

铁基非晶涂层的研究进展与应用

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摘要: 铁基非晶涂层可突破尺寸及室温脆性限制, 其优异的力学性能可改善基体材料表面性能, 有效拓展铁基非晶合金应用范围。针对非晶合金成分设计准则进行了较为系统的总结, 归纳了铁基非晶涂层材料体系, 介绍了铁基非晶涂层常用的制备技术, 分析了热喷涂和激光熔覆技术对非晶涂层力学性能的影响。综述了铁基非晶涂层耐磨性和耐蚀性的研究现状。影响涂层性能的原因是多方面的, 其制备工艺、元素组成、非晶含量、孔隙率、表面粗糙度、硬度及对涂层的后续处理等因素均会对涂层性能产生影响, 并分别针对涂层的耐磨性和耐蚀性进行详细阐述。在此基础上, 提出高摩擦因数是保证工作人员在甲板正常工作的前提, 针对国内研究现状, 开发制备出更多可同时兼具高耐磨性和高耐蚀性的铁基非晶涂层体系是突破技术封锁的关键问题。讨论了铁基非晶涂层在军事、航天、海洋防护、核工业、储燃及其他工程设备上应用的前景, 介绍了铁基非晶涂层的应用现状及目前存在的问题, 并在最后展望了铁基非晶涂层的发展方向。

关键词: 铁基非晶涂层; 制备技术; 性能; 应用

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Research Progress and Application of Fe-based Amorphous Coatings

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ABSTRACT: Fe-based amorphous alloys have exceptional properties, such as high strength, high hardness, good wear resistance, and corrosion resistance, and have important applications in the fields of tribology and corrosion resistance. However, the relatively poor glass-forming ability of Fe-based amorphous alloys and their inability to be prepared in large

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blocks at room temperature due to their brittleness greatly limit their application as bulk materials. To effectively address this problem, the excellent properties of Fe-based amorphous alloys can be demonstrated in the form of coatings. The Fe-based amorphous coating can overcome the restrictions of size and room temperature brittleness, and its excellent properties such as high wear resistance and high corrosion resistance will be well utilized. This will improve the surface properties of the matrix material and significantly widen the range of applications for Fe-based amorphous alloys.

This paper summarized the design criteria for amorphous alloy components and coating material systems in a more systematic way. The influence mechanism of thermal spraying and laser cladding technology on the properties of Fe-based amorphous coatings was analyzed, and the progress of research and application of wear resistance and corrosion resistance of Fe-based amorphous coatings were reviewed. The prospect of Fe-based amorphous coatings with high wear and corrosion resistance for application on aircraft carrier flight deck and other engineering was also discussed. In addition, the current application status and problems with Fe-based amorphous coatings were introduced, and it is predicted where they will go in terms of future development.

An amorphous alloy is a type of metastable material that is extremely sensitive to composition. A slight variation in composition can result in a significant difference in glass-forming ability. Various compositional design criteria for amorphous alloys have been proposed and applied to improve the glass-forming ability. The incorporation of multiple metallic elements can improve the Fe-based amorphous formation ability due to their size differences and different negative mixing enthalpies, resulting in an increase in the entropy and long-range disorder of the system, which improves the amorphous formation ability.

There are various factors affecting the wear and corrosion resistance of the coatings, such as the preparation process, elemental composition, amorphous content, porosity, surface roughness, hardness, and subsequent treatment of the coatings. The SAM series of Fe-based amorphous coatings has been developed abroad. On this basis, the non-skid deck coating for the warship has been developed. Due to the innovation in the spraying method, the surface of the coating after spraying has a special texture, and the coating has a high coefficient of friction, high abrasion resistance, impact resistance and corrosion resistance that are all superior to the existing organic non-skid coating. The high coefficient of friction is necessary to ensure that employees can perform their jobs on the deck normally. The main challenge to breaking through the technical blockade is the development and preparation of more Fe-based amorphous coating systems with high wear resistance and corrosion resistance, given the current state of domestic research. In China, the plungers of water injection pumps have already been coated with Fe-based amorphous materials by businesses, and the wear resistance is still strong even in extremely corrosive conditions. By applying the same Fe-based amorphous coating to boiler water-cooled wall panels, the equipment can have a 10-fold increase in service life. Currently, Fe-based amorphous coatings are used in the military, aerospace, marine protection, nuclear industry, storage and combustion, tunnel boring machines, boiler wall protection, and other fields.

KEY WORDS: Fe-based amorphous coating; fabrication technology; properties; application

非晶合金 (Amorphous Alloy) 是一种新型金属材料, 有着金属玻璃 (Metallic Glass) 的称号, 非晶合金具有多种特性, 既具有金属特性和玻璃特性, 又具有固体和液体特性等^[1]。1959 年, Duwez 等^[2]第一次尝试利用熔体急冷技术制备出 Au-Si 非晶合金。研究发现, 该非晶合金的原子结构与晶体结构不同, 即长程无序、短程有序。非晶合金的化学、物理和机械性能表现优秀, 因而得到重点关注^[3]。其中, 铁基非晶合金具有优异的机械与化学性能, 在超疏水自清洁^[4]、化学降解^[5-6]、抗冲击断裂^[7]、超精密机械^[8]、医学^[9]、生物^[10]、军事^[11]及海洋^[12]等方面均有广泛的应用前景。受限于铁基非晶合金的玻璃形成能力 (Glass Formation Ability, GFA) 和制备工艺等因素, 一般情况下, 铁基非晶合金的存在形式为粉末或者薄

带等, 仅有少数铁基非晶合金的临界尺寸可达到厘米级别^[13], 且通常具有较高的常温脆性, 作为块体材料的应用受到制约。1981 年, Miura 等^[14]采用火焰喷涂技术首次在水冷铜板上制备了 $(\text{Fe}_{1-x}\text{Ni}_x)_{80}\text{P}_{14}\text{B}_6$ ($0.1 \leq x \leq 0.9$) 非晶涂层。采用涂层的方式可解决室温脆性及非晶合金尺寸限制问题, 并且附着于基体材料表面可使铁基非晶合金的高强度、高硬度和表现优异的耐磨/耐蚀性得以展现, 基体材料的表面性能可明显改善。

本文对铁基非晶涂层近年来的发展情况进行梳理。总结了非晶合金成分的设计方法与制备涂层技术, 涂层的耐磨性和耐蚀性的最新研究进展, 介绍了目前铁基非晶涂层的应用现状以及现阶段制备的涂层所存在的问题, 最后展望了铁基非晶涂层未来的发展方向。

1 非晶合金成分设计

非晶合金作为一种亚稳态材料,具有较强的成分敏感性,成分的微量变化都可能引起玻璃形成能力的巨大差异。在非晶合金的开发过程中,基于早期研究的数据积累,各国学者提出多种非晶合金的成分设计准则,并应用于玻璃形成能力的提高。

Greer^[15]最早提出了“混乱”原则,即大块金属玻璃(Bulk Metallic Glass, BMG)中的GFA倾向于随着合金组元数量的增加而增加。大多数具有较高GFA的铁基非晶合金都是含有4~9种元素的多组元合金。

Inoue等^[16]提出非晶合金能够形成块体的经验三原则:第一个原则是指在非晶合金的元素组成体系中,至少要含有3种不同元素;第二个原则是指在整个非晶合金体系中重要组元之间的原子尺寸比一定要高于12%,这对提升非晶合金的GFA有很大帮助;第三个原则是指非晶合金体系中的重要组元之间要满足负混合焓较大。符合这3条经验原则可在一定程度上提高非晶合金GFA^[3]。

汪卫华等^[17]从合金的微结构、热力学和动力学三方面说明了微合金化元素的加入可增加过冷液体的黏度,降低合金的熔点,减缓晶化相的形核与长大,从而提高合金的GFA^[18]。在微观结构上,加入微合金化的元素可以增加合金中原子的密堆结构;在热力学上,加入微合金化的原子使得熔体在能量上比其他金属熔体更接近结晶态,阻碍晶相的形成;在动力学上,少量微合金化原子的添加使熔体更黏滞。这些是影响合金GFA的主要原因。

类似地,相似原子替换同样会提高GFA。Li等^[19]提出相似原子替换原则,是指在同周期或同主族近邻原子之间的替换。一般认为,过大的原子尺寸差异能够导致元素偏析而促进晶化相的析出,相似原子的替换并不会改变非晶合金的基本结构,只是对其结构进行修饰和微调,降低非晶合金的熔点,因此具有相似性质的元素替换能够有效提高GFA。

这些原则本质上具有相似性。从热力学的角度分析可知,在多组元的铁基非晶合金体系中,因为组元数量的增加会造成更大的混乱度和熵,这样的多组元体系可以促进高温稳定性;从动力学角度分析,多组元往往导致更复杂的晶化竞争相,有利于限制晶体的形核与长大,与共晶点原则的基本思想类似^[20]。合金化元素和铁基非晶合金体系中的基础元素之间有相互作用,并且相互作用较强,也就是有较大的负混合焓,这样可以促进局域结构有良好的稳定性,达到阻碍原子扩散和形成长程有序结构的目的。具有一定尺寸差异的元素有利于结构的密堆性,减少自由体积,提高黏度,从而达到阻碍扩散和提高GFA的目的。一般认为,过强或弱的相互作用和过大的尺寸差异能够导致元素偏析而促进晶化相的析出,因此通常具有

相似性质的元素替换的合金化方法能够有效提高GFA^[20-21]。

除此之外,一些学者从原子结构的角度对非晶合金成分设计方法进行大胆创新。Miracle等^[22]在非晶合金的微观结构基础上提出了“团簇密堆”模型,主要关注不同尺寸原子对密堆结构的影响。董闯等^[23]在此模型基础上,设计出“团簇加连接原子”模型,此模型将每个非晶合金体系中具有最佳GFA合金的平均成分还有结构用团簇式的方式来表达,这样可以对大量块体非晶合金成分进行合理优化。

2 铁基非晶涂层的制备

2.1 制备涂层的材料体系

铁基非晶合金主要基于3种二元合金体系,分别是Fe-B、Fe-P和Fe-C^[24],合金化元素主要包括前过渡族元素(Early Transition Metal, ETM,如Y、Nb、Cr、Mo、W等)、后过渡族元素(Late Transition Metal, LTM,如Mn、Co、Ni等)以及类金属元素(Metalloid, M,如B、P、Si、C等)。简言之,以上3组元素与Fe组成的合金体系可以为Fe-ETM-M、Fe-LTM-M以及Fe-ETM-LTM-M。本文找出一些已经成功制备的并且较为典型的铁基非晶涂层合金体系,如表1所示。

表1 典型的铁基非晶涂层合金体系
Tab.1 Typical Fe-based amorphous coating alloy system

Material system	Composition	Year	Reference
Fe-ETM-M	Fe-(Nb)-(Si,B)	2013	[25]
	Fe-(Nb)-(P,Si,B)	2017	[26]
Fe-LTM-M	Fe-(Cr, Mo)-(C,B)	2016	[27]
	Fe-(Cr, Mo,Ni)-(P, C,B,Si)	2017	[28]
	Fe-(Cr)-(B)	2017	[29]
Fe-ETM-LTM-M	Fe-(Cr,Mo,W,Mn)-(B,Si,C)	2021	[30]
	Fe-(Nb)-(Cr)-(Si,B)	2017	[31]
	Fe-(Nb)-(Co)-(Si,B)	2021	[32]
	Fe-(Y)-(Cr,Mo)-(B,C)	2021	[33]

前过渡族金属因原子半径大,并与Fe及类金属元素间负混合热焓较大,能够与近邻原子形成较强结合能力的近程有序结构,这种结构可增加非晶相形成的倾向。其中,Y、Nb、W与Fe原子半径差异较大,通常作为微合金化元素,含量相对较低;Cr、Mo与Fe原子半径差异相对较小,既可作为相似元素替换,也可以作为微合金化元素。后过渡族金属由于d电子层的屏蔽效应,原子半径随原子序数的变化较小,Mn、Co、Ni等元素与Fe半径相差较小,且性质相似,一般作为相似元素替换。多种类金属元素的加入可提高非晶形成能力,这是由于其尺寸差异以及不同

的负混合热焓, 导致系统的熵值及长程无序性增加, 提高了非晶形成能力。这种“Fe-ETM/LTM-M”型非晶合金体系, 金属与类金属之间的原子键会促进原子团簇更加牢固, 过冷液相的稳定性也随之得到显著提高^[34]。

2.2 铁基非晶涂层常用的制备技术

2.2.1 热喷涂技术

热喷涂技术是利用热源(如电弧、火焰等)将喷涂材料加热至熔化或半熔化状态, 并以一定的速度喷射沉积到经过预处理的基体表面形成涂层的方法, 高温喷涂粒子高速飞行撞击到基体表面, 撞击后粒子形状扁平化, 冷却速率可达 $10^5 \sim 10^7$ K/s, 具有很高的冷却速度^[25]。

超音速火焰喷涂(High Velocity Oxygen Fuel, HVOF)是现阶段较为常用的热喷涂技术。Nayak 等^[35]采用 HVOF 技术制备 FeCrPBC 非晶/纳米晶复合涂层, 发现在非晶涂层上形成分布均匀的纳米晶相, 而此纳米晶相的尺寸和体积分数随送粉率的增加而变小, 得到最低孔隙率为 $(2.9 \pm 0.5)\%$, 非晶含量最高的复合涂层具有较好的耐蚀性。杨曦等^[36]通过 HVOF 制备 $\text{Fe}_{51.1}\text{Cr}_{18.1}\text{Mo}_{30.8}$ 非晶涂层, 其非晶相含量和硬度分别为 94.8% 和 1 159HV0.2, 同时涂层具有较低的孔隙率, 为 1.22%, 其硬度和耐磨性均比基体 316L 不锈钢优异。

等离子喷涂(Air Plasma Spray, APS)是热喷涂技术的一种, 也是热喷涂制备涂层经常使用的技术之一。APS 可产生大于 10^4 K 的火焰温度和 $10^5 \sim 10^7$ K/s 的超高冷却速度, 使热应变程度降低, 有利于形成非晶态涂层。爆炸喷涂(Detonation Spray, DS)也是制备非晶涂层的有效方法, 可显著提高铁基非晶涂层和基体间的黏接强度^[37]。

解路等^[38]在不锈钢基体上分别采用 HVOF、APS 和 DS 技术制备了 $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$ 非晶涂层, 发现 3 种技术制备的涂层非晶含量分别为 85.26%、79.39% 和 88.14%, 孔隙率分别为 1.9%、2.5% 和 1.5%。DS 制备的涂层非晶含量最高、孔隙率最低, 涂层表现出最优异的耐磨性。3 种热喷涂工艺制备的涂层的耐磨性均优于不锈钢基体。

2.2.2 激光熔覆技术

激光熔覆(Laser Cladding, LC)技术是指以不同的填料方式在被涂覆基体表面上放置选择的涂层材料, 经激光辐照使之和基体表面一薄层同时熔化, 并快速凝固后形成稀释度极低并与基体材料成冶金结合的表面涂层。它的能量密度高, 制备的涂层和基体变形小, 其冷却速度可达 10^6 K/s^[39]。

Paul 等^[40]采用 LC 在 AISI 1018 钢基体上制备了

3 种不同结构的 $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{Y}_2\text{C}_{15}\text{B}_6$ 非晶涂层。结果表明, 3 层结构的非晶涂层硬度较其他 2 种最高可达 1 100HV0.3, 单层与双层的硬度仅约为 650HV0.3, 硬度较低。但因 3 层结构的涂层内部存在大量孔洞和裂纹, 导致所制备的涂层耐磨性明显低于单层和双层结构。Ibrahim 等^[41]在 4 种不同粗糙度的基体表面制备了 FeCrMoCB 非晶涂层, 发现基体表面粗糙度会改变涂层本身的非晶含量, 当喷涂表面粗糙度大时, 非晶含量相应提高, 涂层硬度在较光滑表面最高可达 1 278HV0.1。

Zhu 等^[42]在低碳钢基板上采用 LC 制备了厚度为 0.6 mm 的 $\text{Fe}_{34}\text{Co}_{34}\text{B}_{20}\text{Si}_5\text{C}_3\text{Nb}_4$ 非晶涂层。由于 LC 过程中凝固条件极不平衡, 导致熔覆层化学成分和显微组织不均匀, 涂层的硬度与耐磨性出现分层现象。结果表明, LC 涂层的硬度平均值达 1 245HV0.05, 摩擦因数最低可为 0.1(摩擦对偶为 Al_2O_3 陶瓷块), 涂层表现出良好的耐磨性, 但分层现象严重影响了涂层的耐磨稳定性。Liu 等^[43]在碳钢基板表面基于 LC 技术制备了 FeCrNiCoBMoCu 非晶涂层, 涂层厚度为 15 mm。结果表明, 涂层是由富 Fe-Cr 非晶和多种硼化物形成的复合涂层, 且涂层表面的热应力低于基体碳钢。该非晶态复合组织有利于形成具有较强保护作用的 Cr_2O_3 氧化膜, 在高温工作环境中可有效阻止腐蚀性物质向基体内扩散, 从而表现出良好的耐热蚀能力。

3 涂层的耐磨性

铁基非晶涂层的制备工艺、非晶含量、孔隙率及后续处理等因素对涂层的耐磨性会造成直接影响。Li 等^[44]采用 APS 和 LC 分别在 45 钢基体表面制备 FeCrMoCB 体系非晶涂层。摩擦磨损数据中, 基体 45 钢、LC 和 APS 涂层表面的磨损面积分别为 67 000、4 800、6 800 μm^2 。2 种工艺制备的非晶涂层的磨损量为基体的 1/10 左右, 而 APS 制备的涂层表现出最优异的耐磨性。Zhou 等^[45]在 HVOF 喷涂中, 通过同步喷丸方式, 将 ZrO_2 陶瓷颗粒注入火焰低温区强化 $\text{Fe}_{69}\text{B}_{22}\text{Si}_5\text{Nb}_4$ 非晶涂层。结果表明, 该工艺不仅提高了非晶涂层的致密性和硬度, 降低其残余应力, 同时明显提高其耐磨性。在低负荷、低频率磨损试验条件下, 喷丸处理和未喷丸处理涂层的磨损机理均为磨粒磨损与氧化磨损相结合。当喷丸速率为 50 g/min 时, 涂层的磨损率是未喷丸涂层的 1/3。

Nayak 等^[46]发现粉末进给率越高, 制备的铁基非晶/纳米晶复合涂层的硬度越高, 耐磨性越好。主要是由于高速率降低了玻璃化程度, 使非晶内键结合更好, 生成的纳米晶 α -Fe 相减少。由于较软的纳米晶 α -Fe 相体积分数的降低, 在提高进给速率时, 复合涂层的耐磨性增加。当粉末进给速率为 50 g/min 时,

复合涂层的非晶相含量最高,为81%,摩擦因数由 0.23 ± 0.04 (进给率15 g/min)降低到 0.13 ± 0.01 (摩擦对偶为 $\phi 25$ mm Al_2O_3 磨球)。Li等^[47]利用爆炸喷涂制备了FeCrMoCB非晶涂层,发现涂层与粉末具有几乎相同的宽峰形非晶形貌,表明在喷涂过程中没有明显的结晶行为,涂层中存在大量完整的非晶组织(图1a)。因此涂层保持着良好的耐磨性,其磨损率是基体的1/6,涂层摩擦因数(摩擦对偶为 $\phi 6$ mm Si_3N_4 磨球)比基体稳定且小,为0.71(图1b)。

Liang等^[48]制备了 $\text{Al}_2\text{O}_3/\text{FeBSiNb}$ 和 $\text{Al}_2\text{O}_3/\text{FeCrBSiNb}$ 铁基非晶复合涂层。结果表明,当 Al_2O_3 的质量分数为30%时,涂层致密,孔隙率仅为0.5%,涂层耐磨性好。Xie等^[49]制备了FeCrMoCBY和FeCrBSiCuMoCuNi 2种非晶涂层,发现通过增加非晶相含量,降低涂层孔隙率,可获得硬度高、磨损率低

的铁基非晶涂层。涂层的磨损机理不是固定不变的,非晶含量和孔隙率的不同都会对磨损机理造成影响。当涂层非晶含量在81.32%以下时,涂层的主要磨损机制会变成黏着磨损;当非晶含量在84.35%以上时,主要为疲劳磨损;同时,高孔隙率($\geq 2.1\%$)导致了严重的疲劳磨损(图2)。氧化磨损发生在整个摩擦过程中,特别是随着Fe、Cr、Mo等金属含量的增加,铁基非晶涂层发生严重的氧化磨损。Li等^[50]分别在150℃和250℃下,对FeCrMoCB非晶涂层进行热处理。结果表明,低温热处理后的涂层均为非晶结构,且热处理后涂层孔隙率低于未退火非晶涂层。当热处理温度为250℃时,涂层孔隙率降低到0.5%,此时非晶涂层的磨损率最低,为 $4.3 \times 10^{-6} \text{ mm}^3/(\text{N} \cdot \text{m})$,耐磨性显著提高,比未处理非晶涂层提高了2个数量级。

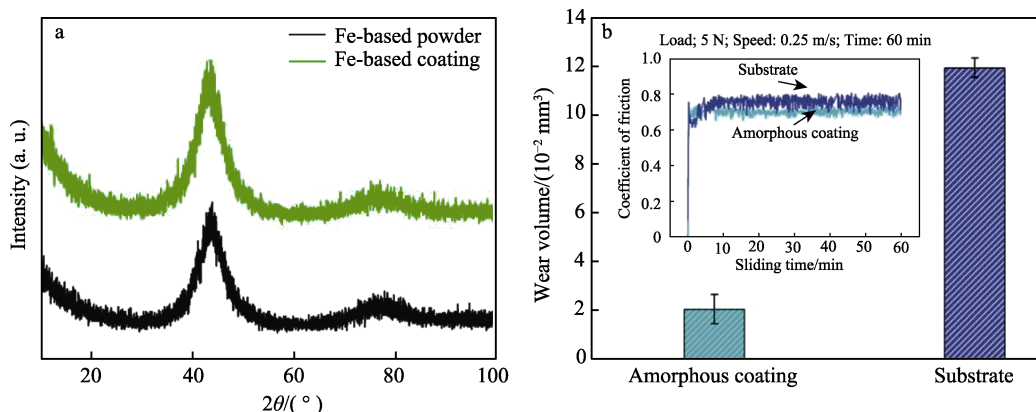


图1 FeCrMoCB非晶粉末与喷涂态涂层的XRD比较(a)和涂层与9Ni钢基体的磨损率与摩擦因数比较(b)^[47]

Fig.1 XRD comparison of FeCrMoCB amorphous powder and spray coating and comparison of wear rate and friction coefficient between the coating and 9Ni steel substrate^[47]: a) XRD of the Fe-based amorphous feedstock powders and as-sprayed coating; b) wear volume and coefficient of friction of the Fe-based amorphous coating and 9Ni steel substrate at normal load of 5 N and sliding speed of 0.25 m/s

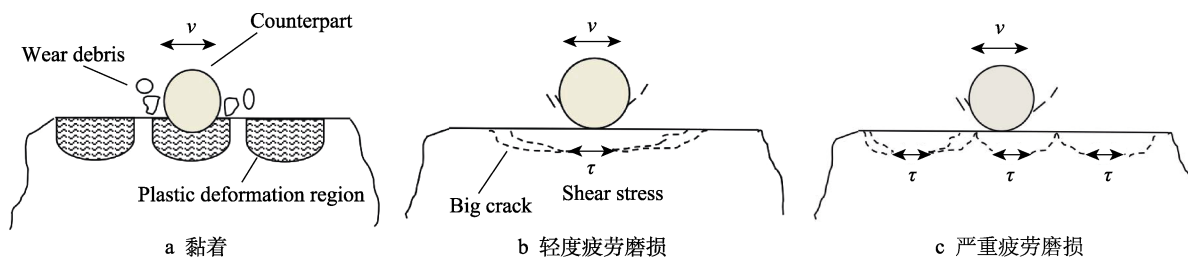


图2 铁基非晶涂层的磨损机理^[49]

Fig.2 Schematic illustrations of the wear mechanisms of Fe-based amorphous coatings^[49]: a) adhesive wear; b) mild fatigue wear; c) serious fatigue wear

4 涂层的耐蚀性

在铁基非晶合金体系中,具有钝化能力的金属元素和过饱和准金属元素可促进表面氧化膜形成,阻碍离子传输,从而提高涂层的耐蚀性^[51]。非晶含量、孔隙率、制备工艺及涂层表面疏水性等因素对非晶涂

层的耐蚀性同样有重要影响。王勇等^[52]研究了FeCrMoMnWBCSi非晶涂层在NaCl和 H_2SO_4 2种溶液中的钝化行为,发现钝化膜中存在Cr、Mo及W的氧化物,由于钝化区间宽,钝化膜结构稳定可靠,但孔隙的存在会一定程度降低涂层的耐蚀能力。Tian等^[53]利用热喷涂制备了高铬成分的非晶涂层 $\text{Fe}_{49.7}\text{Cr}_{18}\text{Mn}_{1.9}\text{Mo}_{7.4}\text{W}_{1.6}\text{B}_{15.2}\text{C}_{3.8}\text{Si}_{2.4}$,并与SAM2X5

型非晶涂层进行对比。结果表明, SAM2X5 表现出更加稳定的钝化区间, 且在恒电位极化条件下, 表现出更低的自腐蚀电流密度。此外, 对 Mo、W、Mn 和 Cr 元素在钝化膜中的作用进行了系统分析。发现在相对比较低电势下, Mo 和 W 元素有利于形成钝化膜, 且钝化膜的成分主要为 Cr_2O_3 ; 在相对较高的电势下, Mn 元素可增强涂层的钝化能力, 提高其稳定性。

Liu 等^[54]利用低压等离子喷涂技术制备了 $\text{Fe}_{62}\text{Ni}_3\text{Cr}_4\text{Mo}_2\text{W}_3\text{Si}_6\text{B}_{17}\text{C}_3$ 非晶涂层, 涂层在中性和强酸溶液中的耐蚀性效果均佳, 得到涂层致密性对耐蚀性有显著影响的结论。Zhang 等^[55]研究了铁基非晶涂层的耐蚀性与孔隙率的关系, 结果显示, 高孔隙率导致的孔隙贯通是基体优先腐蚀的主要原因。Zhou 等^[56]发现当铁基非晶涂层孔隙率低于 1.22% 时, 涂层的非晶含量相比于孔隙率, 对涂层耐蚀性造成更大的影响。

田芳等^[57]以 CO_2 为载流气体, 利用电弧喷涂技术制备了厚度为 200 μm 的 FeCrBNi 非晶涂层, 探究了非晶涂层耐蚀性与载流气体和喷涂距离之间的关系。由于 CO_2 抑制了晶化, 使非晶含量有一定程度的增加。同时, 喷涂距离的增加使涂层的非晶含量降低, 从而降低了耐蚀性。所以选择适当的喷涂距离对涂层耐蚀性的影响非常重要。Cui 等^[58]在不同氧燃料比 (2.5、2.0 和 1.7) 下, 利用爆炸喷涂制备了 FeCrMoCB

非晶涂层。微观形貌表明, 在氧燃料比为 2.0 时, 涂层致密度最高, 孔隙率约为 0.5%, 自腐蚀电流密度最低为 $5.14 \mu\text{A}/\text{cm}^2$, 涂层耐蚀性良好。Zhang 等^[59]研究了喷涂粉末粒度与 $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ 非晶涂层耐蚀性的关系。结果表明, 原料粉末的粒度对涂层的组织形貌和耐蚀性有显著影响。喷涂粉末最细的涂层结构最致密, 而粉末较粗的涂层具有较好的耐蚀性能。因此, 发现涂层的耐蚀性与涂层的润湿行为密切相关, 即疏水性越强, 涂层的耐蚀性越好 (图 3), 而润湿行为^[60]由涂层的含氧量和粗糙度共同作用。在一定范围内, 较高的粗糙度 (涂层表面凹坑深度大于 0.5 μm) 和较少的氧含量会增强涂层表面的疏水性^[61], 疏水性的提高可阻止涂层与离子接触, 从而产生更好的耐蚀作用。但如果涂层孔隙大到可以吸收水溶液, 则耐蚀性会急剧恶化。

赵仁亮等^[62]根据 Inoue 经验原则, 设计了 Fe-Cr-Ni-Mo-B-Si 非晶合金体系, 通过超音速电弧喷涂技术制备一系列铁基非晶合金涂层, 发现涂层非晶含量的增加会降低涂层孔隙率, 硬度越高时, 涂层与钢基体结合越强, 涂层耐蚀性得到提高。但为了兼顾涂层综合性能, 适当降低涂层非晶含量, 涂层摩擦因数增大, 耐磨性增强。随着体系中 Cr、Ni、B、Si 含量变化, 合金熔点发生改变, 当合金体系熔点升高时, 涂层非晶形成能力降低, 粒子熔融不完全导致涂

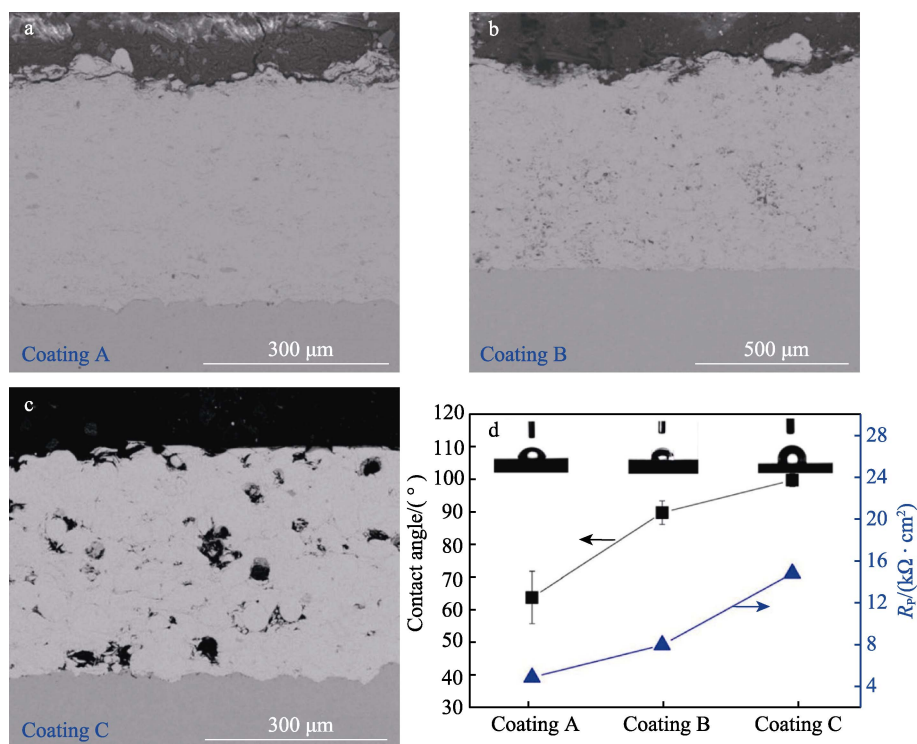


图 3 不同 $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ 铁基非晶涂层的截面形貌 (a—c) 及不同涂层疏水性与耐蚀性的关系 (d)^[59]

Fig.3 The cross section morphology of different $\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$ amorphous coatings (a-c) and the relationship between hydrophobicity and corrosion resistance of different coatings (d)^[59]

层表面粗糙,摩擦因数增大,防滑性增强。同时,非晶形成能力降低导致涂层中弥散分布的纳米晶硬质相 Ni_2SiO_4 含量增加,提高了涂层耐磨性。当非晶含量为 46.3% 时,铁基非晶合金涂层的摩擦因数为 1.0; 当非晶含量为 22.4% 时,涂层摩擦因数高达 1.32 (摩擦对偶为氯丁橡胶条)。因此,铁基非晶涂层摩擦因

数的提高,需要适当牺牲耐蚀性来达到指标。

目前,有报道的高摩擦因数的铁基非晶涂层主要集中在 0.57~0.79,如表 2 所示。具有高摩擦因数(0.85 以上)的铁基非晶涂层在航母甲板领域有着重要应用,高摩擦因数是保证工作人员在甲板可以正常工作的前提。

表 2 典型铁基非晶涂层的摩擦因数
Tab.2 Friction coefficient of typical Fe-based amorphous coatings

Composition	Coefficient of friction	The friction counter body	Prepared methods	Year	Reference
$\text{Fe}_{45.8}\text{Mo}_{24.2}\text{Cr}_{14.7}\text{Co}_{7.8}\text{C}_{3.2}\text{B}_{4.3}$	0.11	Si_3N_4 ($\phi 4$ mm)	Laser cladding	2018	[63]
$\text{Fe}_{32}\text{Cr}_{16}\text{Mo}_{12}\text{B}_{20}\text{Si}_{20}$	0.57	Si_3N_4 ($\phi 6.35$ mm)	Laser cladding	2020	[64]
$\text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Y}_2$	0.60	GCr15 (frictional ring of $\phi 49.22$ mm)	High velocity oxygen fuel	2010	[65]
$\text{Fe}_{49}\text{Cr}_{17.8}\text{Mo}_{7.2}\text{Mn}_{1.8}\text{W}_{1.6}\text{B}_{15.4}\text{C}_{4.6}\text{Si}_{2.5}$	0.60-0.65	GCr15/ Al_2O_3 ($\phi 9.525$ mm)	High velocity oxygen fuel	2015	[66]
$\text{Fe}_{69}\text{B}_{22}\text{Si}_5\text{Nb}_4$	0.74	Si_3N_4 ($\phi 4$ mm)	High velocity oxygen fuel	2020	[45]
$\text{Fe}_{63}\text{Cr}_8\text{Mo}_{3.5}\text{Ni}_5\text{P}_{10}\text{B}_4\text{C}_4\text{Si}_{2.5}$	0.79	Al_2O_3 ($\phi 9$ mm)	Activated combustion-high Velocity air fuel	2017	[67]
$\text{Fe}_{45}\text{Cr}_{19}\text{Ni}_6\text{Mo}_{10}\text{B}_8\text{Si}_{12}$	1-1.32	Chloroprene rubber strip (60 mm×60 mm)	Supersonic arc spraying	2019	[62]
$\text{Fe}_{\text{balance}}\text{Cr}_{25-27}\text{Mo}_{16-18}\text{C}_{2.0-2.5}\text{B}_{2.0-2.2}$	0.71	Si_3N_4 ($\phi 6$ mm)	Detonation spray	2020	[47]

5 铁基非晶涂层的应用现状

5.1 航母上的铁基非晶涂层

海水本身具有很强的腐蚀性,航空母舰长期在海上执行任务,面临潮湿的盐雾海洋大气环境的侵蚀,同时承受着飞机起降对航母甲板的反复冲击,只有兼具高耐磨性、高耐蚀性以及各阶段都能保证良好防滑能力的甲板涂层才能保证航空母舰的正常服役。

现阶段航母甲板表面主要涂覆有机涂层(环氧树脂或聚氨酯)或者金属基陶瓷涂层作为甲板表层。传统有机涂层虽然耐蚀性高、韧性好,但耐磨性、耐高温性和耐紫外线能力差,限制了有机涂层在甲板上的推广应用。金属基陶瓷涂层与甲板钢材有着优异的结合强度与耐磨性,但是耐蚀性差。铁基非晶涂层同时具备有机涂层与金属基涂层两者的优点,是未来航母飞行甲板涂层的重要研究方向。

2003 年,美国国防高级研究计划局、国防科学办公室和美国能源部民用和放射性废物管理办公室共同提出高性能耐腐蚀材料项目,开发了一系列非晶态铁基金属材料,并准备以涂层的形式应用于海洋腐蚀防护。在该项目支持下,研发出比较知名的如 SAM2X5 ($\text{Fe}_{49.7}\text{Cr}_{17.7}\text{Mn}_{1.9}\text{Mo}_{7.4}\text{W}_{1.6}\text{B}_{15.2}\text{C}_{3.8}\text{Si}_{2.4}$) 和 SAM1651 (又称 SAM7, $\text{Fe}_{48}\text{Mo}_{14}\text{Cr}_{15}\text{Y}_2\text{C}_{15}\text{B}_6$), 此外还有其他性能优异的非晶涂层,如 SAM35 ($\text{Fe}_{54.5}\text{Mn}_2\text{Cr}_{15}\text{Mo}_2\text{W}_{1.5}\text{B}_{16}\text{C}_4\text{Si}_5$)、SAM40 ($\text{Fe}_{52.3}\text{Mn}_2\text{Cr}_{19}$ -

$\text{Mo}_{2.5}\text{W}_{1.7}\text{B}_{16}\text{C}_4\text{Si}_{2.5}$)、SAM6 ($\text{Fe}_{43}\text{Cr}_{16}\text{Mo}_{16}\text{B}_5\text{C}_{10}\text{P}_{10}$) 以及 SAM10 ($\text{Fe}_{57.3}\text{Cr}_{21.4}\text{Mo}_{2.6}\text{W}_{1.8}\text{B}_{16.9}$) 等一系列铁基非晶涂层,其中 SAM2X5 和 SAM1651 的耐腐蚀性是不锈钢及镍金属的 4~5 倍,且具有优秀的耐磨性^[68]。

在此项目基础上美国军方成功制备出一种铁基非晶涂层,并将其作为舰船甲板防滑涂层,美国军方在喷涂方式上有创新,喷涂后的涂层表面有特殊的纹理,涂层摩擦因数高,耐磨损能力强、抗冲击和耐腐蚀性能均比现有的有机防滑涂料优秀^[11]。

5.2 核工业防护领域应用的铁基非晶涂层

SAM2X5、SAM10 和 SAM35 等高 B 成分的铁基非晶涂层有利于玻璃形成和中子吸收,该特性使非晶涂层在核废料和高放射性废物运输、老化和处置容器等^[69]方面有着实际的应用(图 4)。核废料储存罐内壁对于核废料的核辐射屏蔽起到至关重要的作用,现阶段该技术相对成熟,制备的 SAM2X5、SAM10 和 SAM35 等涂层已成功用于储存罐内壁。在该涂层的保护下,存储罐寿命得到大大提高,可持续防护 4 000 年。其中, SAM2X5 中子吸收能力尤为突出,是不锈钢和镍基高温合金的 7 倍,比硼化不锈钢高 4 倍,甚至比添加 Gd 的镍基合金高 2 倍^[70](图 5)。在核废料存储罐表面喷涂铁基非晶涂层,其优秀的中子吸收能力可以使存储废核燃料等放射性物质实现长周期安全有效。

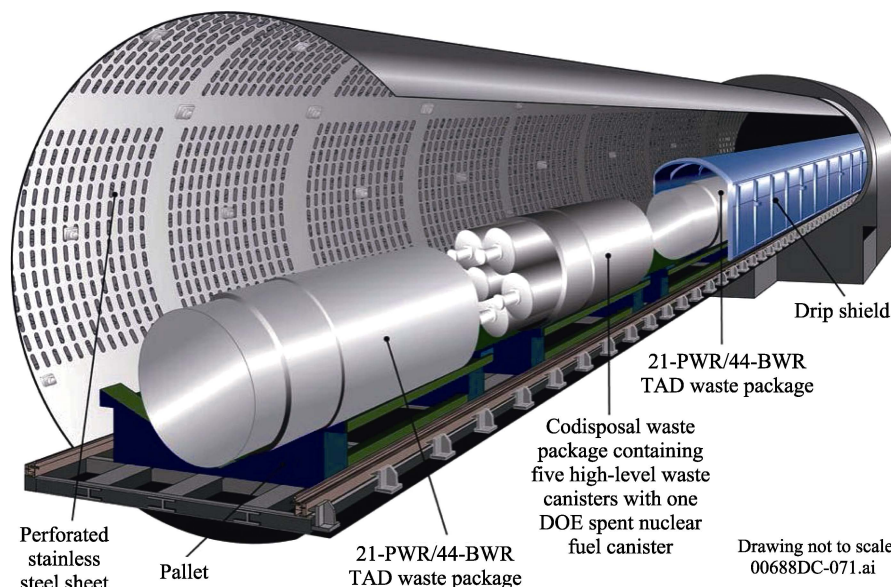


图 4 高放射性废料包三维示意图 (在防护罩外部的 SAM 系列涂层可以提高存储库的性能) [69]

Fig.4 Three-dimensional diagram of the HIGH-LEVEL waste package (SAM series coating on the outside of the shelter can improve the performance of the repository) [69]

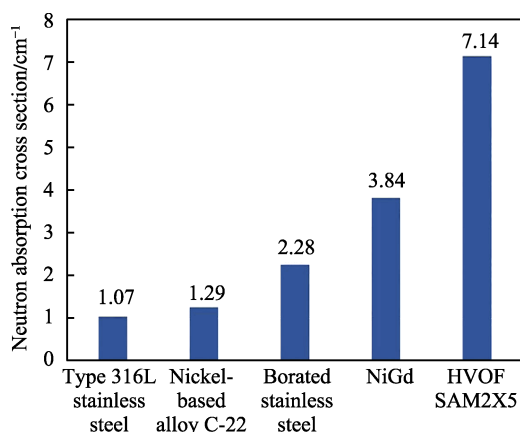


图 5 316L 型不锈钢、镍基合金 C-22、硼化不锈钢、NiCrMoGd 合金和 SAM2X5 透射中子吸收截面的测量平均值 [70]

Fig.5 Average measured values of the neutron absorption cross section in transmission for type 316L stainless steel, Nickel base alloy C-22, borated stainless, a Ni-Cr-Mo-Gd alloy and SAM2X5 [70]

5.3 其他领域的铁基非晶涂层

Khanolkar 等 [71] 基于 SAM 系列合金研发出 SAM2X5-630 ($\text{Fe}_{49.7}\text{Cr}_{17.7}\text{Mn}_{1.9}\text{Mo}_{7.4}\text{W}_{1.6}\text{B}_{15.2}\text{C}_{3.8}\text{Si}_{2.4}$) 非晶合金, 其弹性极限为 (11.76 ± 1.26) GPa, 该特性可用在防弹衣或者航天器护盾等领域。SAM2X5 硬度可达 $1\,100 \sim 1\,300\text{HV}$ [68], 该成分铁基非晶涂层已在隧道掘进机的圆盘切割机上成功应用。

国内, 科盾工业设备制造 (天津) 有限公司将铁基非晶涂层应用在中石油某企业生产的注水泵柱塞, 涂层结合强度可达 70 MPa, 孔隙率小于 1%, 实际运行 12 个月后发现高腐蚀环境下其耐磨性保持非常

好, 设备使用寿命至少提高了 5 倍 [72]。同样, 内蒙古华电乌达热电有限公司, 将铁基非晶涂层应用到锅炉水冷壁面板, 设备运行 26 个月后, 非晶涂层仍未失效, 平均厚度约为原始涂层的 70%。锅炉水冷壁上的铁基非晶涂层在正常工况下, 服役时间能够达到 5 a 以上, 是其他常规的合金材料涂层服役寿命的 10 倍左右。铁基非晶合金涂层的出现解决了该电厂水冷壁管磨损难题, 提高了生产安全性, 节约了大量成本 [73-74]。广西柳州发电有限责任公司运用超音速电弧喷涂技术在煤粉炉的水冷壁上制备出铁基非晶涂层, 工作 1 a 后铁基非晶涂层厚度保持原始厚度 89%, 水冷壁可以安全使用 5 a 以上, 设备寿命同样得到明显提高 [74]。

此外, 铁基非晶涂层还在螺旋泵螺杆修复 (图 6a)、高压球阀修复 (图 6b)、叶轮修复 (图 6c) 等方面得到应用。铁基非晶涂层的高耐磨性和高耐蚀性可有效提高设备使用寿命, 降低运维成本, 可应对

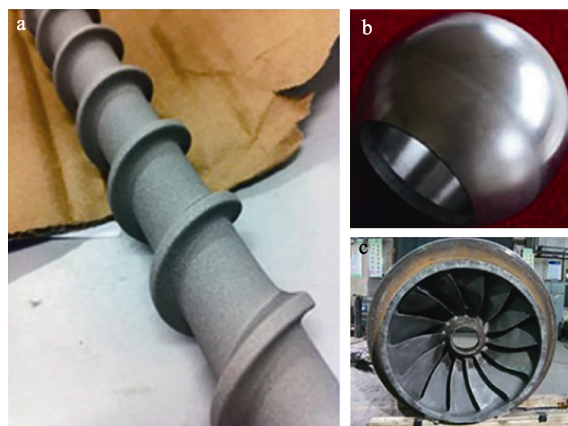


图 6 铁基非晶涂层的几种应用 [70]

Fig.6 Several applications of Fe-based amorphous coatings [70]

复杂工况环境下装备的现实问题,得到制造与再制造业的认可。

6 总结与展望

铁基非晶涂层在军事、航天、海洋防护、核工业、储燃、隧道掘进机、锅炉等领域均有应用。目前针对铁基非晶涂层的应用研究主要集中在以下 3 个方面:

1) 目前已开发铁基非晶的玻璃形成能力已基本满足涂层制备的需求,针对形成能力的成分设计不再是研究重点。未来铁基非晶涂层的成分设计应服务于 2 个方面:基于成分调控的性能设计,以满足具体应用场景的性能指标要求;元素有效利用方法,以提高低纯度原料的适用性,到达降低制备成本的目的。

2) 铁基非晶涂层的制备技术日趋成熟,热喷涂技术可实现涂层非晶含量与原始粉末非晶含量的同步性,涂层的综合性能得到显著提高。那么,只要保证非晶粉末的质量,如降低非晶成分粉体氧含量,控制 S、P 等杂质的含量,控制粉末适当的流动性,可在保证铁基非晶涂层非晶含量的前提下提高涂层的综合性能。

3) 铁基非晶涂层的制备工艺、非晶含量、孔隙率、后处理方法、钝化元素的协同作用及涂层表面疏水性等因素直接影响涂层的综合性能。而设计制备兼具低孔隙率、高非晶含量、高结合强度、高耐磨和高耐蚀的铁基非晶涂层应该成为今后追求的性能指标。目前国际主流报道的铁基非晶涂层的摩擦因数主要在 0.57~0.79 之间。针对国内研究情况,开发制备出更多可同时兼具高耐磨和高耐蚀的铁基非晶涂层体系是突破技术封锁的关键。

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