on magnesium alloys was conducted in inert atmosphere, and the influences of temperature on coating properties were investigated. The microstructure transformed from amorphous to crystalline state with increasing temperature. About 300 ℃ was the transformation temperature, after which face centered cubic Ni、Ni_3B and Ni_2B phases appeared successively. Elements diffusion took place between coating and substrate during heat treatment. The microhardness of Ni-B coating gradually increased with temperature, but exorbitant temperature deteriorated corrosion resistance. Experiment results considered comprehensively, approximate 300 ℃ was selected as the temperature of heat treatment of electroless Ni-B coating on magnesium alloys.

Keywords: Magnesium alloy; Electroless nickel-boron plating; Zinc immersion; Additives; Heat treatment.

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