

氧化物颗粒增强 Ni-W-P/Nb₂O₅ 复合镀层制备及其耐腐蚀性能

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摘要: **目的** 对 NdFeB 磁性材料进行表面防护处理, 改善其耐腐蚀性能。 **方法** 利用化学镀方法, 在 NdFeB 基体材料表面制备氧化物颗粒增强的晶态和非晶态 Ni-W-P/Nb₂O₅ 复合镀层, 对镀层的组织形貌、元素组成分布及物相进行分析, 并通过化学腐蚀失重法对耐腐蚀性能进行测试。 **结果** 当镀液中的次亚磷酸钠含量为 20 g/L 时, 形成了晶态镀层; 为 35 g/L 时, 形成了非晶态镀层。晶态和非晶态 Ni-W-P/Nb₂O₅ 镀层均由胞状突起组成, 其中弥散分布着共沉积的 Nb₂O₅ 颗粒。镀层样品的 XRD 图谱中没有出现与钕铁硼相关的衍射峰。对于制备的晶态和非晶态复合镀层, 镀液中 Nb₂O₅ 质量浓度由 5 g/L 增加到 15 g/L 时, 化学腐蚀速率明显下降; Nb₂O₅ 质量浓度由 15 g/L 增加到 20 g/L 时, 化学腐蚀速率的下降变得缓慢。 **结论** 利用化学镀可以在 NdFeB 磁性材料表面制备致密的 Nb₂O₅ 增强 Ni-W-P 复合镀层, 且随着 Nb₂O₅ 含量的增加, 复合镀层的耐腐蚀性能提高。

关键词: 化学镀; Ni-W-P/Nb₂O₅ 复合镀层; 耐腐蚀性能; 钕铁硼; 颗粒增强; 共沉积

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Preparation of Oxide Particles Enhanced Ni-W-P/Nb₂O₅ Composite Coatings by Electroless Plating and Its Corrosion Resistance

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ABSTRACT: **Objective** To protect the surface of NdFeB permanent magnetic materials and improve its corrosion resistance. **Methods** The oxide particles enhanced crystalline and amorphous Ni-W-P/Nb₂O₅ composite coatings were deposited on the NdFeB substrate using electroless plating, respectively. The microstructure, chemical elements distribution and the existed phases of the coatings were analyzed. The corrosion resistance of the composite coatings was also evaluated using weight loss experiments. **Results** The crystalline and amorphous composite coatings were formed correspondingly while the mass concentration of NaH₂PO₂ ·

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H₂O was 20 g/L and 35 g/L, respectively. The dissimilar Nb₂O₅ particles were dispersed inside the crystalline and amorphous Ni-W-P/Nb₂O₅ composite coatings which showed closely nodules structure. The XRD patterns of the coatings indicated that there was no diffraction peak related to the NdFeB substrate. When the Nb₂O₅ mass concentration was increased from 5 to 15 g/L, the corrosion rate of the crystalline and amorphous coatings formed decreased markedly, whereas the corrosion rate of the coatings decreased tardily when the Nb₂O₅ mass concentration was increased from 15 to 20 g/L. **Conclusion** The consolidated Nb₂O₅ particles enhanced Ni-W-P/Nb₂O₅ composite coatings could be prepared by electroless plating. And its corrosion resistance was improved with increasing Nb₂O₅ concentration.

KEY WORDS: electroless plating; Ni-W-P/Nb₂O₅ composite coating; corrosion resistance; NdFeB; particle enhancement; co-deposition

化学镀方法制备的镀层在化学和力学方面的性能优良,因此具有自催化化学反应过程的化学镀被广泛应用于防护薄膜的制备^[1-3]。近年来,在化学镀镍的基础上逐步发展了以 Ni-P 二元系为基的三元、四元甚至多元镀层体系,如 Ni-P-Ag, Ni-B-P, Ni-P-PTFE-nano-Al₂O₃ 等^[4-6]。另一方面,氧化物、碳化物及氮化物等颗粒增强的化学镀层也引起了广大研究者的兴趣,如 Al₂O₃, SiC, ZrO₂ 及 Si₃N₄ 等颗粒的增强显著改善了镀层体系的综合性能^[7-11]。

NdFeB 材料的磁性能优异,但常温耐腐蚀性能较差,如在潮湿、酸碱环境中容易被腐蚀粉化等,这影响了其使用寿命^[12-14],因此对磁体进行表面防护处理,改善 NdFeB 磁性材料的耐腐蚀性能具有实际意义。Song 和 Chen 等人在 NdFeB 表面制备了 Ni-P/TiO₂ 镀层及多层 Ni-P 镀层,显著改善了其耐腐蚀性能^[13,15]。相比之下,Nb₂O₅ 颗粒具有更好的耐化学环境腐蚀能力。笔者采用化学镀方法在 NdFeB 材料基体上制备了不同 Nb₂O₅ 含量的氧化物颗粒增强晶态和非晶态 Ni-W-P/Nb₂O₅ 复合镀层,并通过腐蚀失重法对镀层的耐腐蚀性能进行测试,分析了 Nb₂O₅ 含量对复合镀层耐腐蚀性能的影响规律。

1 实验

基材为工业用 NdFeB,名义成分(以质量分数计)为: Nd 26.7%, Fe 72.3%, B 0.99%。用 DK7732 型电火花线切割机将其切割成 20 mm×10 mm×10 mm 的施镀样品。施镀前,样品用 800#—1000# 砂纸打磨平整,然后利用超声波清洗并活化。所用 Nb₂O₅ 粉末由宁夏东方钼业生产,粒径为 400~600 nm。

化学镀液的配方见表 1,用 NH₄OH 调节 pH 值至 9。在施镀过程中,将数字显示水浴锅的温度维持在 85 ℃,镀液用可调节转速的金属棒搅拌,搅拌速率为 140 r/min。

表 1 Ni-W-P/Nb₂O₅ 复合镀配方
Tab. 1 Bath formulation used for Ni-W-P/Nb₂O₅ deposition

成分	质量浓度/(g·L ⁻¹)	
	晶态镀层	非晶态镀层
NiSO ₄ ·6H ₂ O	20	35
Na ₂ WO ₄ ·2H ₂ O	20	35
NaH ₂ PO ₂ ·H ₂ O	20	35
Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	35	62.5
(NH ₄) ₂ SO ₄	30	52.5
CH ₄ N ₂ S	5×10 ⁻³	5×10 ⁻³
C ₁₂ H ₂₅ NaO ₃ S	5×10 ⁻³	5×10 ⁻³
Nb ₂ O ₅	5, 10, 15, 20	5, 10, 15, 20

施镀完成后,用 KYKY-2800B 型扫描电子显微镜(SEM,中科院产)对镀层进行组织形貌、面扫描分析,用 D/MAX2200PC 型 X 射线衍射仪(XRD,日本理学)对镀层进行物相分析。镀层的耐腐蚀性能通过全浸失重法测试的腐蚀速率进行表征,所用化学腐蚀溶液为硝酸酒精溶液,V(HNO₃):V(酒精)=1:9。

2 结果与讨论

2.1 镀层微观形貌

图 1 和图 2 为在两种镀液中制备的 Nb₂O₅ 颗粒增强 Ni-W-P 合金复合镀层的微观形貌。由图可见,所有样品的镀层形貌均呈现典型的化学镀层组织形貌,即由不同尺寸的胞状突起组成,Nb₂O₅ 颗粒弥散分布于 Ni-W-P 合金中。此外,晶态和非晶态镀层中弥散颗粒的含量随镀液中颗粒浓度的增加而呈增加趋势,其中,在颗粒质量浓度为 20 g/L 的镀液中制备的非晶态 Ni-W-P/Nb₂O₅ 复合镀层颗粒团聚现象较为严重。具有自催化化学反应的化学施镀一般包含两

个基本过程:一是金属离子和酸根离子获得电子的还原过程,即 $M^{2+} + 2e \leftrightarrow M$;二是氢气析出,即 $2H^+ + 2e \leftrightarrow H_2$ 。当金属原子 M 被吸附沉积到基体活化点处时便开始形核,超过临界形核半径时,开始沉积长大并顺势蔓延,同时悬浮于表面的 Nb_2O_5 颗粒被捕获,从而

形成 Nb_2O_5 颗粒增强 Ni-W-P 合金的胞状突起单元,当许多胞状突起单元蔓延至相互接触时,便形成 Nb_2O_5 颗粒增强 Ni-W-P 合金镀层覆盖在 NdFeB 基体的表面,形成有效的腐蚀防护屏障。

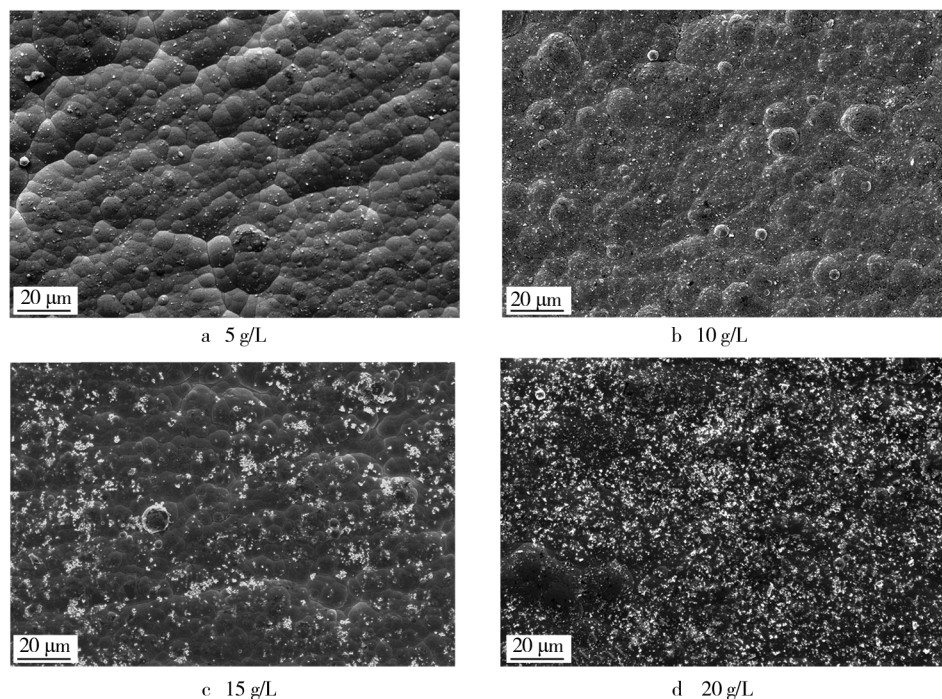


图1 Nb_2O_5 用量不同所得晶态 Ni-W-P/ Nb_2O_5 复合镀层的微观形貌

Fig. 1 Microstructure of crystalline Ni-W-P/ Nb_2O_5 composites prepared with different Nb_2O_5 content

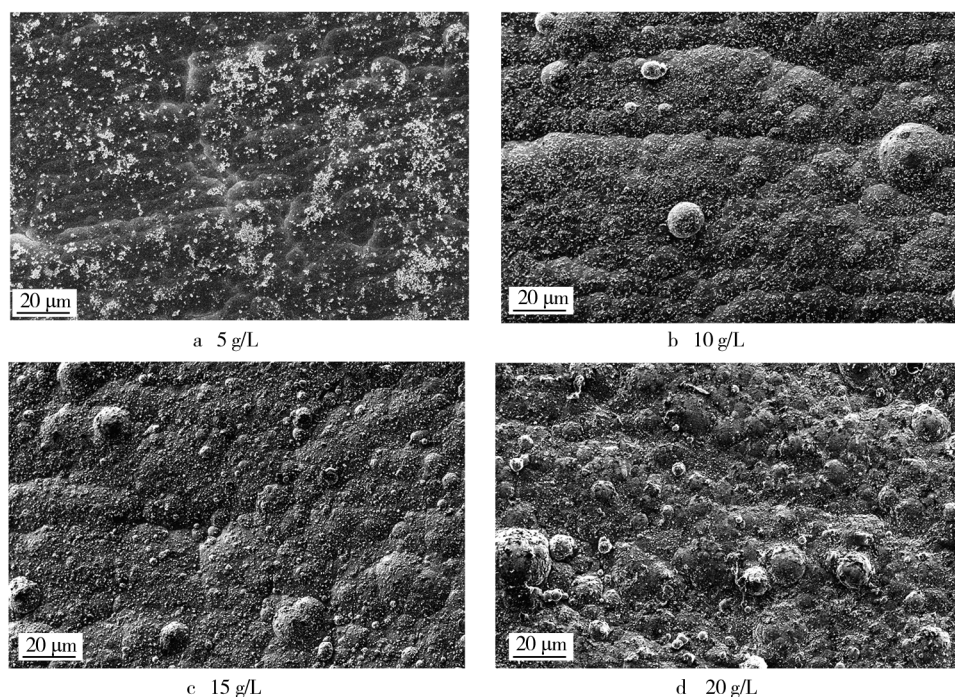


图2 Nb_2O_5 用量不同所得非晶态 Ni-W-P/ Nb_2O_5 复合镀层的微观形貌

Fig. 2 Microstructure of amorphous Ni-W-P/ Nb_2O_5 composites prepared with different Nb_2O_5 content

2.2 镀层化学元素面分布

为了进一步确认所制备晶态和非晶态 Ni-W-P/Nb₂O₅ 镀层对基体的覆盖效果,利用扫描电镜的面扫描功能对两种镀层(Nb₂O₅ 颗粒质量浓度为 10 g/L, 施镀时间为 2 h)的化学元素分布进行了分析,结果见

图 3 和图 4。如图所示,检测到了 Ni,P,W,Nb 和 O 元素,且组成 Nb₂O₅ 颗粒的 Nb 和 O 元素弥散分布于 Ni,P,W 背景元素中。此外,没有检测到 Nd,Fe,B 元素,这也进一步说明所制备的 Ni-W-P/Nb₂O₅ 防腐蚀镀层完全覆盖了 NdFeB 基体表面,形成了有效的腐蚀防护表面层。

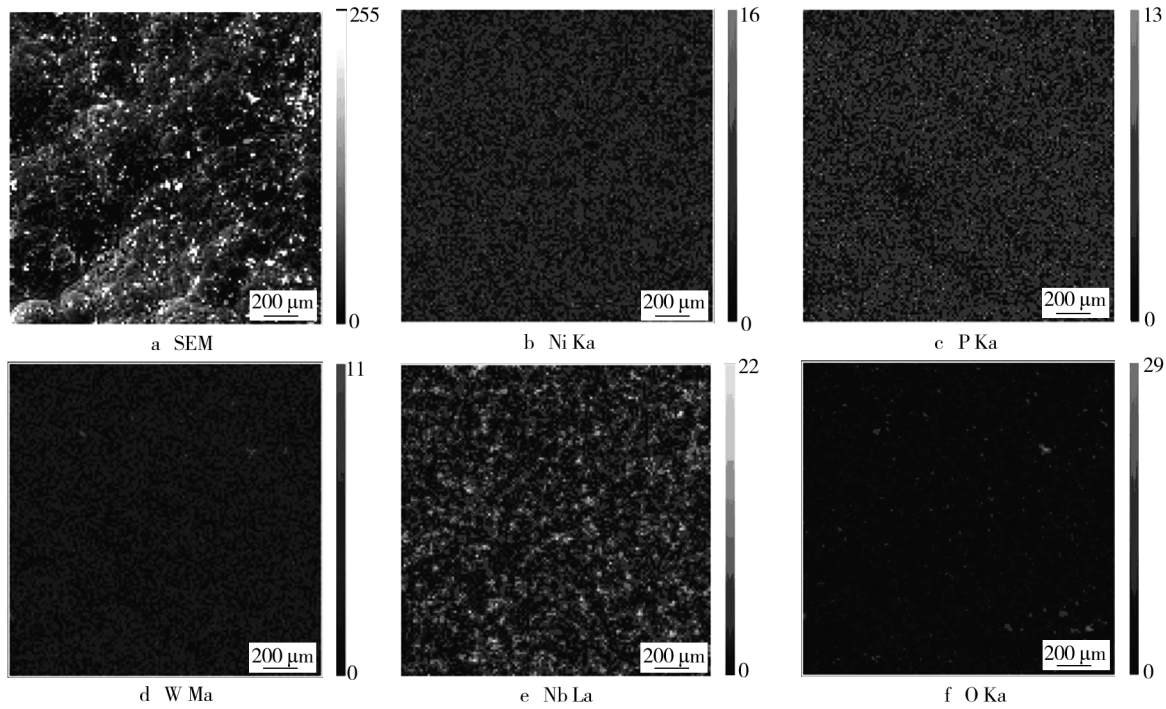


图 3 晶态 Ni-W-P/Nb₂O₅ 复合镀层面扫描

Fig. 3 Chemical elements distribution of crystalline Ni-W-P/Nb₂O₅ composites

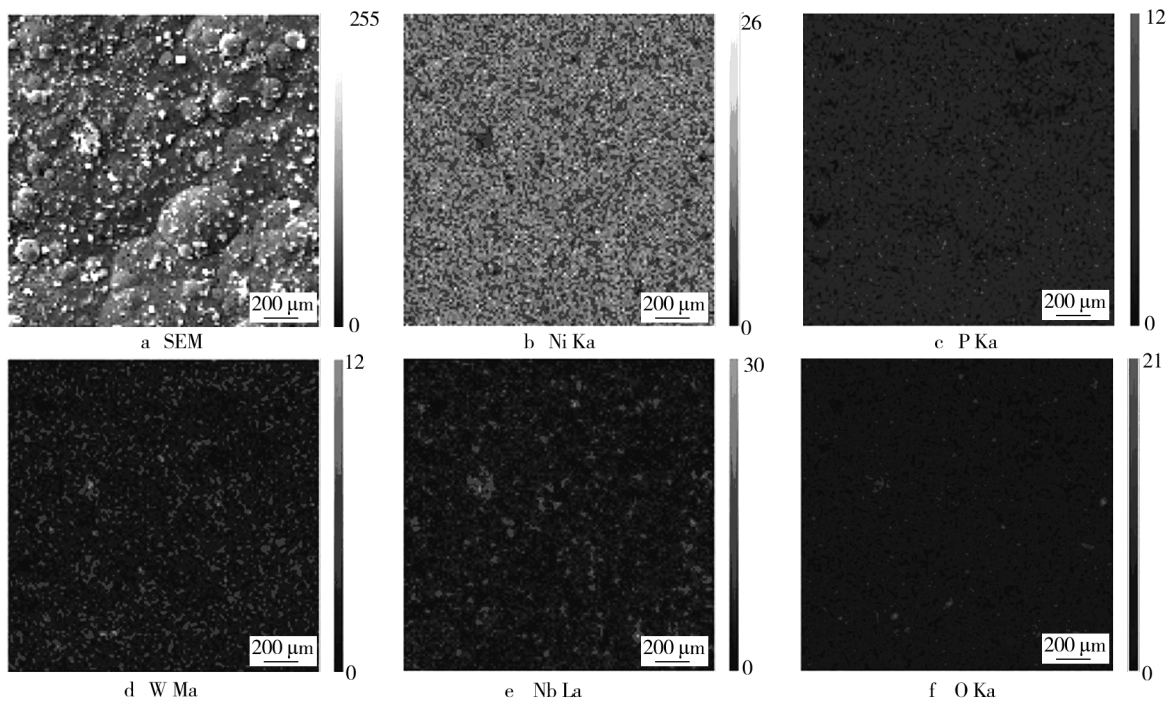


图 4 非晶态 Ni-W-P/Nb₂O₅ 复合镀层面扫描

Fig. 4 Chemical elements distribution of amorphous Ni-W-P/Nb₂O₅ composites

2.3 复合镀层的结构

化学镀层的结构往往与施镀过程中磷酸根离子被还原释放出的P元素的含量有关,P元素含量超过一定值便形成非晶态结构的镀层。文中选用次亚磷酸钠含量不同的两种镀液进行施镀,所制备的 Nb_2O_5 颗粒增强Ni-W-P合金复合镀层的X射线衍射图见图5a,b(化学镀过程中 Nb_2O_5 质量浓度为10 g/L)。

当镀液中次亚磷酸钠质量浓度为20 g/L时,镀层中的P含量较低,形成了晶态镀层(图5a)。其衍射图中出现了Ni(111),Ni(200)和Ni(220)三个主峰,说明Ni-P-W固溶体为晶态结构,且衍射图中有峰值强度相对较低的 Nb_2O_5 相的特征峰,其三强线强度明显低于Ni-W-P合金的衍射峰强度,这可能是由于镀层中 Nb_2O_5 颗粒含量低或者被Ni-W-P合金包覆的

缘故。

当镀液中次亚磷酸钠质量浓度为35 g/L时,镀层中的P含量较高,形成了非晶态镀层(图5b)。其衍射图中只有Ni(111)主峰,没有 Nb_2O_5 相的特征峰。另外,晶态和非晶态两种镀层中均没有检测到与钨铁硼相关的衍射峰,说明施镀后得到了致密的Ni-W-P/ Nb_2O_5 复合镀层,与面扫描结果一致,这也说明镀层完全覆盖了NdFeB基体。

进一步对制备的晶态和非晶态复合镀层进行能谱分析,如图5c,d所示,除了杂质C外,清晰可见Ni, W, P, O和Nb元素的谱峰,没有检测到Nd, Fe, B等基体元素。其中对于非晶态样品,由于检测选区位置为氧化铌颗粒所处的位置,因此对应的Nb和O元素计数率相对较高。

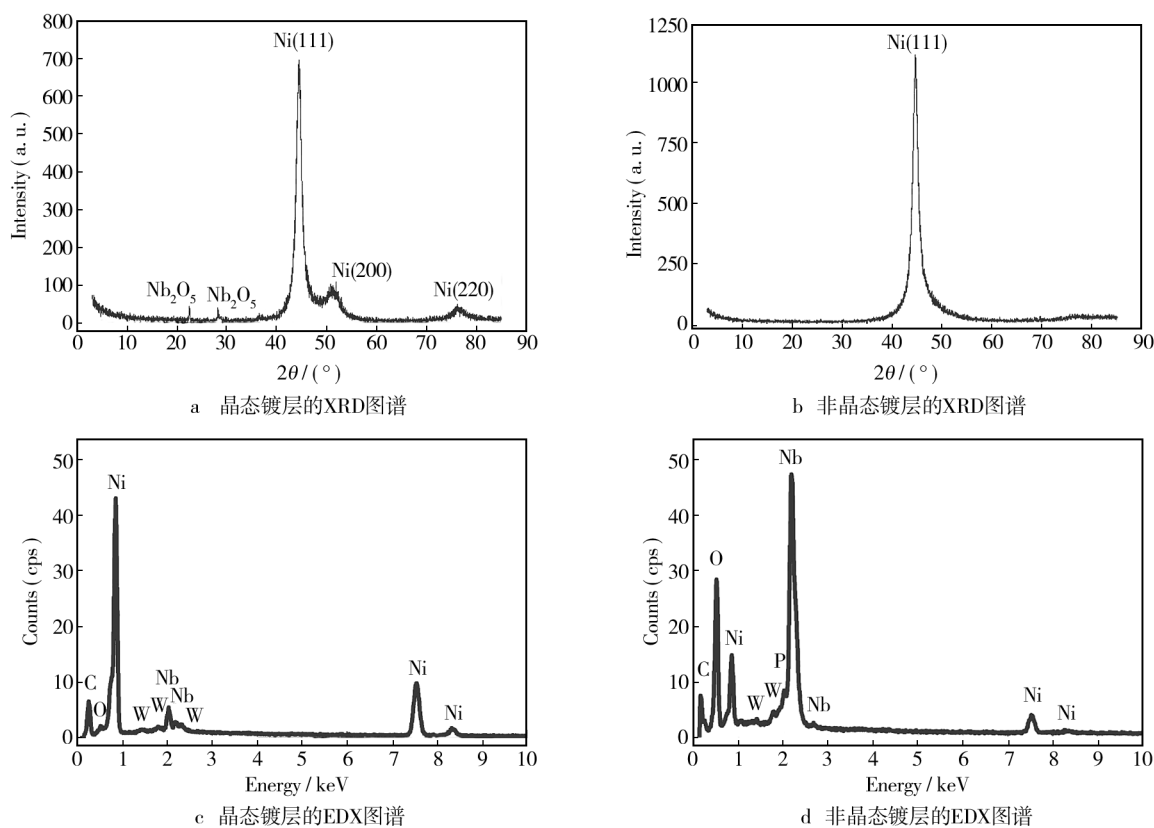


图5 晶态和非晶态Ni-W-P/ Nb_2O_5 复合镀层的XRD和EDX图谱

Fig. 5 XRD and EDX patterns of Ni-W-P/ Nb_2O_5 composite coatings: a) XRD pattern of crystalline coating,

b) XRD pattern of amorphous coating, c) EDX pattern of crystalline coating, d) EDX pattern of amorphous coating

2.4 复合镀层的耐腐蚀性能

通过腐蚀失重法对制备的 Nb_2O_5 颗粒增强Ni-W-P合金镀层进行耐腐蚀性能测试,过程为:有机溶剂清洗→干燥→表面积测量→称量→腐蚀后冲洗→

无水乙醇脱水→干燥→称量。计算腐蚀前后单位时间、单位面积内的质量变化,作为镀层的腐蚀速率。

图6为晶态和非晶态 Nb_2O_5 颗粒增强Ni-W-P合金镀层的腐蚀速率随镀液中颗粒浓度的变化关系。总体上看,在相同颗粒浓度条件下获得的非晶态镀层

的腐蚀速率比晶态镀层低,这是由于非晶态 Ni-W-P 合金的耐腐蚀性能优于晶态 Ni-W-P 合金。对于晶态或者非晶态镀层,由于 Nb₂O₅ 陶瓷颗粒在酸、碱等腐蚀环境中具有良好的化学稳定性,因而使得复合镀层的耐腐蚀性能得到进一步改善,随着镀层中 Nb₂O₅ 陶瓷颗粒的增多,腐蚀溶液与合金的接触面减小,因此腐蚀失重减小,镀层的耐腐蚀性能逐渐增强。从耐腐蚀速率的变化规律上看,随着镀液中 Nb₂O₅ 颗粒质量浓度由 5 g/L 增加到 15 g/L,晶态和非晶态复合镀层的化学腐蚀速率均明显下降;当 Nb₂O₅ 颗粒质量浓度由 15 g/L 增加到 20 g/L 时,化学腐蚀速率的下降变得缓慢。

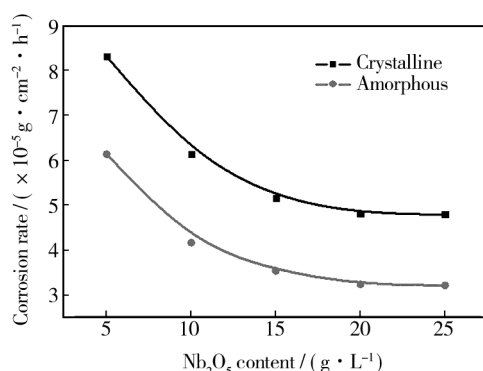


图6 Ni-W-P/Nb₂O₅ 复合镀层在 10% HNO₃+90% 酒精溶液中的腐蚀速率

Fig. 6 Corrosion rates of Ni-W-P/Nb₂O₅ coatings in 10% HNO₃+90% ethanol solution

3 结论

1) 采用化学镀制备了完全覆盖 NdFeB 基体表面的晶态和非晶态 Nb₂O₅ 颗粒增强 Ni-W-P 合金复合镀层。两种复合镀层中 Nb₂O₅ 颗粒的含量均随镀液中颗粒浓度的增加而呈增加趋势,且颗粒弥散分布于 Ni-W-P 合金中。

2) 随着镀液中 Nb₂O₅ 颗粒质量浓度由 5 g/L 增加到 15 g/L,晶态和非晶态复合镀层的化学腐蚀速率均明显下降;当 Nb₂O₅ 颗粒质量浓度由 15 g/L 增加到 20 g/L 时,化学腐蚀速率的下降变得缓慢。

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