

Al 基准晶薄膜/涂层研究进展*

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摘要: 准晶材料固有脆性限制其作为结构性材料的应用,广泛用于表面薄膜/涂层,而得到高纯度准晶相与控制准晶相变仍是应用难点。围绕 Al 基准晶在表面薄膜/涂层应用方面,介绍真空蒸镀、溅射镀膜、热喷涂、激光熔覆等常用制备工艺,总结各工艺的特点。分析准晶薄膜/涂层的成分、冷却速度、热处理对准晶相变的影响,合理的制备工艺和适当的后续热处理对薄膜/涂层中形成高纯度准晶有显著提升。讨论相变对薄膜/涂层的力学性能、疏水性、摩擦性、耐腐蚀性和抗氧化性的影响,分析准晶薄膜/涂层在减磨耐磨涂层、热障涂层、太阳能选择性吸收薄膜等领域的应用前景。综述了近 30 年准晶薄膜/涂层的制备技术及改性研究的重要结果和研究现状,提出了准晶薄膜/涂层应用方面存在的问题并进行了展望。

关键词: 准晶材料; 薄膜/涂层; 制备技术; 相变; 应用

中图分类号: TG156;TB114

Research Progress on Al-based Quasicrystal Films/coatings

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Abstract: The inherent brittleness of quasicrystal materials limit their application as structural materials, so they are widely used in surface films/coatings. However, it is still difficult to obtain high purity quasicrystal phase and control the transformation. In terms of Al-based quasicrystal on surface film/coating applications, the common techniques for the preparation such as vacuum vapor deposition, sputtering coating, thermal spraying, and laser cladding were introduced, and the characteristics of each techniques were summarized. The effects of the composition, cooling rate, and heat treatment on the phase transition of quasicrystal films/coatings were analyzed. Reasonable preparation process and appropriate subsequent heat treatment can significantly improve the formation of high purity quasicrystals in the film/coating. The effects of phase transformation on the mechanical properties, hydrophobicity, tribability, corrosion resistance and oxidation resistance of the films/coatings were discussed. The application prospects of quasicrystal films/coatings in the fields of wear reduction and wear resistance, thermal barrier coatings and solar selective absorption films were analyzed. The important results and research status of preparation technology and modification of quasicrystal films/coatings in recent 30 years were reviewed. The existing problems in application of quasicrystal films/coatings and prospects in the future were put forward.

Keywords: quasicrystal materials; film/coating; preparation technology; phase transformation; application

0 前言

1984 年以色列科学家 SHECHTMAN 等^[1]在急

冷 Al-Mn 合金中首次发现了一种具有五次对称的单晶电子衍射图谱,该结构具有二十面体对称性,且有明锐的衍射斑点,具有长程有序的特点,但衍射斑

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点的排列并不具备周期性,人们将这种具有长程准周期平移序和非晶体学旋转对称性的固态有序相称为准晶^[2]。准晶同超导体、C60 巴基球一起被列为 20 世纪 80 年代凝聚态科学领域三大突破,至今仍然被认为是材料科学领域的科学前沿。

准晶特殊的原子排列结构使其具有低表面能^[3]、低摩擦因数^[4]、耐磨损^[5]、弥散强化、高硬度、耐腐蚀、高电阻等特性,具备广泛的应用前景。但准晶的固有脆性限制了其作为结构材料方面的应用,目前准晶材料主要应用于表面薄膜/涂层和复合材料强化,如法国 Sitram 公司研发的准晶不粘锅专利和瑞典的 Sandvik 公司研发的新型马氏体时效钢,另外在催化^[6-8]、润滑^[9]、热电^[10-11]、金属研磨^[12-13]等应用领域也有一定的拓展应用。准晶表面膜层方面的研究不少,但仍存在问题,如膜基结合不牢、涂层孔隙率高、结构成分难以精准控制、摩擦、腐蚀等机理还有待深入研究等。

本文重点综述近 30 年来准晶薄膜/涂层的制备技术及改性研究的重要结果和研究现状,并指出准晶薄膜/涂层应用方面存在的问题及未来的研究趋势。

1 准晶薄膜/涂层的制备技术

薄膜和涂层通常以厚度区分,一般薄膜的厚度在几微米以内,而涂层的厚度在数十微米以上^[14]。薄膜主要以原子、离子、分子和粒子集团等原子尺度的粒子形态在基体上凝聚、成核、长大,最终成膜,成膜技术主要有真空蒸镀和溅射镀膜。涂层主要指以宏观尺度的熔化液滴或细小固体颗粒在外力作用下于基体材料表面凝聚、沉积或烧结而成的覆盖层,主要制备技术有热喷涂和激光熔覆。薄膜和涂层的性能因制备技术的不同而存在很大的差异,同时受制备工艺和后续热处理等等影响。

1.1 薄膜的制备工艺

真空蒸镀通过在真空容器中把欲镀金属、合金或化合物加热熔化,使其呈分子或原子状态逸出,沉积到被镀材料表面而形成固态薄膜,按加热方式分类可分间接加热和电子束加热两种。间接加热蒸发制备的薄膜质量好、效率高;电子束蒸发适合制备高熔点薄膜材料和高纯薄膜材料,但真空蒸镀难以控制薄膜成分,膜基结合力小,在沉积金属合金薄膜时,组成元素的相对蒸汽压十分关键,Al 元素的相对蒸汽压值小,容易优先蒸发汽化,对于以铝为组成元素之一的金属合金,起始合金应以其他组成元素富集,以补偿铝的优先汽化。USHAKOV 等^[15]用真空电弧等离子体蒸发法制备 Al-Cu-Fe 准晶薄膜,在

沉积过程中,由于 Al 元素的蒸发速度高导致 Al 元素的损耗快,起始材料的化学成分和相组成发生变化,薄膜中的准晶相几近于无。KANJILAL 等^[16]利用富集 Fe 元素的 $\text{Al}_{40}\text{Cu}_5\text{Fe}_{55}$ 母合金分别用间接加热法和电子束加热法制备组分为 $\text{Al}_{62.9}\text{Cu}_{24.6}\text{Fe}_{12.5}$ 和 $\text{Al}_{63.1}\text{Cu}_{24.5}\text{Fe}_{12.4}$ 的非晶态薄膜,经过 700 °C 退火 1 h 后两组薄膜都转变为准晶态薄膜,室温下电阻率提高了近 10 倍。YADAV 等^[17]利用闪蒸法在玻璃衬底上沉积 Al-Ga-Pd-Mn 薄膜,沉积的薄膜为非晶态,准晶 i 相晶粒细小,在 300 °C 下退火 120 h 后,薄膜完全转变为准晶薄膜。POLISHCHUK 等^[18]发现由于残余应力的影响,电子束物理气相沉积制备的 Al-Cu-Fe 准晶涂层不超过临界厚度,其内部裂纹可以得到有效抑制。

溅射镀膜是利用气体放电产生气体电离,正离子在电场作用下高速轰击阴极靶体,使靶材发生溅射,靶材表面的原子脱离原晶格而逸出,转移到基体表面沉积成薄膜。磁控溅射是较为常用的一种镀膜方式,相对其他溅射技术镀膜速率更高,可以精准控制薄膜成分,膜基结合力强,可在大面积连续基板上制取均匀的膜层,但沉积效率低,薄膜质量得不到保证。ČEKADA 等^[19]利用三级溅射交替沉积 Al/Cu/Fe 薄膜,在惰气保护下进行退火处理,成功制备 Al-Cu-Fe 准晶薄膜。LU 等^[20]利用磁控溅射在液氮冷却的基体上制取 $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{25}$ 准晶薄膜,直接沉积的薄膜为非晶态薄膜,在经过 600 °C 退火后完全转变为准晶态薄膜。MOSKALEWICZ 等^[21]在钛合金上通过非反应性磁控溅射镀 Al-Cu-Fe、Al-Cu-Fe-Cr 和 Al-Co-Fe-Cr 多组分薄膜,镀层均为非晶态镀层,经过适当的热处理后转变为准晶态和晶态镀层。OLSSON 等^[22]在 Al_2O_3 和 Si 基体上利用磁控溅射制备了 Al/Cu/Fe 多层薄膜,经过退火后分别形成了准晶相和准晶近似相。PHILLIPS 等^[23]利用非平衡磁控溅射沉积 10 μm 的 Al-Cu-Fe 薄膜,在经过 500 °C、32 h 的退火处理后转变成准晶薄膜。成膜后的后续热处理是形成准晶薄膜的关键因素,热处理的时间和温度都对薄膜的组织有巨大的影响。

1.2 涂层的制备技术

热喷涂是将喷涂材料加热为熔融状态,通过高速气流将熔融状态下的喷涂材料雾化喷射在金属工件表面上,形成具有特殊性能的涂层。热喷涂可以满足准晶合金系较高冷却速度的需求,主要制备手段有爆炸喷涂、超音速火焰喷涂和等离子喷涂等。其中爆炸喷涂制备的涂层质量好,膜基结合力强,但生产成本低;超音速火焰喷涂制备的涂层质量较好,

涂层致密度高,但气体消耗量大,粉末熔融程度相对较低;等离子喷涂温度高、喷涂材料范围广泛,工艺相对简单,但涂层的微小孔洞和裂纹较多。傅迎庆等^[24]采用爆炸喷涂制备 Al-Cu-Cr 准晶涂层,涂层中出现了两种新相:一种是具有体心立方结构的晶体相 $\alpha\text{-Al}_{69}\text{Cu}_{18}\text{Cr}_{13}$,另一种是 Al_3O_2 相。GOMES 等^[25]使用超音速火焰喷涂制备 $\text{Al}_{59.2}\text{Cu}_{25.5}\text{Fe}_{12.3}\text{B}_3$ 准晶涂层,发现涂层中的裂纹与氧燃料比有关,使用轻微氧化火焰制备的涂层裂纹密度更高。FEITOSA 等^[26]提出当氧燃料比为 0.98 时,制备的 Al-Cu-Fe-B 准晶涂层质量最好,硬度为 700 HV,孔隙率为 1.5%。FU 等^[27]分别用超音速火焰喷涂和等离子喷涂制备 Al-Cu-Cr 准晶涂层,发现随着功率的增大,两种方法制备的涂层准晶 ψ 相含量都会减少,相比之下超音速火焰喷涂制备的涂层更致密。LEPESHEV 等^[28-30]用等离子喷涂制备 Al-Cu-Fe 准晶涂层,发现涂层二十面准晶体含量与基体温度有关,喷涂态涂层中主要是二十面体准晶 ψ 相和立方 β 相,随着基体温度的升高准晶 ψ 相的比例增加,当基体温度为 700 °C 时准晶 ψ 相含量达到峰值,高达 80%。

激光熔覆通过在基材表面添加熔覆材料,并利用高能密度的激光束使之与基材表面薄层一起熔凝,在基层表面形成冶金结合的添料熔覆层。激光重熔能改善涂层的孔洞和裂纹,可控性好,精准控制涂层成分。FATOBA 等^[31-32]采用 3D 打印在钛合金表面构筑 Al-Cu-Fe 准晶涂层,结果表明通过改性激光工艺可得到无裂纹的 Ti-6Al-4V/Al-Cu-5Fe 涂层,其耐磨性是基体的 2.8 倍,极化电阻是基体的 1 538.3 倍。FU 等^[33]用选择性激光熔覆(SLM)制备 Al-Cu-Fe-Cr 准晶涂层,研究不同涂层厚度下的微观结构,发现随着涂层厚度的增加,颗粒熔融充分时孔隙率减小,但当厚度增加到一定程度时,涂层反而出现了大孔洞及裂纹。

2 准晶薄膜/涂层相变的影响因素

2.1 组成成分

准晶相有严格的成分范围,微量成分的偏移会导致准晶相向其他类似相和晶体相转变^[34-35]。BRADLEY 等^[36]首次揭示了较为完整的 Al-Cu-Fe 三元相图,但其中 ψ 相结构未定,表 1 中总结了一部分重要的相。TSAI 等^[37]在 1987 年首次报道了稳定的二十面体 ψ 相,如图 1 所示,该相的衍射斑点图具有五次对称的特点。后来人们发现 TSAI 报道的 ψ 相与 BRADLEY 揭示的三元相图中的 ψ 相成分范围相近。FAUDOT 等^[38]系统地研究了 ψ 相和 ω 相附近的成分范围,发现 ψ 相就是 TSAI 报道的 ψ 相。BRADLEY 在缓慢冷却中观察到成分为 $\text{Al}_{65}\text{Cu}_{22.5}\text{Fe}_{12.5}$ 的 ψ 相,它是由 β 相和液相发生包晶反应得到的。DONG 等^[39]在 $\theta\text{-Al}_{13}\text{Fe}_4(\text{Cu})$ 相和液相的包晶反应中观察到二十面体 $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ 相。自此,二十面体准晶相由 β 相+液相通过包晶反应生成这一说法得到认可。经大量学者研究,Al-Cu-Fe 三元相图逐渐完善^[40],如图 2 所示。

表 1 Al-Cu-Fe 体系中最重要二元相和三元相及其结构^[42]

Table 1 Most important binary and ternary phases and their structures in the Al-Cu-Fe system^[42]

Phase	Ideal formula	Structure, composition
η	AlCu	Orthorhombic, related to γ -type Ni_2Al_3
τ	AlCu(Fe)	
θ	Al_2Cu	Tetragonal
λ	Al_7Fe_2	Orthorhombic
λ_1, λ_2	Al_3Fe	Different amounts of Cu dissolved
λ	$\text{Al}_{13}\text{Fe}_4$	Monoclinic
μ	Al_5Fe_2	Monoclinic
β_1	AlFe_3	Body-centered cubic with superlattice
β	$\text{Al}_5(\text{Cu, Fe})_5, \text{AlFe}(\text{Cu})$	Cubic (CsCl type)
φ	$\text{Al}_{10}\text{Cu}_{10}\text{Fe}$	Related to γ -type Ni_2Al_3
χ	$\text{Al}_{18}\text{Cu}_{10}\text{Fe}$	Related to φ
ψ	$\text{Al}_6\text{Cu}_2\text{Fe}$	Icosahedral
ω	$\text{Al}_7\text{Cu}_2\text{Fe}$	Tetragonal

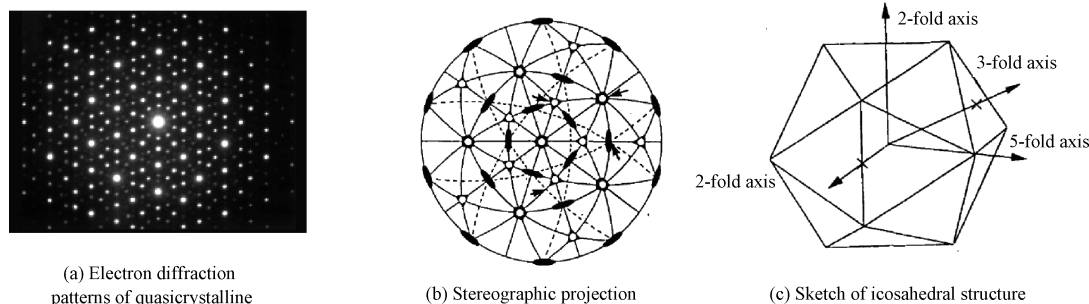


图 1 二十面体准晶的电子衍射图及晶体学特征

Fig. 1 Electron diffraction patterns of quasicrystalline and the sketch of icosahedral structure

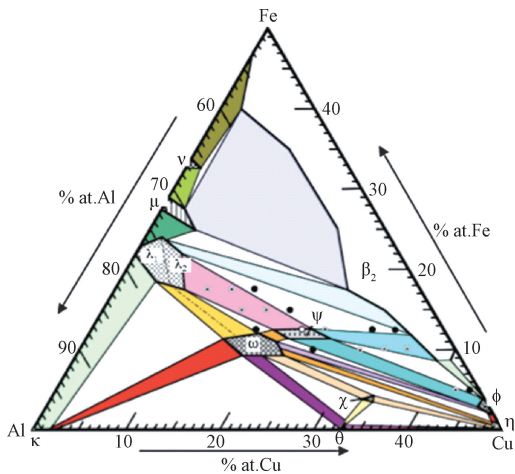


图2 Al-Cu-Fe 在 700 °C 的等温截面图

Fig. 2 Isothermal section of the Al-Cu-Fe phase diagram at $T=700\text{ }^{\circ}\text{C}$

在制备准晶涂层的过程中,不同工艺会导致准晶成分出现不同程度的损耗,如当热喷涂燃料热焓值过高时,低熔点合金组元 Al 元素的蒸发或氧化损失加剧,容易导致涂层内 Al 元素含量下降,涂层成分偏离准晶相的成分范围,继而发生复杂相变,使涂层近似相含量增加,准晶相含量减少^[24,41]。

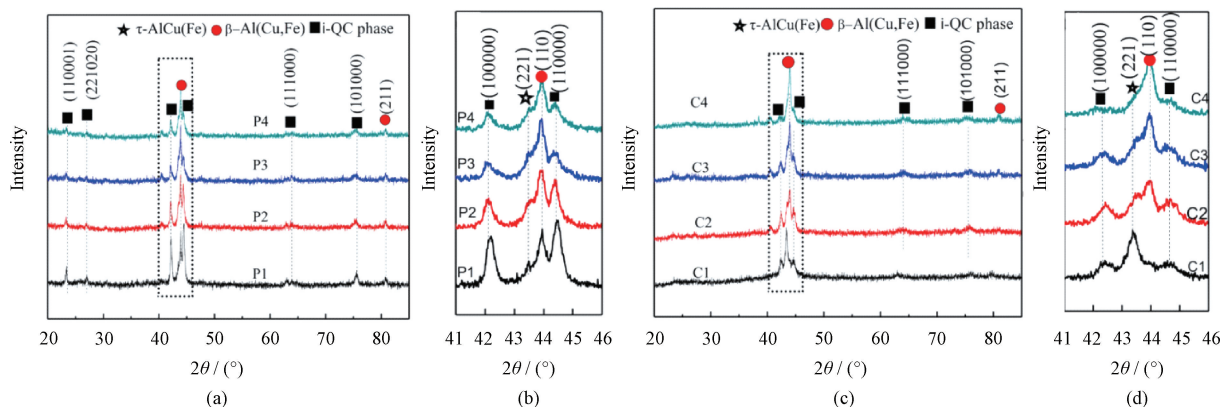
2.2 冷却速度

冷却速度是准晶相形核的重要影响因素,冷却速率越高,过冷度越大。在高冷却速率下,准晶相能直接从熔体中形成^[43-44];在中低冷却速率下,比起一般晶体相和准晶类似相,准晶相的过冷度要小的多^[45],准晶相由包晶反应生成。赵东山等^[46]计算

了 Al-Cu-Fe 准晶 i 相和准晶近似相的自由能,对比了两者的成相驱动力,当温度高于 938 K 时,形成准晶 i 相的驱动力大于形成准晶近似相的驱动力,当温度低于 938 K 时,则相反。采用热导率较低的基体沉积涂层和适当升高基体温度,有利于提高准晶 i 相的含量^[47-48]。USTINOV 等^[49]使用单枪电子束沉积法在不同的基体温度下沉积 Al-Cu-Fe 准晶薄膜,XRD 结果表明随着基体温度的提高,薄膜中的准晶峰更显著。傅迎庆等^[48,50]研究热喷涂中基体热导率和基体温度对涂层准晶相的影响,发现随着基体热导率的减小和基体温度的升高,涂层准晶近似相的衍射强度减小,准晶相衍射强度增大。

MILMAN 等^[51]在电子束沉积的 Al-Cu-Fe 准晶涂层中发现,涂层与基体之间形成了 β 相组织,涂层中间是二十面体准晶 i 相和单斜 $\lambda\text{-Al}_{13}\text{Fe}_4$ 相双相结构,只有涂层表层为准晶 i 相结构,这是因为随着涂层逐渐沉积,热量不断积累,后续沉积的涂层温度冷却更慢。

XIAO 等^[52]利用气体雾化法制备 Al-Cu-Fe-Cr 准晶粉末,并利用高速空气燃料火焰热喷涂制备涂层。图 3 为不同粒度粉末和不同粒度粉末所制涂层的 XRD,研究发现在喷雾造粒的过程中,随着粉末粒度的增大,粉末的冷却速度降低, β 相含量增加,准晶相含量减少。P1 的粉末粒度最小,在喷涂中 Al 元素烧损最严重,且和其他粉末所制涂层的主相 β 相不同,P1 粉末制备的 C1 涂层中主相变为 τ 相。

图3 不同粒度粉末和不同粒度粉末制备涂层 XRD:(a)不同中位径(D50)的 $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{10}\text{Cr}_5$ 粉末的 XRD; $P1_{D50}=9.48\text{ }\mu\text{m}$,

$P2_{D50}=22.48\text{ }\mu\text{m}$, $P3_{D50}=38.47\text{ }\mu\text{m}$, $P4_{D50}=29.65\text{ }\mu\text{m}$, (b) 图(a)的局部放大图, (c) 不同中位径粉末所制涂层的 XRD:

C1 涂层所用粉末为 P1, C2 涂层所用粉末为 P2, C3 涂层所用粉末为 P3, C4 涂层所用粉末为 P4, (d) 图(c)的局部放大图

Fig. 3 XRD of different particle size powders and coatings prepared from different particle size powders: (a) XRD of different

median diameter(D50) $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{10}\text{Cr}_5$ powders: $P1_{D50}=9.48\text{ }\mu\text{m}$, $P2_{D50}=22.48\text{ }\mu\text{m}$, $P3_{D50}=38.47\text{ }\mu\text{m}$,

$P4_{D50}=29.65\text{ }\mu\text{m}$, (b) Partial enlargement of figure (a), (c) XRD of coatings made from different median diameter powders:

Powder used in the C1 coating is P1, Powder used in the C2 coating is P2, Powder used by the C3 coating is P3,

Powder used in the C4 coating is P4, (d) Partial enlargement of figure (c)

2.3 热处理

后续的热处理会对涂层的相变产生重要影响,不同的退火温度和退火时间会对涂层中的相变产生影响。

DING 等^[53]用磁控溅射制备 Al-Cu-Fe 薄膜,观察发现初始薄膜的界面结构为 Al-Cu-Fe 非晶结构,在 750 °C 退火 2 h 后薄膜转变为准晶结构。ČEKADA 等^[54]分别在基体上依次沉积 Al/Cu/Fe 三层金属层,研究了热处理过程中的界面元素扩散。元素扩散行为分为三个阶段(如图 4):第一

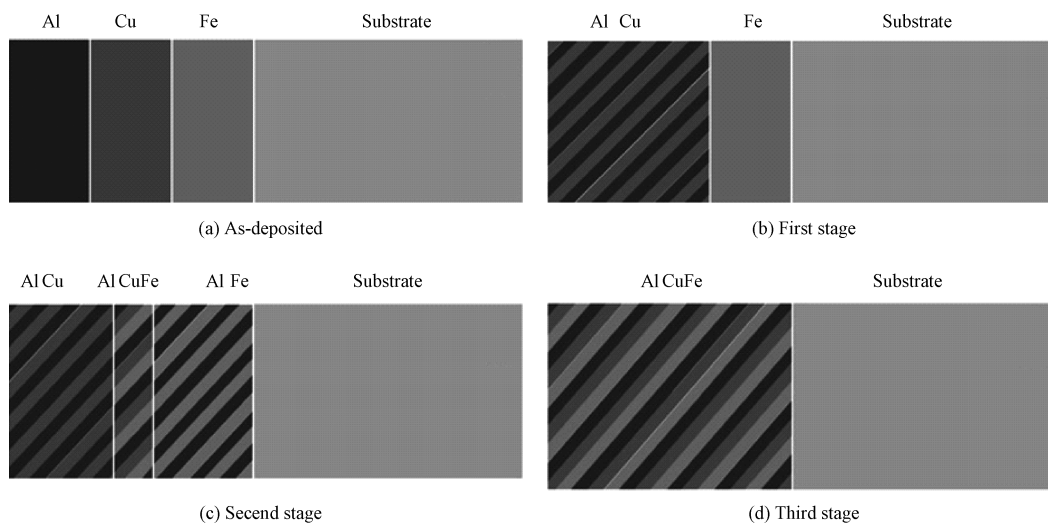


图 4 从沉积三层到完全均匀单层退火过程中的演化模型

Fig. 4 Model of evolution during annealing, from as-deposited trilayer to a completely homogenized single layer stage

PARSAMEHR 等^[55-56]利用热喷涂制备 Al-Cu-Fe 准晶涂层,利用 XRD 进一步研究涂层准晶相的热稳定性(如图 5 所示)。初始阶段时, β 相为主导相;当温度升至 490~650 °C 时, β 相含量减少,准晶 ψ 相含量不断提高,并在 650 °C 时,准晶 ψ 相为主导相;当温度升至 800~870 °C 时,准晶 ψ 相转变为 β 相。

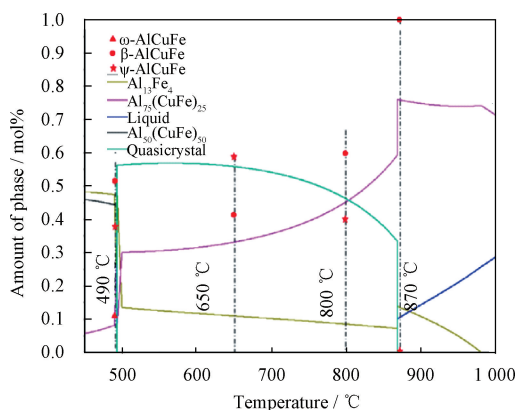


图 5 Al-Cu-Fe 相演化的 XRD

Fig. 5 Phase evolution for Al-Cu-Fe from in-situ XRD

阶段,退火温度为 300 °C 时,Al 向 Cu 层扩散形成 γ -Al₄Cu₉ 相,薄膜呈 AlCu/Fe 双层结构;第二阶段,退火温度为 500 °C 时,Al 继续向下扩散均匀分布在整个薄膜中,与 Fe 层形成 AlFe 层,AlCu 层与 Fe 层间有一层薄薄的过渡层,薄膜中只观察到 β -Al(Cu,Fe) 相,薄膜呈 AlCu/AlCuFe/AlFe 三层结构;第三阶段,退火温度在 600 °C 以上时,中间的过渡层向两边延伸, γ 相和 β 相转变为准晶 i 相,薄膜形成均匀的 Al-Cu-Fe 层,形成二十面体准晶 i 相。

PARSAMEHR 等^[57]对 Al-Cu-Fe 准晶薄膜采取了两步退火法热处理,先在 570 °C 下退火 3 h,然后在 800 °C 下分别进行 5、10、15 h 不同时间的退火处理,发现将试样的退火时间从 5 h 延长至 15 h 后,试样中的 β 相和 ω 相转变为二十面体准晶 i 相, ω 相完全消失,准晶 i 相含量从 24.8% 提高至 84.3%,这表明准晶 i 相在退火 15 h 后达到了热平衡,且准晶 i 相的热稳定性高于 β 相和 ω 相。

3 性能

3.1 力学性能

MILMAN 等^[51]对比了不同的相对 Al-Cu-Fe 准晶涂层硬度和弹性模量的影响,结果表明,无论是弹性模量还是纳米硬度,准晶 i 相都优于 β 相,涂层硬度和准晶 i 相含量成正比关系^[58],比起经 400 °C × 8 h 固溶处理的涂层,经 400 °C × 8 h 固溶 + 200 °C × 16 h 时效热处理的涂层中有更多的 β 相转变为准晶 i 相,涂层硬度也显著更高,达到了 752.8 HV。张秦梁等^[59]优化了高速电弧喷涂 Al-Ni-Mm-Co 准

晶涂层(其中 Mm 为镧系混合稀土元素,质量分别为 48%~52% Ce, 25%~28% La, 14%~17% Nd 和 4%~6% Pr)的工艺参数,涂层出现明显的纳米准晶相,涂层表面组织结构致密,孔隙率仅为 1.13%,硬度可达 392 HV_{0.1}。LEPESHEV 等^[60]研究了 Al-Cu-Fe 准晶涂层的力学性能,发现涂层硬度随着二十面准晶 ψ 相含量增加而增加,当 ψ 相含量达到 80% 时,涂层显微硬度达到了 900~1 000 HV。

3.2 疏水性

薄膜/涂层的疏水性取决于其表面结构和表面能,其中表面结构是主导因素^[61-68],同时低表面能也会提升膜层的疏水性^[69]。

蔡明伟等^[70]用超音速火焰喷涂制备 Al-Cu-Fe-Si 准晶涂层,对比准晶涂层和 45 号钢基体的接触角,测量结果发现准晶涂层的接触角最大为 95°,而 45 号钢的接触角仅为 79°。准晶涂层显著提高了基体的疏水性,此外不同喷涂工艺参数制备的准晶涂层接触角也存在差异。陈泰盛^[71]用等离子喷涂制备 Al-Cu-Fe 准晶涂层,疏水性试验结果表明,未经退火处理的涂层疏水角为 109.1 °C,如图 6a 所示。经 800 °C 退火 1 h 以上的涂层疏水角提高到 135 °C,如图 6b 所示。相比未退火的涂层经退火处理的涂层准晶 ψ 相含量显著增加,两者都在涂层表面观察到 10~200 nm 的纳米级粒子,表面形成了微纳米结构。

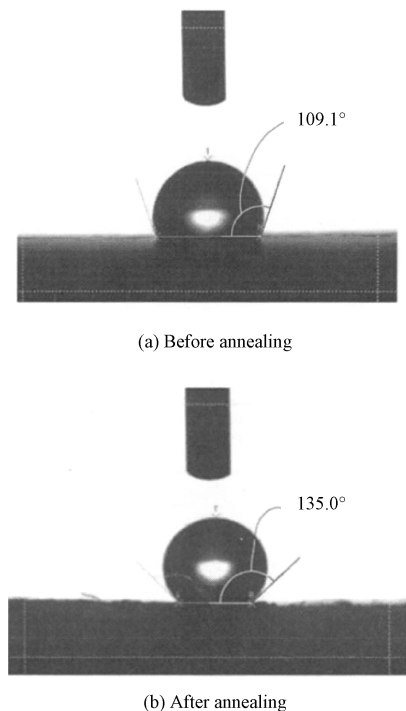


图 6 退火前后 Al-Cu-Fe 准晶涂层水接触角

Fig. 6 Water contact angle of Al-Cu-Fe quasicrystal coating before and after annealing

PARSAMEHR 等^[57]对 Al-Cu-Fe 准晶薄膜采用两步退火法,并对比不同退火时长的涂层,结果表明随着退火时间的延长,准晶相的含量提高,薄膜的接触角增大,退火 15 h 的薄膜接触角达到了 121 °C,大于聚四氟乙烯的涂层的 108.9 °C^[61],证明了准晶具有低表面能的特性。

3.3 摩擦磨损性能

准晶键合性质与金属对磨偶件的键合性质差异显著,当二者组成摩擦副时,具有良好的摩擦相容性,在磨损过程中不易与金属对磨偶件产生黏着,加上准晶具有较高的硬度(HV_{0.05}>700)和较低的塑性,能显著提升复合材料的摩擦磨损性能,但过高的准晶含量反而会适得其反^[72],因为准晶的耐磨性很大程度上取决于其硬度和脆性。热喷涂制备的准晶涂层具有较高的室温硬度,但其固有脆性影响了涂层的磨损性能。在 Al-Cu-Fe 准晶涂层中添加少量的 Fe-Al 相会使涂层硬度有所降低,但可以使涂层磨损模式从脆性断裂向塑性流动转变^[73]。因此兼顾硬度和塑性,可以使准晶涂层具有良好的耐磨性。

罗军明等^[74]利用低压等离子喷涂制备 Al_{62.8}Cu₂₅Fe₁₂Y_{0.2} 稀土准晶涂层,并同钛合金对比耐磨性,研究表明稀土准晶涂层具有优异的室温干滑动磨损耐磨性,且随着磨损时间的延长,稀土准晶涂层的磨损失重相比于钛合金试样的磨损失重增加要缓慢的多,涂层具有良好的耐磨性。DELIMA 等^[75]用超音速火焰喷涂在钢基体上制备 Al₅₉B₃Cu_{25.5}Fe_{12.5}/Al₄Cu₉ 复合涂层,并进行划痕试验,结果表明,准晶涂层明显变形,但准晶涂层并未被穿透,涂层表现出良好的自润滑能力。一是因为燃料煤油中分离出来的 C 提高了涂层的自润滑性能,减小了涂层的磨损,二是因为涂层中间的 Al₄Cu₉ 层有效的平衡了 Al₅₉B₃Cu_{25.5}Fe_{12.5} 准晶涂层和钢基体之间的应力^[76]。FEHRENBACHER 等^[77]等利用磁控溅射制备 Al-Cu-Fe 准晶涂层,研究准晶含量和摩擦因数之间的关系,发现涂层在无退火、450 °C 下退火 2 h、500 °C 下退火 1 h 后摩擦因数分别为 0.45、0.23、0.17,检测结果表明在 450 °C 下退火后涂层中形成了准晶近似相,在 500 °C 退火后,涂层中各相向二十面体准晶相转变,摩擦因数的降低与准晶相的含量提高有关。

SALES 等^[78]分别研究了 Al-Fe-Cu 涂层单相(准晶 ψ 相)涂层和双相(准晶 ψ 相+立方 β 相)涂层的摩擦磨损性能,两组涂层的摩擦因数在 0.2~0.3 范围内波动,相差不大,双相涂层的磨损率明显

小于单相涂层。观察发现双相涂层上的磨痕轨迹是光滑的,没有脆性断裂或黏着磨损的迹象(图 7a),最大磨损深度仅为 $4\text{ }\mu\text{m}$ 。通过剖面(图 8a)分析可知,在摩擦试验中,双相涂层仅上部被磨损,而单相涂层磨痕出现了转移膜(图 7c),发生了黏着磨损,最大磨损深度达到了 $23\text{ }\mu\text{m}$,同时磨痕周围出现了脆性裂纹(图 8b)。这与 KYUNGJUN^[79]提出的 β 相比准晶相更软,能够提高涂层的断裂韧性,减少脆性裂纹拓展的观点一致。在考虑涂层硬度的同时兼顾一定的韧性能够获得更好的耐磨性。

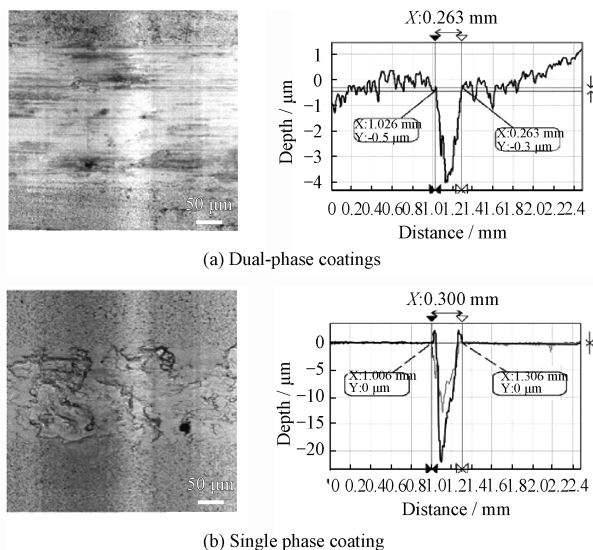


图 7 涂层磨损轨迹扫描电镜图和摩擦试验后的磨损轨迹图
Fig. 7 SEM micrographs of wear tracks on coatings and profiles of the track on coatings after the friction test

3.4 耐蚀性

准晶涂层的耐蚀性与准晶相含量和涂层的致密度有关,准晶相含量及涂层致密度越高,涂层耐蚀性越好。

丁亚茹等^[80]在镁合金 AZ91 D 的表面熔覆 $\text{Al}_{65}\text{Cu}_{20}\text{Fe}_{15}$ 涂层并进行腐蚀试验。结果表明与镁合金基体相比,准晶涂层耐蚀性反而下降。原因是熔覆层内存在较多杂相导致形成电偶加速了腐蚀,同时涂层金相组织呈网状分布,且密度及均匀程度不一致,腐蚀液从致密度低的区域首先侵入,加速熔覆层的腐蚀。WOLF 等^[81]研究超音速火焰喷涂 Al-Cu-Fe 和 Al-Cu-Fe-Cr 涂层的耐蚀性,两组涂层在无氯的酸性和碱性的介质中具有良好的耐蚀性,自腐蚀电流密度为 $\mu\text{A}/\text{cm}^2$,含 Cr 涂层的自腐蚀电位要高于不含 Cr 的涂层。RYABTSEV 等^[82-84]研究了 Al-Cu-Fe 和 Al-Cu-Fe-Sc 准晶涂层的耐蚀性,结果表明 Al-Cu-Fe 涂层耐蚀性高于准晶铸态合金;Sc 元素的加入显著提高了 Al-Cu-Fe

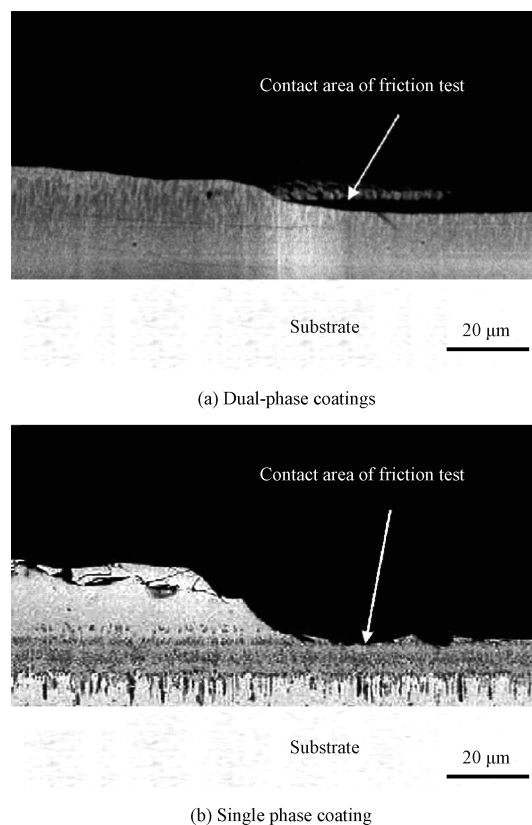


图 8 摩擦试验后接触面积的扫描电镜显微图

Fig. 8 SEM micrograph of the contact area after the friction test

体系在 Cl^- 离子环境下的耐蚀性。吕威闫等^[85]在研究微合金化调控铝基准晶合金成分中发现,在 $\text{Al}_{86}\text{Ni}_6\text{Y}_{4.5}\text{Co}_2\text{La}_{1.5}$ 体系中添加原子分数 0.5% 的 Mo、Cr 元素后,不仅准晶涂层的点蚀电位提高,涂层的自腐蚀电流密度减小,而且容抗弧显著增大(如图 9 所示),钝化膜的稳定性相较于其他涂层更高,耐蚀性更好。

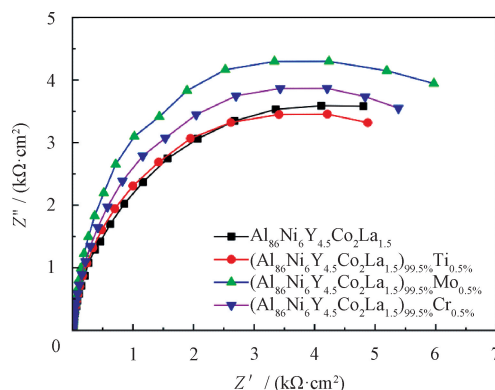


图 9 4 种合金样品的 Nyquist 图

Fig. 9 Nyquist plots of four alloy samples

3.5 抗氧化性

准晶薄膜/涂层的抗氧化性主要归功于 Al 的氧化,在表面形成了一层致密的 Al_2O_3 薄膜。于洋

等^[86]研究了 Al-Cu-Fe-Cr 准晶涂层在高温下的抗氧化性能,静态氧化试验的恒温氧化增重曲线表明,准晶涂层有效提高了基体在高温下的抗氧化性,涂层表面形成一层薄薄的氧化层。MOSKALEWICZ 等^[21]研究了 Al-Cu-Fe、Al-Cu-Fe-Cr、Al-Co-Fe-Cr 多组分薄膜对钛合金抗氧化性的影响,750 °C、300 h 的静态氧化试验结果表明,钛合金表面出现了氧化皮剥落现象,表面沉积了准晶薄膜的钛合金无剥落现象。高温下 Al-Co-Fe-Cr 准晶薄膜的抗氧化性效果最显著,在其薄膜表面发现 α - Al_2O_3 晶粒密集分布在薄膜表面,而 Al-Cu-Fe、Al-Cu-Fe-Cr 薄膜形成的 α - Al_2O_3 晶粒呈鳞片状分布于薄膜表面。KHARAT 等^[87]研究 Al-Cu-Fe 准晶薄膜和 Al-Ni-Co 准晶薄膜的氧化行为发现亲氧元素 Al 扩散到薄膜表面优先和氧气反应生成金属氧化物,在薄膜表面形成一层致密的 Al_2O_3 层,薄膜的抗氧化性得到显著提升。

4 Al 基准晶薄膜/涂层的应用前景

4.1 减磨耐磨涂层

准晶的低表面能和良好的摩擦性能是减磨耐磨涂层的关键^[88],如 Al-Pd-Mn 准晶的不粘性可以与不粘性最好的材料聚四氟乙烯 (Teflon) 相媲美,法国 Sitram 公司研发的 Al-Cu-Fe-Cr 准晶不粘锅,代替了之前的特氟龙 (Teflon) 不粘锅,相比于聚四氟乙烯,准晶不粘锅的效果更好,使用寿命更长。低摩擦因数和高硬度的准晶涂层也可用于汽车发动机的气缸套和活塞涂层^[89]。DUBOIS 等^[40]利用准晶的摩擦特性在碳化钨刀片上制备了多层准晶薄膜,使其寿命提高了 25%。

4.2 热障涂层

虽然准晶体系大多由金属元素组成,但其特殊的微观结构导致准晶有别于其他金属原子的电子传输过程,相比普通金属材料,准晶的热导率更低,比不锈钢低一个数量级,比普通铝合金低两个数量级,与目前常用的热障涂层材料 ZrO_2 相近。准晶的低热导率和接近金属的热膨胀系数,使准晶在热障涂层方面有很好的应用潜力。如图 10 所示,小型涡轮叶片的表面覆盖一层 Al-Co-Fe-Cr 准晶复合材料涂层后,完全可以满足 700 °C 高温的工作环境需求^[40]。王全胜等^[90]在 ZL109 基体上制备 Al-Cu-Co-Si 准晶涂层,热障试验结果表明涂层具有良好的抗热冲击性,涂层的热导率比其纯金属组元的热导率低近两个数量级,与常规 YSZ 热障涂层的热导率

相近。WOLF 等^[91]利用超音速火焰喷涂在钢基体上制备 $\text{Al}_{71}\text{Co}_{13}\text{Fe}_8\text{Cr}_8$ 准晶涂层,结果表明涂层由十面体的准晶近似密排六方相 Al_5Co_2 和单斜相 $\text{Al}_{13}\text{Co}_4$ 组成,涂层的显微硬度接近 500 HV,摩擦因数优异 (0.05 左右),达到了良好的隔热效果 (比基体碳钢温度降低了 30%)。



图 10 小型涡轮叶片

Fig. 10 Small turbine blade

4.3 太阳能工业薄膜

太阳能工业薄膜材料不仅要求材料能够吸受短波、反射长波,而且还要有良好的热稳定性。DEMANGE 等^[92]研究了 Al-Cr-Fe 体系中几种金属间化合物在宽频率范围内的导光性,发现准晶在低频处没有 Drude 峰,这与传统金属形成明显的对比,且 Al-Cu-Fe 准晶在低频段对红外线的吸收率高,反射系数 R 低至 0.6。EISENHAMMER 等^[93]以 Cu 为基体,设计绝缘层/准晶薄膜/绝缘层多层结构,并制备 $\text{Al}_2\text{O}_3/\text{Al-Cu-Fe}$ (薄膜厚度约为 10 nm)/ Al_2O_3 多层结构薄膜,测试发现材料的选择、薄膜的厚度和不同薄膜材料的组合影响薄膜对太阳光的吸收率和反射率。这些薄膜具有高的热吸收率 α_s 、低的热发射率 ε_h 和足够高的热稳定性,与目前使用的 Ti-N-O 薄膜相比还具有抗高温氧化、耐腐蚀和与基体结合力好的优点。

5 结论与展望

准晶独特的力学性能备受表面学家的关注,关于 Al 基准晶薄膜/涂层开发了以 Al-Cu-Fe 和 Al-Co-Ni 为主的三元合金体系,掺杂的 Cr、Si、B、Sc 等元素提高了三元体系的综合性能。结合已有报道,准晶薄膜/涂层研究的主要问题如下:

(1) 现有的常规真空蒸镀、溅射镀膜、热喷涂、激光熔覆等制备技术,在制备准晶薄膜/涂层过程中存在着技术局限性。Al 元素熔点低,高温下易于蒸发,造成准晶成分偏离理论值,降低了准晶相纯度。因此,能够研发出输出能量既低,减少 Al 元素消耗,又能保证质量的制备工艺是现阶段亟待解决的问题。

(2) 准晶薄膜/涂层的相变和界面结构难于控

制。提高工艺重复性,精准控制涂层相结构、提高界面结合力并调控制备高质量涂层是发展准晶应用重点需要解决的关键问题。

(3) 经济性与工艺性的矛盾。预期获得高纯度准晶薄膜/涂层不可避免地需要长时间退火,经济成本提高。协调薄膜/涂层性能与经济性也是限制准晶应用的客观现实问题。

为了推动 Al 准晶薄膜/涂层的应用,可考虑以下几个方面的研究工作:① 薄膜/涂层制备工艺的叠加,采用复合工艺,发挥各工艺的优势,做到精准调控;② 添加少量陶瓷微颗粒,弥补准晶疏松多孔缺陷,或在薄膜/涂层表面进行封孔处理,提高表面致密性;③ 结合表面构筑微纳米结构,增强涂层综合性能,降低热处理成本。

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