

储氢合金表面修饰方法的研究进展

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摘要: 金属储氢合金是迄今为止储氢密度高、安全性好、使用便捷的最佳储氢候选材料。为了改善储氢合金的活化性能、吸放氢性能、抗腐蚀性能、抗氧化性能以及抗杂质气体毒化性能等, 研究人员常对储氢合金进行表面修饰。表面修饰通常是通过调控合金表面的微观结构、化学组成以及物理状态来改善合金的理化性质。对近几十年储氢合金的表面修饰相关研究成果进行梳理、分析, 并加以归纳和分类。将储氢合金的表面修饰方法大体分为两大类: 物理表面修饰和化学表面修饰。其中, 物理表面修饰方法包括气相沉积技术、激光处理技术、机械合金化技术和剧烈塑性变形技术。化学表面修饰方法包括化学镀技术、电镀技术、阳极氧化技术以及其他化学修饰方法(酸处理、碱处理、盐处理、氟化处理等)。这些方法是通过在合金表面形成保护层, 引入纳米晶结构、增加活性位点等来提高合金的综合性能。对这些表面修饰方法进行了详细的综述, 并对照了不同修饰方法对部分储氢合金的性能影响, 同时对储氢合金的表面修饰方法在今后的发展进行了展望。

关键词: 储氢合金; 表面修饰; 储氢性能; 微观结构; 电化学性能

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Research Advances of Surface Modification Methods for Hydrogen Storage Alloys

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ABSTRACT: Hydrogen energy is a kind of secondary energy which is abundant, green and low carbon and widely used. The key to application of hydrogen energy is hydrogen storage. Metal hydrogen storage alloys are by far the best hydrogen storage candidate materials with high hydrogen storage density, high safety and ease of use. In order to improve the activation

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properties, hydrogen absorption and release properties, corrosion resistance, oxidation resistance and anti-impurity gas toxicity properties of hydrogen storage alloys, researchers often modify the surface of hydrogen storage alloys. Surface modification refers to the method of changing the surface structural characteristics of an alloy by physical, chemical or composite methods in order to improve one or several properties of the alloy, such as removing the oxidized layer of the alloy, increasing the active sites, and coating the film layer. There are many kinds of surface modification methods for hydrogen storage alloys, and the improvement degree of properties is different. In this paper, the research results of surface modification of hydrogen storage alloys in recent decades are reviewed, analyzed, summarized and classified. The surface modification methods of hydrogen storage alloys can be roughly divided into two categories: physical surface modification and chemical surface modification. Among them, the physical surface modification methods include vapor deposition technology, laser treatment technology, mechanical alloying technology and severe plastic deformation technology. Chemical surface modification methods include electroless composite plating technology, electroplating technology, anodizing technology and other chemical modification methods (acid treatment, alkali treatment, salt treatment, fluoride treatment, etc.). These surface modification methods are reviewed in detail, and the future development of surface modification methods for hydrogen storage alloys is also prospected.

The physical surface modification methods include vapor deposition technology, laser treatment technology, mechanical alloying technology and severe plastic deformation technology. Vapor deposition technology is to melt or sputter the coating material into a vapor phase, so that it can quickly condense on the surface of the hydrogen storage alloy. However, some coating materials are brittle, likely to crack or even spalling under complex stress, and have strict technical requirements. Laser treatment technology is the use of laser scanning on the alloy surface to make it remelt, promote the appearance, microstructure and other changes of the alloy, so as to improve the performance of the alloy. However, laser treatment technology is easily limited by equipment or materials. Mechanical alloying method is to make the alloy produce plastic deformation by high-energy ball milling to provide more active sites and improve the hydrogen absorption and discharge rate of the alloy. However, the treatment time of the mechanical alloying method is long, which is likely to introduce impurities to oxidize the alloy. Severe plastic deformation technology is to apply extreme pressure to the alloy, so that the alloy material grain refinement, grain boundary increase, thereby enhancing the hydrogen storage capacity of the material, but the technology has more stringent requirements for the preparation process, and is not conducive to the long-term stability of the material.

Chemical surface modification methods include electroless composite plating technology, electroplating technology, anodizing technology and other chemical modification methods (acid treatment, alkali treatment, salt treatment, fluorination treatment, etc.). Electroless composite plating uses the redox reaction of plated elements to form a film on the alloy surface, while electroplating with the alloy material to be plated as the cathode and the plating element as the anode, and deposits it on the surface of the alloy by setting an appropriate current density. Electroplating can correct the defects of poor uniformity and insufficient adhesion of chemical coating. However, the waste liquid produced by the plating process may contain harmful substances, which should be handled safely during the application process. Anodizing is suitable for light metals, also known as the micro-arc oxidation process, but essentially is an oxidation reaction between the metal substrate and the electrolyte of the plating solution, the oxidation film formed by the method is thick and uniform, but its scope of application is small. Acid, alkali and fluoride treatment is more common, generally the alloy is directly soaked in the method, the operation is relatively simple. However, the pH value of the solution is more strictly controlled during the operation, which will cause a certain degree of corrosion on the surface of the alloy.

KEY WORDS: hydrogen storage alloys; surface modification; hydrogen storage properties; microstructure; electrochemical performance

能源是人类社会赖以生存和发展的基石,而目前主要使用的化石能源不仅即将枯竭而且还会加剧对环境的污染^[1-2]。人类迫切需要寻求一种储量丰富、绿色低碳的新型替代能源。在众多新能源中,氢能因具有储量丰富、高效、清洁等优点被人们认为是未来极具发展潜力的新型能源^[3-6]。在氢能利用过程中,

氢能的储存和运输是关键^[7]。在储氢技术中,利用金属储氢合金储氢是近 50 年来被公认的一种高效储氢技术,非常适合于储能和转换系统,该合金可以用作镍氢电池的负极材料、氢燃料电池的催化剂等^[8-9]。根据储氢特性和晶体结构的不同,一般将金属储氢合金分为以下几类:具有 CaCu_5 型晶体结构的 AB_5 型储

合金、具有 Laves 相结构的 AB_2 型储氢合金、具有超结构型的 A_2B_7 型储氢合金、AB 型的 TiFe 基合金、镁系合金以及钒系固溶体等^[10]。以上分类中的 A 是指构成储氢合金的吸氢类元素, B 是指不吸氢类元素。

金属储氢合金储氢主要是基于物理吸附和化学吸附来储存、释放氢气, 在吸附氢的过程中会涉及氢分子在合金表面的吸附、解离以及扩散等。而对不同种类的储氢合金来说, 在实际应用中仍然面临着诸多问题, 如循环稳定性差、吸放氢动力学性能差以及表面易氧化腐蚀等。其储氢性能与合金表面的理化性质密切相关, 合金的表面形貌如多孔结构、缺陷程度会决定氢吸附位点的数量以及氢扩散的路径, 合金的表面组成成分会影响氢分子解离的难易程度。而合金的活化性能、吸放氢性能、抗腐蚀性能、抗氧化性能以及抗杂质气体毒化性能等都主要受合金表面组成和微观结构的影响^[11]。因此在不改变储氢合金内部性质的条件下, 可以通过表面处理技术去除合金表面的氧化层^[12]、或覆盖具有催化等性能的材料来调整合金表面的理化性质。如利用气相沉积技术可以使合金表面镀膜均匀致密的保护层, 从而抑制合金的粉化与氧化^[13]; 利用激光处理技术可以使合金表面发生重熔现象, 产生裂纹、增加新的活性位点等^[14]。表面修饰是指通过物理、化学或者复合方法改变合金的表面结构特征以提高合金某一种或几种性能的方法。储氢合金的表面修饰方法种类繁多、性能改善程度不同。近年来, 对储氢合金进行表面修饰越来越受到人们的关注。

对储氢合金进行表面修饰的方法有很多。选择合适有效的表面修饰方法是改善储氢合金性能的关键。本文将详细梳理近几十年对储氢合金进行表面修饰方法的研究成果, 并对储氢合金表面修饰方法的未来发展趋势进行展望。

1 表面修饰方法

研究人员对储氢合金的表面修饰方法有很多种, 如气相沉积技术、激光处理技术、机械合金化处理技术、剧烈塑性变形处理技术、化学镀处理技术、电镀处理技术、阳极氧化处理技术以及其他化学处理技术(酸、碱、盐、氟化处理)等。这些表面修饰方法大体上可以划分为两大类: 物理表面修饰和化学表面修饰, 本文将重点对这两大类的表面修饰方法进行梳理。

1.1 物理表面修饰方法

物理表面修饰是指通过物理手段, 如热力、电磁力等作用于材料表面, 使其外部形态、表面组成成分和表面特性发生改变, 以提高材料的性能。具体表现在材料表面沉积膜层、增大比表面积、引入晶格缺陷、改变晶粒尺寸等。常见的物理修饰方法有气相沉积法以及激光处理等。物理修饰通常不涉及化学反应和化学键的形成与断裂, 而是通过改变材料的物理状态来

优化材料的性能。但是, 在实际应用过程中, 也会涉及少部分化学反应。在此, 将重点梳理气相沉积技术、激光处理技术、机械合金化法和剧烈塑性变形技术。

1.1.1 气相沉积

气相沉积技术是一种可以获得厚度在微米数量级薄膜的技术^[15]。具体方法是将所需涂层材料熔融或是溅射成为气相, 在储氢合金表面快速凝结, 以抑制合金粉化, 提高储氢能力。气相沉积技术可以分为物理气相沉积和化学气相沉积, 其中物理气相沉积是将物质热蒸发或是使用离子束轰击物质表面使其发生原子溅射的现象; 而化学气相沉积是通过原子、分子之间的化学反应以生成固态薄膜的技术^[15]。化学气相沉积技术通常会涉及高温高压、激光辅助等物理手段, 因此本文将其归类为物理表面修饰方法。

按照物理机制的差别, 物理气相沉积技术一般分为真空蒸发镀膜、真空溅射镀膜、离子镀膜、分子束外延、离子束增强沉积、电火花沉积、电子束物理气相沉积以及多层喷射沉积技术等^[16]。不同的沉积技术有不同的特点, 可适用于不同的材料, 例如, 离子束增强沉积技术的主要优点是工艺温度低, 对所有衬底结合力强, 可在室温得到高温相、亚稳相及非晶态合金, 化学组成便于控制, 方便控制生长过程等。但是, 离子束增强沉积技术具有直射性, 因此在处理形状复杂的表面时比较困难^[17]。杨凯^[18]、吴锋等^[19]通过真空蒸发镀膜技术分别在 $MINi_{3.6}Co_{0.7}Mn_{0.3}Al_{0.4}$ (Ml 为富镧混合稀土) 电极上镀覆 Ni 膜和 Ag 膜, 考察了镀覆膜层的合金对镍氢电池性能的影响。研究表明, 该方法在合金上镀覆的膜层并不会对储氢合金的体相结构产生影响, 但却都提高了合金的放电容量以及放电平台电压, 内阻也都有相应的降低, 对于合金的表面修饰, 不仅改善了电池的放电性能, 同时也抑制了合金的粉化和氧化, 起到了电池保护层的作用, 提高了电池的循环稳定性。他们还利用等离子体技术对 $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ (Mm 为富铈混合稀土) 镀覆了 Ni 膜^[20], 同样发现电池的性能有了明显的改善。Zhang 等^[21]采用磁控溅射法在 La_2Mg_{17} 合金表面溅射了钇金属。研究发现, 通过磁控溅射、表面吸收和热处理成型 3 个步骤, 在合金表面形成了新的金属间化合物。在储氢性能方面, 掺杂样品的可逆容量和循环稳定性均得到提高, 氢的解吸活化能降低。Zhang 等^[22]还利用磁控溅射法在 $LaMgNi$ 基合金上溅射了纳米钼, 研究发现, 电极表面会出现花状沉积颗粒。随着溅射时间的延长, 沉积颗粒的分布更加密集、致密, 获得的合金性能已超过大多数 AB_5 、 AB_3 型合金, 且与 A_2B_7 型合金非常接近。

化学气相沉积技术可分为热 CVD 技术、等离子辅助化学气相沉积技术、激光辅助、金属有机化合物沉积、低温沉积、中温沉积、高温沉积以及超高温沉积等^[23]。在实际反应过程中, 如果想要得到具有特定

性质的薄膜,就要选择合适的反应方式,并科学确定温度、气体组成、浓度、压力等参数^[24]。Davids 等^[25]采用金属有机化学气相沉积技术对钛铁基储氢材料进行了表面改性。研究发现,合金形成了由 Pb 纳米粒子构成的涂层,即使暴露在空气中也能提升材料的加氢能力,这是由于改性表面对 H_2 解离的催化活性提高了。Zhang 等^[26]研究了多壁碳纳米管的电化学储氢,采用化学气相沉积法,以钨镍合金为催化剂,在 C_2H_2/H_2 气氛下合成了 MWNTs, 研究结果表明在 200 mA/g 充电电流密度和 100 mA/g 放电电流密度条件下,纯化的 MWNTs 具有 380 mAh/g 的高储氢容量,放电曲线具有近似 0.8 V 的电压平台,放电容量随着循环次数的增加而增加,这些曲线显示了 CNTs 具有良好稳定的充放电性能。

1.1.2 激光处理

对于金属合金的激光表面处理,一般会促进材料形貌、显微组织以及残余应力的变化,经激光处理后的合金,硬度、耐腐蚀性、耐磨损性和抗氧化性都会得到一定程度的提高^[27-28]。而合金主要的变化是由于激光扫描合金表面发生了重熔现象,熔化区在冷却时发生收缩,且激光重熔会影响合金表面的残余应力,从而导致出现裂纹^[14]。激光会与金属合金之间产生相互作用,以改善合金表面的某些特性,但目前利用激光技术处理储氢合金表面的研究还少有报道。Silva 等^[27]首次研究了脉冲激光激活法(PLA)如何影响暴露在空气中 $Ti_{11}V_{30}Nb_{28}Cr_{31}$ 合金的储氢行为。他们将样品暴露在空气中 30 d,并保证一定的湿度条件,使用激光器以一定的速度进行了纳米脉冲激光扫描。实验结果表明,经激光处理的合金样品,相结构并未发生改变,但却明显地改变了合金颗粒的表面,如图 1 所示,颗粒边缘发生重熔且快速凝固,并存在几处微

裂纹。性能测试分析发现,经激光处理后,已经氧化的合金可以完全恢复储氢能力。Makridis 等^[29]采用激光烧蚀法在聚合物基体上合成了新型的镁纳米颗粒。测试结果表明,该方法合成的镁纳米颗粒表现出更快的氢吸收速度(在 250 °C 下,吸收氢量的 96% (体积分数) 在 20 min 内被解吸),且在真空状态和较低的温度下(相比于镁块体材料所需的 330 °C, 250 °C 是相对较低的温度)具有优异的可逆性。

1.1.3 机械合金化

机械合金化法是将原料粉末与镀覆元素混合放入球磨罐,通过高能球磨的方式,使混合粉末发生强烈的机械碰撞而产生塑性形变的一种常用方法,在整个球磨过程中,混合粉末之间碰撞会导致材料晶粒细化,材料的比表面积在一定程度上增大,且细化后的材料会有更多的缺陷,可提供更多的氢化成核位点和较短的氢扩散距离,增强材料的吸放氢速率,提高储氢合金的储氢性能^[30]。Wang 等^[31]采用机械合金化法复合石墨烯、多壁碳纳米管与 Mg_2Ni 储氢合金。研究结果表明,经高能球磨后,成功将石墨烯与多壁碳纳米管掺入合金表面,在球磨过程,产生了表面缺陷,并建立了更多储氢通道以促进氢的吸收和解离,且复合合金晶粒细化,活化时间缩短,动力学性能显著提高。Lucaci 等^[32]通过机械合金化法在镁基合金中添加 Ti、Fe、Ni 等元素以提高储氢能力,将 $Mg_{76}Ti_{12}Fe_{12-x}Ni_x$ ($x=4, 8$) 合金分别在石油醚介质中机械合金化 10、20 和 60 h,接着又在 450 °C 氩气中热处理 3 h。实验结果表明,随着球磨时间的增加合金不断形成新相,且合金的非晶化程度也在增加,经过热处理后,合金发生相变,从非晶相又转变为晶相。所加入的元素经球磨后,在合金表面形成了层状的复合涂层,有效提高了该合金的储氢能力。

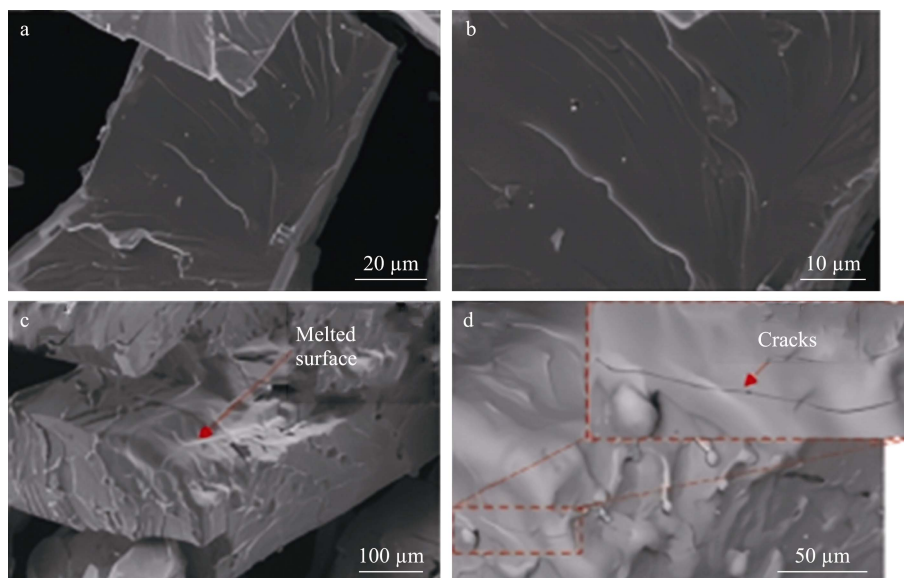


图 1 激光处理样品的 SEM 图像分析: a~b) 原始合金; c~d) 激光处理后合金^[27]
Fig.1 SEM image analysis of laser treated sample: a-b) original alloy; c-d) laser treated alloy^[27]

1.1.4 剧烈塑性变形

剧烈塑性变形技术 (Severe Plastic Deformation, SPD), 简称 SPD 方法。该方法是通过合金材料施加极端的压力, 使该材料晶粒细化、晶界增多, 在基础合金里引入较多的晶格缺陷以增强材料的储氢能力^[33]。常见的 SPD 方法包括等通道角挤压 (ECAP)、高压扭转 (HPT)、横轧挤压 (CRE)、悬臂辊挤压 (CGP)、累积滚接 (ARB) 等, 但用于修饰储氢合金表面以改善性能的方法非常有限^[33]。Cengeri 等^[34]采用两种 SPD 方法, 即高压扭转 (HPT) 和搅拌摩擦加工 (FSP), 对镁合金 ZK60 进行了塑性变形, 探究其储氢容量和动力学的变化。研究表明, 不同的 SPD 方法得到的结果不同, 其中 FSP 较 HPT 的容量大 30% 左右。经 XRD 和 DSC 分析表明, SPD 处理后的合金, 储氢的机制主要表现为: 经 SPD 处理产生的晶格缺陷对氢气的选择性俘获, 且处理后的合金都保持有高稳定性和长时间的储存稳定性, 分析是由于 SPD 引起的晶格缺陷具有较高的热稳定性, 且会优先形成氢化物^[35]。Edalati 等^[36]采用高压扭转法 (HPT) 对 TiFe 合金进行处理, 如图 2 所示, 加工过的合金含有纳米颗粒; 表面含有许多孤立的富铁团以及裂纹。处理后的合金可以长时间暴露在空气中而不失活, 但是在加氢过程中, 样品易发生碎裂现象。该研究也验证了塑性变形对储氢激活的意义。Silva 等^[37]采用搅拌摩擦 (FSP) 对 ZK60 合金进行了处理, 随后又进行了手动锉削。研究表明, 经 FSP 处理后, 样品的微观结构更加精细, 且更加均匀, 内层也更薄。由于薄的内层以及更精细的第二相颗粒分布, 使处理后的合金显示出更快的氢吸收动力学。

综上所述, 气相沉积技术、激光技术以及机械处理的方法作为储氢合金表面的物理修饰手段, 均可以改善合金的微观结构、增强力学性能、提高耐腐蚀性以及抗氧化性, 每种方法都较为成熟且均有各自独特的优点, 气相沉积是通过在合金表面形成致密均匀的

涂层以提高合金的抗腐蚀性、抗氧化性、循环稳定性等, 在沉积过程中, 可能会形成纳米晶或非晶结构, 在一定程度上可以提高合金表面的催化活性。激光处理是通过将合金表面熔融形成细晶或非晶层, 增加较多活性位点, 可以显著增加合金表面的硬度以及抗粉化性。机械合金化是通过引入纳米晶和非晶结构, 增加合金表面的粗糙度, 纳米晶或非晶一方面可以极大程度增加合金表面反应的活性位点, 另一方面可以增加氢扩散的路径以促进氢的吸收和解离。剧烈塑性变形技术对合金施加极端的压力, 使晶粒显著细化, 增加氢扩散路径的同时提高合金的抗腐蚀性。但也面临着一些挑战, 例如, 气相沉积技术, 一些涂层材料脆性较高, 在复杂应力下易产生裂纹甚至剥落, 且涂层技术要求有较为严格的工艺条件等, 加工过程较为复杂; 而激光技术, 对精密度要求较高, 也易受到设备或是材料的限制; 机械处理方法可以使材料晶粒细化, 例如 SPD 方法处理后的合金材料具有均匀的超细晶或纳米晶结构, 该方法有利于提高储氢合金的储氢容量以及吸放氢动力学性能。但机械合金化法通常需要较长的球磨时间, 且在球磨过程中, 随着设备和磨球的磨损, 易在材料当中引入不纯物; 而 SPD 方法通常需要专门的操作设备且工艺较为复杂, 经 SPD 方法处理后的样品可能导致材料内部残余应力, 会影响材料的长期稳定性, 不宜大规模生产。因此, 在应用这些技术的同时, 需考虑各自的优缺点, 例如 SPD 方法所带来的材料内部残余应力可以通过热处理来降低, 而不同的 SPD 方法之间也可以相互复合以弥补单一方法的缺点。根据所需条件适当选择相应的技术手段, 以克服现有技术的局限, 实现高效率、高质量的储氢合金表面改性。

1.2 化学表面修饰方法

化学修饰即通过化学反应改变材料表面的微观结构与组成成分, 如氧化还原反应、溶解沉淀、络合

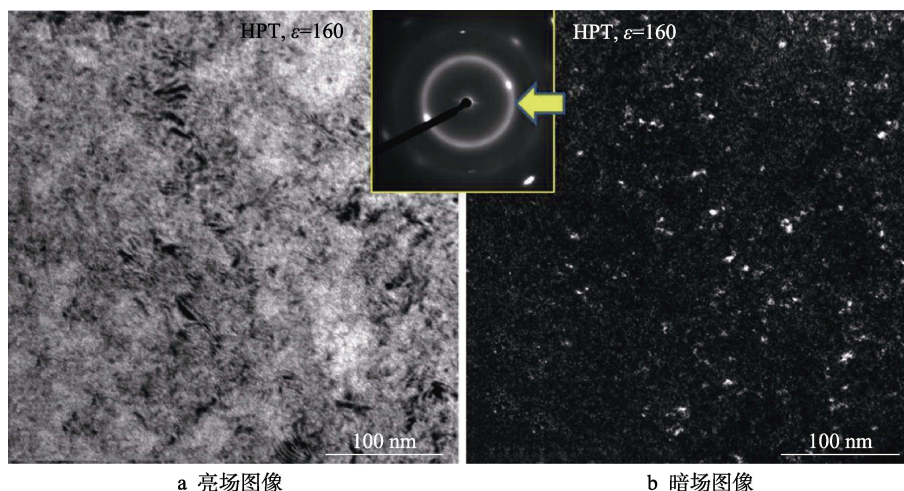


图 2 HPT 处理样品的 SAED 图案^[36]

Fig.2 SAED patterns of HPT treated samples^[36]: a) bright field image; b) dark field image

反应等,通常会涉及材料表面与化学试剂之间化学键的形成与破坏。常见的化学修饰方法包含化学镀、电镀、氧化处理以及酸碱盐处理等,通过化学修饰对合金表面产生深度影响,如涉及材料表面的重排与重构,以此来改善合金的性能。

1.2.1 化学镀

化学镀是指合金在镀液中反应,利用镀覆元素的氧化还原反应在合金表面形成一层金属膜。所形成的膜层主要有 3 个作用:一可以作为阻挡层,防止合金的氧化以及在反应过程中的粉化;二可以作为微电流的集流体,促进合金表面的电化学反应,并且改善电极的导电、导热性;三可以提高放电电压,改善大电流的放电特性^[38]。将所要镀覆涂层的合金颗粒与涂层粉末或是含涂层元素的溶液均匀混合,通过搅拌将涂层元素镀覆在合金表面。

Yang 等^[39]为了提高 La-Mg-Ni 基储氢合金的整体电化学性能,对 $\text{La}_{0.88}\text{Mg}_{0.12}\text{Ni}_{2.95}\text{Mn}_{0.10}\text{Co}_{0.55}\text{Al}_{0.10}$ 合金粉末进行化学复合镀 Ni-Cu-P 处理。研究表明,复合处理使合金表面沉积了密集的球形颗粒,即 Ni-Cu-P 化合物,这些颗粒涂层不仅起到了保护层的作用,还提高了合金的导电性和催化活性,合金电极的放电容量由 338 mA/g 显著提高到 361 mA/g。200 次充放电循环后的容量保持率和 1 500 mA/g 放电电流密度下的高倍率放电率(HRD)分别由 76.0%和 27.7%提高到 84.8%和 37.0%。Zhao 等^[40]为了改善 La-Ni-Al 储氢合金的表面结构和电化学性能,在其表面镀覆了 Ni-P 颗粒。研究表明,在充放电循环前,处理过的合金电极的开路电位均降低,导致金属氢化物形成,增强了基体合金的抗腐蚀能力。与未处理的合金电极相比,处理后的合金电极表现出更高的交换电流密度和更低的电荷转移电阻。表面处理后形成的活性表面有利于氢在基体合金内部和通过合金表面扩散。Wang 等^[41]研究了不同沉积浓度 Pb 涂层对 ZrCo 合金表面形貌、显微组织和储氢性能的影响。结果表明,球形 Pd 颗粒在 ZrCo 合金表面成功沉积,随着 PdCl_2 浓度的增加, Pd 颗粒由稀疏排列转变为连续致密膜。与裸合金相比,镀 Pd 合金的氢化动力学性能得到改善;随着沉积浓度的增加,样品的氢化速率先升高后降低。可见,镀液浓度会显著影响镀层的均匀性,使合金的性能有不同程度的改变。Wu 等^[42]研究了热 KOH 刻蚀和化学镀镍改性的 AB 型储氢合金的电化学性能,先用热 KOH 溶液处理,接着化学镀镍,研究表明,用热氢氧化钾溶液改性的合金具有快速活化的特点,但其循环寿命稳定性较差。镀镍后的合金改善了循环寿命稳定性和放电容量。与未处理的合金电极相比,通过热 KOH 溶液浸渍或化学镀镍改性的合金电极可以提高交换电流密度和极限电流密度,具有较高交换电流密度和限制电流密度的电极可改善高倍率放电性能。Zhang 等^[43]对 AB_5 型储氢合金进

行化学镀铜处理,通过调整工艺条件研究合金性能的变化规律。结果表明,随着温度、pH 值以及镀液浓度的增加,镀层的沉积速率增大,得出最佳的工艺条件为:温度为 75 ℃, pH 值为 8.5, Ni^{2+} 质量浓度为 1.2 g/L。处理过的合金循环稳定性由 60.66%增加到 75.58%,且表现出更好的耐腐蚀性。

1.2.2 电镀

化学镀处理后的合金,镀层存在均匀性差、附着力不足等问题,电镀处理则是为了弥补化学镀的缺陷。在电镀过程中,待镀覆的合金材料作为阴极,镀层元素作为阳极,通过设置合适的电流密度,将要镀覆的元素沉积在合金表面形成金属镀层。Ding 等^[44]对 $\text{La}_{0.88}\text{Mg}_{0.12}\text{Ni}_{2.95}\text{Mn}_{0.10}\text{Co}_{0.55}\text{Al}_{0.10}$ 进行了电镀钴、镍镀层处理,研究其对合金电化学性能的影响。研究表明,在合金表面形成了致密的球形钴颗粒层以及片层状的镍层,如图 3 所示,使钴涂层合金的最大放电容量提高了 19 mAh/g,且 2 个涂层合金的高放电率都得到较大提升,改善了合金的电化学性能。Shen 等^[45]采用聚苯胺(PANI)包覆 $\text{La}_{0.80}\text{Mg}_{0.20}\text{Ni}_{2.70}\text{Mn}_{0.10}\text{Co}_{0.55}\text{Al}_{0.10}$ 合金,以期提高电化学动力学性能。实验结果表明,经电镀处理,苯胺单体在合金表面形成了聚苯胺薄膜,聚苯胺颗粒呈珊瑚状。电镀过程在 1 500 mA/g 的放电电流密度下,在经 200 次充放电循环后,容量保持率以及高速率放电能力均有一定程度的提高,且经处理后的电极交换电流密度、极限电流密度、氢扩散系数以及阳极峰值电流都较未处理的电极有所提高。Kim 等^[46]采用电镀的方法将 Ni-PTFE 复合层镀覆在 AB_5 型合金上,通过控制用量镀覆合适的镀层。研究表明,经处理后的合金呈现出多孔结构,且较为明显地提高了合金的耐腐蚀性能,这是由于 PTFE 的疏水性阻止了碱液在合金表面发生直接反应。此外,合金的电化学性能也明显改善,特别是提高了活化性能。Derakhshani 等^[47]研究了电镀电流密度对镍钴涂层形貌和电催化性能的影响。研究表明,随着电流密度的增加,活性表面积增加了 5 倍,电催化性能得到了一定的提升。其中电流密度为 500 mA/cm² 时,得到了孔隙率好、表面活性高的涂层。Zhang 等^[48]研究了平均电流密度等不同工艺参数对电镀银镀层效果的影响。结果表明,电流密度的变化程度会影响镀层颗粒大小以及沉积程度,通过调整合适的工艺参数会得到结构更为致密的镀层,从而提高合金的耐腐蚀性等,达到最优的电镀效果。

1.2.3 阳极氧化

阳极氧化一般用于轻金属,主要目的是在金属表面形成一层致密均匀坚硬的氧化膜,而在使用这项工艺时,可以根据环境的侵蚀性,额外进行密封或者是涂漆^[49]。阳极氧化虽然与电镀一样是一种电解过程,但是阳极氧化过程是将金属作为阳极放置于溶液中,通过施加电流密度形成一层氧化膜,这层氧化膜较自

然形成的氧化膜更厚且更均匀。阳极氧化过程也被称为微弧过程,因为在处理过程中镀液会有火花现象,但是本质上还是金属衬底与镀液电解质的一种氧化反应^[50]。目前,阳极氧化技术多用于镁基合金,且核心技术在不断更新完善,研究者们通过控制镀液以及操作的条件,不断突破该技术的局限性^[51-58]。

Zhang 等^[59]采用阳极氧化的方法在镁基合金表面制备了铝镁混合氧化物的膜层,在该膜层的基础上又制备了双氢氧化物膜。研究结果表明,由阳极氧化工艺制备的膜层为多孔结构,且大多孔隙并不规则,如图 4 所示,会引起环境的侵蚀,并不能达到长时间有效的保护,通过额外的密封处理,才能够达到较为理想的保护效果。Kale 等^[60]采用阳极氧化技术在铝表面制备了镍镁银复合膜层,并与镍镁复合膜层进行了对比。研究结果表明,多元素的复合膜层会减少缺陷数量,且电沉积的合金由六边形转变为细颗粒型,更大程度地提高了材料的耐蚀性。

1.2.4 其他化学表面修饰方法

在化学修饰中,除了镀覆膜层,还可以将合金浸泡在溶液里,通过腐蚀合金表面的氧化层来提高合金的性能。如酸处理可以去除合金粉表面的稀土类浓缩层,使表面变得疏松多孔,比表面积增大,让合金粉能够露出新的活性位点。常用的酸可以分为无机酸和有机酸,其中无机酸有盐酸、硝酸等。常见的有机酸

有甲酸、乙酸、氨基乙酸等。对于碱处理,通常改变合金表面成分以形成富镍层,从而提高电极的放电容量、快速放电能力以及循环寿命等。一般用盐溶液处理会在合金表面形成以金属氧化物为主的耐腐蚀薄膜,常用的溶液有磷酸盐、钼酸盐、钒酸盐、铬酸盐,以及稀土等。氟化处理即是将合金浸泡在含氟溶液中,使合金表面形态改变,引进新的活化中心以提高合金的性能。表 1 总结了其他表面化学处理的方法。

综上所述,化学修饰操作方式较为简单,是表面修饰常选择的一种方法。例如化学镀与电镀均可以在合金表面均匀地镀覆涂层,涂层的化学组成和特殊结构都会使合金性能有不同程度的改善,比如化学组成若含有催化元素(Ni、Pb 等)会增加合金表面的活性位点,并一定程度促进氢分子解离,提高速率,如球形钴颗粒镀层、呈珊瑚状的聚苯胺颗粒等特殊的镀层结构都会显著提升合金表面的化学性质。阳极氧化是通过在合金表面形成一层致密的氧化层,减少合金表面的氧化和腐蚀。酸碱盐处理以及氟化处理是通过去除表面氧化物、改变合金表面形态使合金表面产生新的活化中心,提高吸放氢的速率,提升合金综合性能。化学表面修饰方法相较物理表面修饰方法工艺较为简单,成本也相对较低,但有些方法也会给储氢性能带来负面影响。其中化学镀不需要外加电源,电镀方法可以通过调整电流、时间等相关参数,精确控制

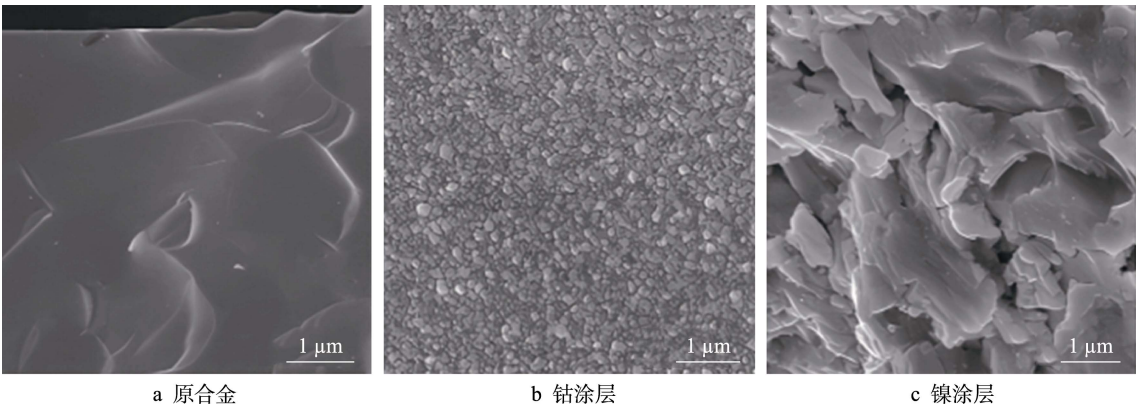


图 3 电镀处理合金粉末的 FESEM 图像^[44]
Fig.3 FESEM image of electroplated alloy powder^[44]: a) primary alloy; b) cobalt coating; c) nickel coating

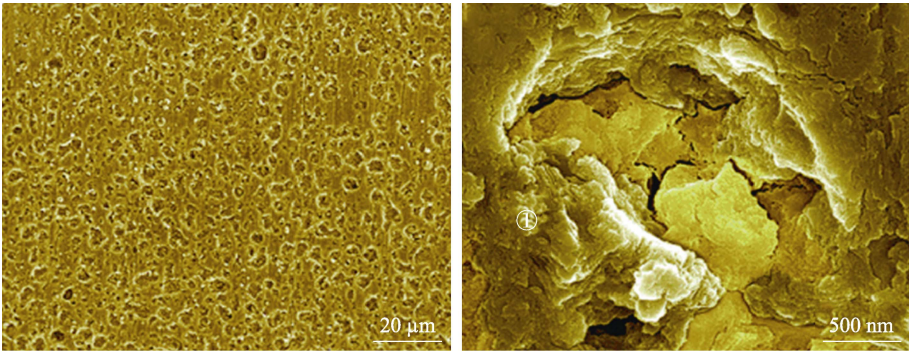


图 4 阳极氧化制备膜层的 SEM 表面图像^[59]
Fig.4 SEM surface image of anodic oxidation film^[59]

表 1 其他表面化学处理方法分析总结
Tab.1 Analysis and summary of other surface chemical treatment methods

Process modes	Processing solutions and base alloys	Treating processes	Microstructures	Performance changes
Acid treatment	Treatment of LaY ₂ Ni _{9.7} Mn _{0.5} Al _{0.3} alloy with dilute hydrochloric acid solution ^[61]	The alloy is treated in dilute hydrochloric acid solution with pH=1 at room temperature for different times (30, 60, 120 min)	With the extension of acid treatment time, the content of Ni in the alloy increases	After acid treatment, the activation properties of the alloy were improved significantly, and the initial discharge capacity increased by about two times, but the maximum discharge capacity also decreased with the extension of the treatment time
	Mm(NiMnCoAl) ₅ alloy was treated with organic acids such as formic acid, acetic acid, oxalic acid and amino acetic acid ^[62]	The optimum conditions for soaking at room temperature were obtained by changing the concentration and time of acid treatment solution at room temperature	The surface oxide layer is removed, and each element of the alloy dissolves to different degrees, of which nickel dissolves relatively least, so nickel-rich layer is formed on the surface of the alloy	After acid treatment, the initial discharge capacity of the alloy electrode is significantly increased, the discharge platform is obviously negative shift, and the activation performance is enhanced
Alkali treatment	LiOH, NaOH, KOH treatment of rare earth magnesium nickel base alloys ^[63]	The same concentration of 6 (mol/L) alkali solution is used, and the treatment time is different.	After the alkali treatment of the alloy, some elements are dissolved in the solution, and re-precipitated on the surface of the alloy, in the form of rods, needles, columns	All the alloys showed excellent electrochemical properties, among which the alloy treated with NaOH solution had the best performance, and the sample treated with LiOH had the best corrosion resistance
Salt treatment	NiSO ₄ , MnCl ₂ and MmCl ₃ process TiFe alloy ^[64]	Choose different salt solutions to treat for the same time	After salt solution treatment, the oxide layer on the surface of the alloy has a certain degree of destruction, and the metal atoms or ions in the solution enter the alloy surface in different ways, such as Mm segregation on the alloy surface to form a new phase	The activation properties of the alloys were improved effectively by the three salt solutions
Fluoride treatment	NH ₄ F and NaF, NHF and NaF treatment of AB ₃ alloy ^[65]	Configuration of different concentrations and different components of fluorinated liquid handling La _{0.94} Mg _{0.06} Ni _{3.49} Co _{0.73} Mn _{0.12} Al _{0.20} alloy	After fluoride treatment, the surface of the alloy becomes rough and uneven, and the granular material appears, and the phase structure of the alloy changes, and a new phase appears	The maximum discharge capacity of the alloy electrode is increased, the cycle stability is also improved, and the formed fluorination layer weakens the corrosion and powder of the alloy

镀层的厚度，且电镀速度快，适应于大规模生产。但二者的缺点在于，镀液可能含有有害物质，镀覆过程所产生的废液、废气均需安全处理，而电镀对设备的要求也比较高。阳极氧化所形成的氧化膜虽然具有良好的耐腐蚀性，但应用范围较小，且部分氧化层可能会阻碍氢扩散。酸碱盐等处理方式较为常见且操作简单，但对溶液的 pH 值要求较为严格，且操作不当易引起合金表面腐蚀。因此，未来应用这些方法进行表面修饰时，要考虑该工艺的环保性、效率等，也可考虑多种化学修饰方法相结合，以提高综合性能。

1.3 不同修饰方法的具体对照

储氢合金表面修饰方法的本质都是通过改变合金表面的微观结构、化学组成或物理状态等来优化合金表面的理化性质，有的方法是通过在表面镀覆膜层，有的方法是通过细化晶粒或引入纳米晶非晶等结

构，虽然表面修饰方法的切入点不同，但都是通过改善氢气的吸附、解离、扩散以及材料的稳定性来实现合金性能的优化。表 2 总结了不同修饰方法对部分储氢合金的性能影响，可以明显发现，不同表面修饰方法各有优缺点，对储氢合金的修饰作用也有相同之处，选择合适的表面修饰方法不仅要关注技术本身的特质，还要结合不同合金的性质特点。

2 结论与展望

改善储氢合金性能的方法众多，包括合金本身元素置换、不同元素的组成比例，以及电解液的种类、浓度甚至是测试条件。储氢合金表面修饰方法也是一个前景较好的研究领域，通过表面修饰技术改变合金表面形貌以及组成成分，可以有效提高储氢能力。目前的表面修饰技术仍有较多局限，如气相沉积技术，

表 2 不同修饰方法对部分储氢合金的性能影响
Tab.2 Effects of different modification methods on properties of some hydrogen storage alloys

Modification methods	Specific technologies	Modified target	Microstructures	Comprehensive performances
Vapor deposition technology	Vacuum evaporation coating	The $\text{MlNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.3}\text{Al}_{0.4}$ (Ml is lanthanum-rich rare earth mixture) electrode is coated with Ni film ^[18] and Ag film ^[19]	The film layer on the surface of the alloy has micropores and cracks, and is not particularly dense	Ni film: After modification, the discharge capacity of the electrode at 5 C is increased by 255 mA·h, the discharge platform voltage is increased by about 0.12 V, and the cycle stability is increased Ag film: After modification, the discharge capacity of the electrode at 5 C is increased by 200 mA·h, the discharge platform voltage is increased by about 0.10 V, and the internal resistance of the battery is reduced by 31.5%
	Plasma technique	$\text{MmNi}_{3.6}\text{Co}_{0.7}\text{Mn}_{0.4}\text{Al}_{0.3}$ (Mm is cerium-rich rare earth mixture) coated with Ni film ^[20]	After 500 weeks of charge and discharge cycle, the powder degree of the modified electrode alloy is better than that of the unmodified electrode	After modification, the discharge capacity of the electrode at 5 C is increased by 200 mA·h, the discharge platform voltage is increased by about 0.14 V, the internal resistance of the battery is reduced by 24%, and the cycle stability is increased.
	Magnetron sputtering	$\text{La}_2\text{Mg}_{17}$ alloy is sputtered with Y metal ^[21]	The yttrium metal on the surface of the sample was pin-like particles, and gradually distributed evenly	With the increase of sputtering time, the amount of hydrogen absorption and dehydrogenation of the alloy increases first and then decreases. When the sputtering time is 20 minutes, the comprehensive properties of the alloy are the best. The modified alloy has higher hydrogen diffusion activity
	Metal-organic chemical vapor deposition	Metal Pb was deposited on the surface of TiFe-based alloy ^[25]	Pb particles aggregate on the surface of the alloy to form a dense coating. With the increase of Pb loading, the morphology of the coating is obviously different, from a uniform but discontinuous morphology to a dense and multi-layer structure	Appropriate loading can improve the activation performance and anti-poisoning ability of TiFe-based alloys
	Laser processing	Laser ablation	Synthesis of Mg nanoparticles on polymer matrix ^[29]	—
Mechanical alloying		Composite graphene and multi-walled carbon nanotubes on the surface of Mg_2Ni alloy ^[31]	After ball milling, graphene and multi-walled carbon nanotubes were incorporated into the surface of the alloy, and the grains were gradually refined. With the increase of the composite content, the agglomeration and welding phenomenon are greatly reduced	The ball milling process produced more surface defects, which promoted the absorption and desorption of hydrogen. The activation time of the composite alloy is significantly shortened, the kinetic performance is significantly improved, and the temperature required for hydrogen absorption is also reduced accordingly

表 2 不同修饰方法对部分储氢合金的性能影响 (续)

Tab.2 Effects of different modification methods on properties of some hydrogen storage alloys

Modification methods	Specific technologies	Modified target	Microstructures	Comprehensive performances
Severe plastic deformation	High Pressure Torsion (HPT) and Friction Stir Processing (FSP)	Plastic deformation of ZK60 magnesium alloy ^[34]	—	The capacity of FSP is about 30% larger than that of HPT treated alloy, and the alloy treated by SPD method maintains high stability and long-term storage stability
	High Pressure Torsion (HPT)	TiFe alloy ^[36]	The processed alloy contains nanoparticles, and there are isolated iron-rich clusters and cracks on the surface	The treated alloy can be exposed in air for a long time without deactivation
Chemical plating		La _{0.88} Mg _{0.12} Ni _{2.95} Mn _{0.10} Co _{0.55} Al _{0.10} alloy powder for electroless composite plating Ni-Cu-P ^[39]	Dense spherical particles are deposited on the surface of the alloy	The discharge capacity of the alloy electrode was significantly increased from 338 mA/g to 361 mA/g. The capacity retention rate after 200 charge-discharge cycles and the high rate discharge rate (HRD) at 1 500 mA/g discharge current density increased from 76.0% and 27.7% to 84.8% and 37.0%, respectively
		Pb coating was deposited on the surface of ZrCo alloy ^[41]	With the increase of the concentration of the plating solution, the spherical Pd particles change from sparse arrangement to continuous dense film	The hydrogenation kinetic properties of the alloy after Pd plating were improved. With the increase of deposition concentration, the hydrogenation rate of the sample increased first and then decreased
Electroplating		La _{0.88} Mg _{0.12} Ni _{2.95} Mn _{0.10} Co _{0.55} Al _{0.10} electroplating of cobalt and nickel coatings ^[44]	A dense spherical cobalt particle layer and a lamellar nickel layer were formed on the surface of the alloy	The maximum discharge capacity of the cobalt-coated alloy is increased by 19 mAh/g, and the high discharge rate of the two coated alloys is greatly improved
		La _{0.80} Mg _{0.20} Ni _{2.70} Mn _{0.10} Co _{0.55} Al _{0.10} alloy coated polyaniline (PANI) ^[45]	The aniline monomer forms a polyaniline film on the surface of the alloy, and the polyaniline particles are coral-like	At the discharge current density of 1 500 mA/g, the capacity retention rate and high rate discharge capacity are improved to a certain extent after 200 charge-discharge cycles
Anodic oxidation		Preparation of Al-Mg mixed oxide film on the surface of magnesium-based alloy ^[59]	The film is a porous structure, and most of the pores are irregular	—

虽然可以按照需求选择较多种类的材料和工艺,且能一定程度上提高合金的耐腐蚀性以及吸放氢动力学,但是涂层制备过程较为复杂,所制备的涂层可能由于附着力不够而脱落,影响最终的修饰效果;机械合金化虽较大程度上提高了合金比表面积,但却降低了合金的抗氧化能力,甚至导致合金产生裂纹,从而影响合金的长期稳定性;在化学修饰中,虽然可以较为简单地调节处理条件以及溶液配比,但化学试剂大多具有腐蚀性,有一定的安全隐患,也可能会影响合金本身的晶体结构和性能。综上,不同的表面修饰方法都

有其独特的优点和缺点,需要根据实际应用需求,逐步调整修饰的方法以实现储氢合金表面性能的有效调控。未来,可以将多种方法相结合以避免单一方法带来的不足,比如可以通过热处理来降低 SPD 方法所带来的材料内部残余应力;可以先对合金进行机械球磨,增加表面粗糙程度,以提供更多的活性位点,接着通过化学镀或电镀等方式改善合金表面的催化活性、耐腐蚀性等;也可以对合金先进行镀覆膜层,比如阳极氧化等,接着可以利用热处理改善膜层与基体之间的结合力,增强抗腐蚀性。还可以通过探究更

多的表面修饰方法或者新型的涂层材料以提高性能,比如聚合物涂层,如聚吡咯、聚苯胺等,其柔韧性好可以达到更为理想的抗腐蚀性;碳基材料、二维材料等均为储氢合金的表面修饰提供了更多的可能性,利用不同涂层材料的优势,改变合金表面的理化性质,以期更大程度地改善合金的性能。

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