超疏水表面技术在腐蚀防护领域中的研究进展

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摘　要：提高材料表面疏水性有利于降低其与水分等腐蚀性介质的相互作用，从而增强材料的耐腐蚀性。近年来，超疏水表面由于其非润湿性、自清洁性等特殊表面性质而受到广泛的关注，并且越来越多的研究已经将超疏水表面应用于腐蚀防护领域。材料表面的浸润性主要取决于表面化学性质及表面微观结构，因此提高材料表面的疏水性也往往通过降低材料的表面能、改变表面微观结构这两个方面入手。阐述了超疏水表面的浸润性机理，介绍了不同建立表面微观粗糙结构，增强材料疏水/超疏水性的方法，总结了超疏水表面技术在腐蚀防护领域的最新进展和存在的一些问题，并展望了超疏水防腐表面技术的未来发展方向。

关键词：超疏水；涂层表面改性；腐蚀防护

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Research Progress of Superhydrophobic Surface Technologies in the Field of Corrosion Protection

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ABSTRACT: Increasing the hydrophobicity of materials surfaces can reduce their interactions with corrosive media such as water, thereby enhancing their corrosion resistance. In recent years, superhydrophobic surfaces have received widespread attention because of its non-wetting and self-cleaning surface properties. A growing number of studies have been focused on applying superhydrophobic surfaces for anticorrosion purposes. Wettability on the surface of the material mainly depends on the surface chemical properties and surface microstructure, thus improvement of the material surface hydrophobicity is often achieved by lowering the surface energy and changing the surface microscopic structure. This article expounds the mechanism of wettability on superhydrophobic surfaces, introduces different methods for establishing a rough surface microstructure and reinforcing material hydrophobic/super hydrophobic property, summarizes the recent progresses and the existing problems in superhydrophobic anticorrosive surface technologies in the field of corrosion protection, and prospects the future development of superhydrophobic anticorrosive surface technologies.

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KEY WORDS: superhydrophobic; coating surface modification; corrosion protection

近年来,在“生物仿生学”启发下,超疏水表面引起了大量研究者的兴趣。超疏水表面在自清洁、防雾、防冻、低粘性、减小阻力等领域得到了广泛应用,其特有的疏水性能够减少水等腐蚀性介质对金属材料表面的侵蚀[1—4],因此,将超疏水表面技术应用于金属腐蚀防护领域是一种重要的突破,具有广阔的发展前景。

评价材料表面疏水性的主要参数是浸润性。浸润性是指水在固体表面的铺展能力,是固体表面的重要性质之一[5]。一般认为,水接触角 $\theta<90°$ 的材料表面亲水,$90°<\theta<150°$ 的材料表面疏水,而 $\theta>150°$ 的材料表面定义为超疏水表面。在自然界中,荷叶、蝉翼、蚊子复眼等都能展现出超疏水现象,这些现象对超疏水理论的完善与超疏水表面的开发具有重大的启示作用。例如,露水在荷叶表面凝集后会形成水珠,随着荷叶的摇动而顺着斜面滚动下去。这种性质可以对荷叶表面进行一定程度的清洁,带走污物,正所谓“出淤泥而不染”。Barthlott 和 Neinhuis 等人研究发现[6—7],这种疏水性与荷叶的表面形貌密切相关,他们将超疏水性能与表面微米级的粗糙结构联系在一起。Jiang 等发现荷叶表面的结构包括微米乳突表面和纳米蜡,形成微米-纳米结构,这样的结构对荷叶表面的浸润性有重大影响[8]。

文中介绍了超疏水表面技术在腐蚀防护领域的最新进展与存在的一些问题,并探讨了超疏水防腐表面技术未来的发展趋势,拟为制备长效、耐久的超疏水防腐表面提供一定的借鉴。

1 超疏水表面的浸润性机理

1.1 光滑表面的浸润性

在一般的固体表面,接触角都是固定值,其大小由表面张力决定。光滑表面接触角 θ_0 满足 Young′s 方程[9—10]:

$$\cos\theta_0=\frac{\gamma_{SA}-\gamma_{SL}}{\gamma_{LA}}$$

式中:γ_{SA},γ_{SL},γ_{LA} 分别为固体-气体、固体-液体、液体-气体的界面张力。

1.2 粗糙表面的浸润性

为了定量表征粗糙表面的浸润性,在 20 世纪 40 年代,Wenzel 和 Cassie 分别对 Young′s 方程进行了修正。Wenzel 将表面粗糙度的概念引入到浸润理论中,建立了 Wenzel 模型,可以对液滴在均匀粗糙表面的接触角进行定量计算。Wenzel 方程可表述为[11—12]:

$$\cos\theta_w=\frac{r(\gamma_{SA}-\gamma_{SL})}{\gamma_{LA}}=r\cos\theta_0$$

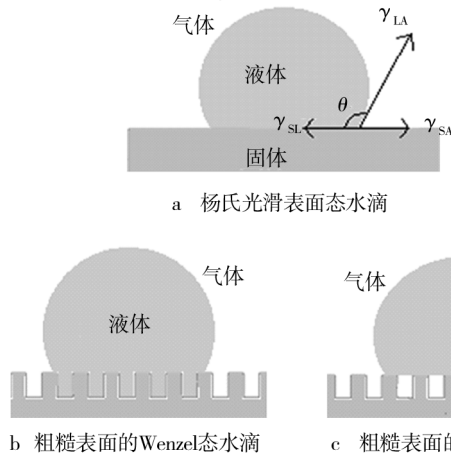
式中:θ_0 为本征接触角(Young′s 接触角);θ_w 为表观接触角(Wenzel 接触角);r 为表面粗糙因子,其值为表面的实际面积与几何投影面积之比。

1944 年,Cassie 和 Baxter 将相面积分数(f)的概念引入到浸润性中。相面积分数是指非均匀表面上每一相(组分)的接触面积占总接触面积的百分比[13]。如果复合表面由两种不同组分组成,两种组分表面的本征接触角分别为 θ_1 和 θ_2,占总面积的百分数分别是 f_1 和 f_2($f_1+f_2=1$),则表观接触角方程可写成:

$$\cos\theta_{CE}=f_1\cos\theta_1+f_2\cos\theta_2$$

当粗糙表面的凹槽内存留有空气时,液滴不能够填满凹槽,此时材料表面由固、气两相组成,液滴的实际接触面积包括了水滴与空气的接触面积和水滴与固体部分的接触面积。液滴与空气的本征接触角为 180°,因此达到平衡时的表观接触角满足 $\cos\theta_{CE}=f_{SL}\cos\theta_0+f_{SL}-1$。

疏水光滑表面及粗糙表面的 Wenzel 态、Cassie 态水滴如图 1 所示。在粗糙表面,Wenzel 态水滴始终充满微观凹槽,这些凹槽增大了水与表面的接触面积,



a 杨氏光滑表面态水滴

b 粗糙表面的Wenzel态水滴 c 粗糙表面的Cassie态水滴

图 1 光滑表面和粗糙表面的水滴状态

Fig. 1 The states of water droplets on smooth surface and rough surface: a) the Young′s model; b) the Wenzel model; c) the Cassie model

在几何上放大了疏水效应,使水滴的接触角更大。随着表面粗糙度的增大,水滴在疏水表面会实现从 Wenzel 态到 Cassie 态的转变。Cassie 态水滴无法填满粗糙表面的微观凹槽,水滴下截留了一定空气,呈现出对材料表面的复合接触,接触角滞后变小,滚动角变小,材料表面自清洁能力增强[14—16]。在 Cassie 态,通过调节材料表面微观形貌减小固-液接触界面所占比例,可以使表面达到 θ>150°的超疏水状态[5]。此外,超疏水性不能只用静态接触角来衡量,而应同时考虑水滴在材料表面的滚动行为。滚动角可以用来衡量水滴在固体表面移动的难易程度。滚动角越小,水滴在固体表面移动越容易,表面的非润湿性和自清洁性越好。

2　超疏水表面技术在腐蚀防护领域的应用

材料表面的浸润性主要取决于表面化学性质及表面微观结构,因此提高材料表面的疏水性也往往通过这两个方面入手:1)降低材料的表面能,如选用低表面能物质对表面进行修饰[17—20],包括含有机硅类树脂(表面能可低至 22 mM/m[21—22])、含氟树脂(表面能可低达 10 mN/m[23]);2)改变表面微观结构,增加表面粗糙度。光滑疏水表面的水接触角大多难以超过 120°,疏水性能不尽如人意,而通过表面粗糙化可以改变表面的浸润状态,使疏水表面的接触角升高,甚至大于 150°,达到超疏水的状态。利用不同的方法建立表面微观粗糙结构,增强材料疏水/超疏水性,在腐蚀防护领域是一个较新的研究方向[24—26]。常见的方法有转化膜法和蚀刻法,此外还包括模板法、溶胶凝胶法等[26—30]。

2.1　转化膜法

尹衍升等人在铜的表面制备了一系列具有微米粗糙结构的正十四烷酸盐转化膜,随着转化膜的生长,铜表面实现了亲水—疏水—超疏水的转变,其耐海水腐蚀能力随之增强[31]。Ishizaki 等在镁合金表面制备纳米氧化铈转化膜,并用氟硅烷加以修饰,获得了超疏水结构(图 2),水接触角达到 153.2°。在 5%(如无说明,文中涉及含量的百分数均为质量分数)NaCl 溶液中浸泡 24 h 后,经超疏水处理的镁合金低频区阻抗模量比未处理的镁合金高出 5 个数量级。极化曲线测试表明,经超疏水处理的镁合金腐蚀电流比未处理的镁合金小很多(图 3)。这些结果都说明经过超疏水处理,镁合金表面的耐蚀性大大提高[32]。He 等将铝试样在 15% 硫酸溶液中进行阳极氧化,氧化电流为 0.32 A/cm^2,然后用肉豆蔻酸进行低表面能修饰,获得了带有超疏水氧化铝膜的试样,极化曲线测量结果表明试样的耐蚀性增强[33]。Zhao 等将镁基片浸入到氯化铁、十四烷酸、去离子水和乙醇配制的溶液中,镁表面生成了由十四烷酸铁组成的超疏水膜。电化学测试结果表明,生成十四烷酸膜的镁基片在 3.5% NaCl 溶液中浸泡 24 h 后,腐蚀电流仍然远小于未处理的镁基片,显示出良好的耐蚀能力[34]。

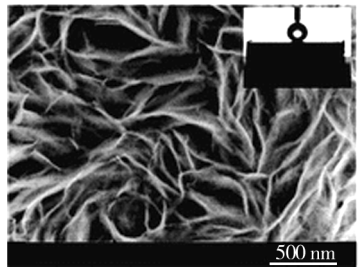


图 2　超疏水表面的微观形貌以及水滴在表面的状态

Fig. 2 Microscopic morphology of superhydrophobic surface and the state of water droplets on the coating surface

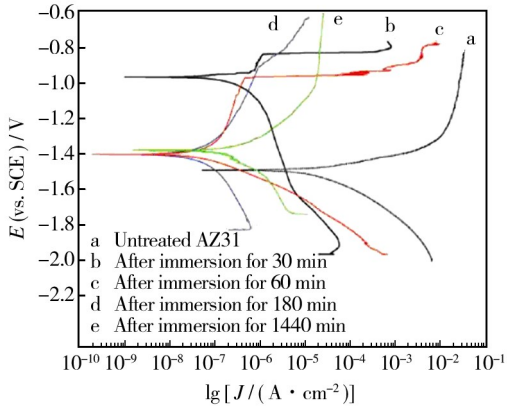


图 3　镁合金超疏水表面的极化曲线

Fig. 3 The polarization curves of magnesium alloy with superhydrophobic surfaces

Zhang 等人以钛箔为基体,在含有 0.5% NH_4F 的乙二醇/水电解质溶液中进行恒电位阳极处理,电位为 20 V。处理 5 h 后,钛箔基体表面形成了二氧化钛转化膜,最后他们用苯基三乙氧基硅烷进行低表面能修饰[35]。测试发现,水滴在转化膜表面的接触角达到了 160°。电化学阻抗测试表明,试样在 3.5% NaCl 溶液中浸泡 90 天后,仍然表现出良好的耐蚀性。Wang 等人以铜基片为阳极,铂片为阴极,在十四烷酸中进行恒电位阳极处理,铜基片表面形成了超疏水转

化膜[36]。图 4 为裸铜片在 NaCl 溶液中(BS)、超疏水转化膜铜片在 NaCl 溶液中(SS)和超疏水转化膜铜片在去除了空气的溶液中(DS)的极化曲线,由于转化膜微观结构上能存储大量空气,铜片腐蚀速率大大降低。孙佳等人以 NaBr 为电解液,通过阳极氧化法在 AZ31 镁合金基体表面制备粗糙结构的转化膜,再经过氟硅烷修饰后,成功获得超疏水表面,且实验表明其耐蚀性大大加强[37]。实验中,随着电解液电流密度不同,所得转化膜的接触角大小也不同(图 5)。图 6 中对比了不同表面的动电位极化曲线,当接触角为 155.5°时,腐蚀电流最小。苏冬等人采用 γ-氨基丙基三乙氧基硅烷和含氢硅油,在二月桂酸二丁基锡的催化下,经过反应、水解、喷涂后,获得具备超疏水能力的环氧涂层[38]。该涂层试样在 1 mol/L NaOH 和 HCl 溶液中浸泡 25 min 后,质量损失仅分别为 0.214% 和 0.243%。Liang 等人[39]将铝板浸入到不同比例的 $Zn(NO_3)_2 \cdot 6H_2O$和 $CO(NH_2)_2$ 混合液中,在 95 ℃的条件下搅拌 1.5 h,铝板表面生成了氢氧化碳酸锌转化膜层。经过接触角测量,二者摩尔比为 2∶1 时的接触角最大,实现了超疏水特性。图 7 为转化膜铝板的微观形貌,其与裸铝板在 3.5% NaCl 溶液中的极化曲线如图 8 所示,可见转化膜铝板的腐蚀速率显著降低。

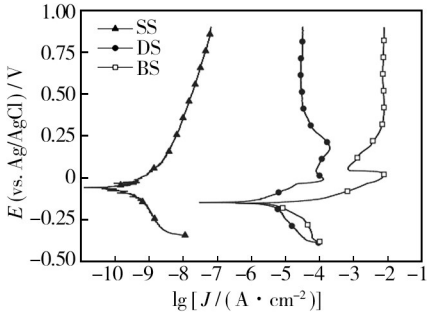


图 4 超疏水处理前后的铜基片在 NaCl 溶液中的极化曲线

Fig. 4 The electrochemical polarization curves of copper substrate before and after superhydrophobic treatment in NaCl solution

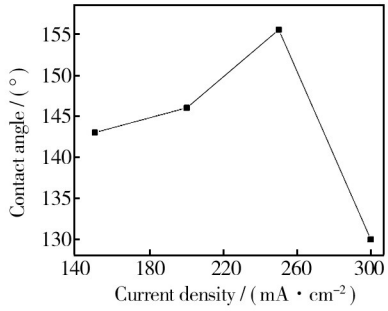


图 5 不同电解液电流密度条件下所得表面的接触角

Fig. 5 Contact angles of surfaces treated in electrolyte with different current density

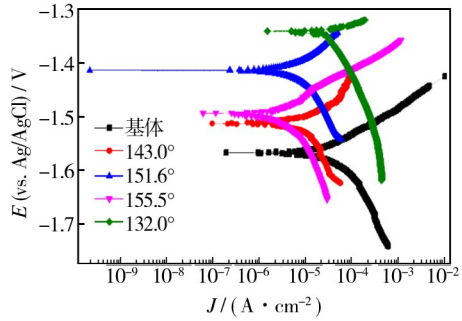


图 6 不同接触角表面对应的极化曲线

Fig. 6 Polarization curves of surfaces with different contact angles

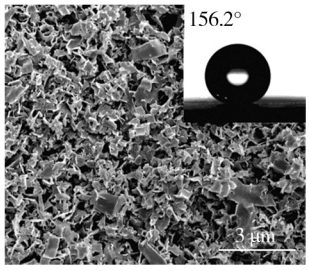


图 7 超疏水转化膜铝板表面微观形貌

Fig. 7 The surface microstructure of superhydrophobic aluminum plate: a) Untreated aluminum; b) Superhydrophobic surface

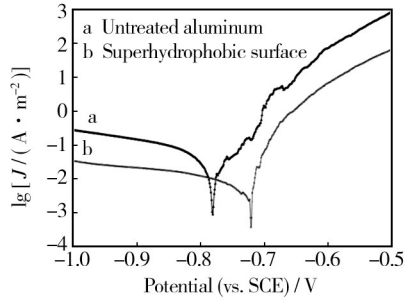


图 8 裸铝板超疏水处理前后在 NaCl 溶液极化曲线

Fig. 8 Polarization curves of aluminum plate before and after superhydrophobic treatment in NaCl solution

2.2 蚀刻法

Feng 等人利用沸水蚀刻使铝合金表面粗糙化,并用十八酸加以修饰,得到了一系列的超疏水表面[40],提升了铝合金耐蚀性。Liu 等人用 0.1 mol/L 的盐酸蚀刻 Mg-Li 合金表面,经过 N_2 干燥后,在含有 FAS ($CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$)的 1% 乙醇溶液中浸泡 12 h,随后在 100 ℃条件下加热,得到了稳定的超疏水表面。该超疏水表面在空气中暴露不同时间后的接触角如图 9 所示,经过 180 天后,水滴仍然难以在表面停留,滚动角小于 5°,疏水性仍然很强[41]。

王青芬等人通过水热法[42]在镁合金表面构建具有一定腐蚀防护性能的氢氧化物层,并用 1H,1H,

2H,2H-全氟辛基三氯硅烷对其进行低表面能化处理,镁合金表面达到超疏水效果,如图 10a 和 b 所示。另外,利用硝酸蚀刻法进行粗糙化处理,同样经 1H,1H,2H,2H-全氟辛基三氯硅烷处理,也得到超疏水表面,如图 10c 和 d 所示。经过电化学测量发现,粗糙表面经过低表面能修饰后,腐蚀电流急剧降低,耐蚀性增强。与蚀刻法相比,水热法所得超疏水结构由于兼具超疏水的气垫阻隔作用和氢氧化镁层的物理屏障作用,腐蚀防护效果更佳。此外,Ou 等人也通过水热法和蚀刻法使钛、铝、镁等轻合金形成超疏水表面,对比发现,水热法生成的转化膜对腐蚀介质具有更好的屏障作用[43]。

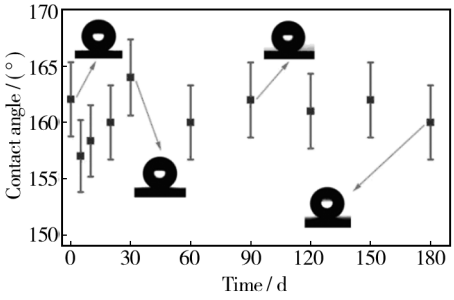
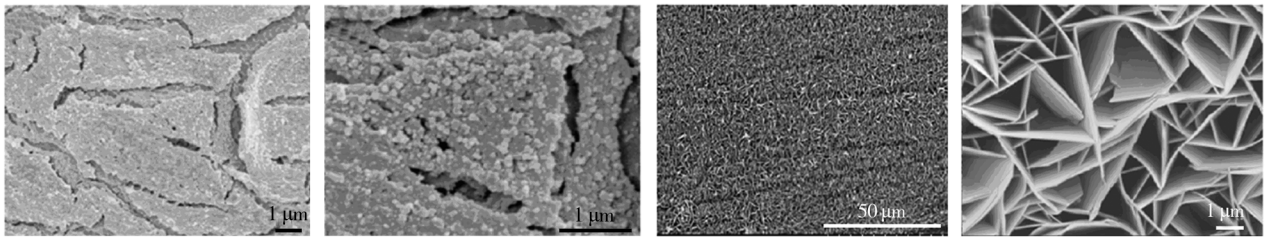


图 9　Mg-Li 合金超疏水表面接触角随暴露时间的变化

Fig. 9 Variation of contact angle on superhydrophobic surface of Mg-Li alloy along with the exposure time

2.3　其他方法

模板法也是一种较为常见的超疏水结构制备方法。通过模板浇注—固化—剥离,模板法可以实现对表面粗糙结构的精确复制[44—45]。例如,Yeh 等人以千年芋树叶为母板,利用 PDMS 软模板,在环氧涂层表面复制叶子乳突的微观结构(图 11),显著提高了涂层的疏水/超疏水性,增强了环氧涂层的阻水能力[46—48],提升了涂层对金属基底的防护能力。



a　硝酸刻蚀样品10 000 ×　　b　硝酸刻蚀样品 30 000 ×　　c　水热法样品1000 ×　　d　水热法样品10 000 ×

图 10　不同处理方式所得超疏水镁合金样品的表面微观形貌

Fig. 10 The surface microstructure of superhydrophobic magnesium alloy samples obtained with different processing methods: a) etched sample (Magnification of 10 000); b) etched sample (Magnification of 30 000); c) hydrothermal sample (Magnification of 1000); d) hydrothermal sample (Magnification of 10 000)

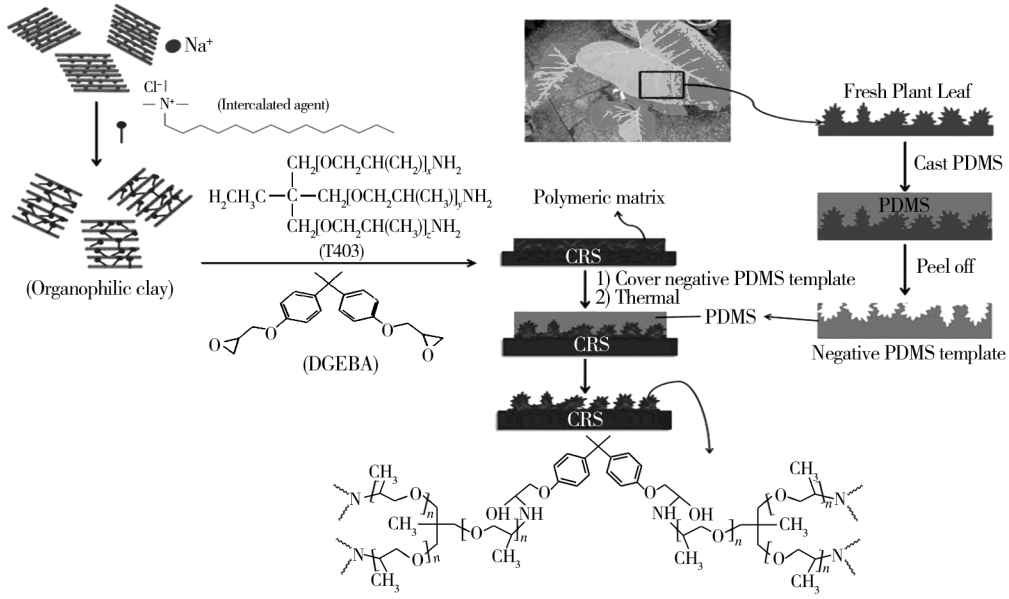


图 11　以千年芋树叶为模板制备超疏水环氧涂层的过程

Fig. 11 The preparation process of superhydrophobic epoxy coating using taro leaves as the template

李松梅等人在覆有阿洛丁膜的铝合金表面刷涂含氟聚氨酯,然后将铝合金板浸入经偶联剂修饰的纳米 SiO_2 的二甲苯溶液中,形成了具有微米-纳米结构的表面[49]。测量发现,其接触角达到了 156°,滚动角小于 5°;电化学阻抗谱的测量结果表明,铝合金的耐蚀性大大提高。Su 等人通过电化学沉积法在铜基体表面制备了微米-纳米双层结构,经过氟硅烷修饰,达到超疏水结构,电化学测量结果显示该膜层具有良好的防腐作用[50]。Rao 等人利用溶胶-凝胶法,以甲基三乙氧基硅烷、甲醇和氨水为溶胶主体,在铜基体表面构筑了二氧化硅基超疏水涂层(图 12)[51]。涂层的接触角达到 155°,滚动角小于 7°。50% 盐酸环境润湿 100 h 后,涂层仍然保持了超疏水性;空气中暴露 90 天后,接触角仍然大于 90°。

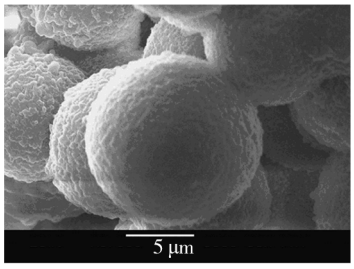


图 12 溶胶-凝胶法制备的超疏水二氧化硅膜表面形貌

Fig. 12 The surface morphology of the superhydrophobic silica films prepared by sol-gel method

2.4 存在的问题

尽管越来越多具有微观粗糙度的超疏水表面被应用于金属腐蚀防护领域,但人们对这些微观结构在提高物理屏障效应、抑制腐蚀萌生发展进程中的关键作用还缺乏深入的探讨[52—53]。一般认为,对于暴露在大气下的超疏水表面,其微米、纳米结构可以驻留大量空气,大大减小水滴与表面的接触面积,而由此产生的自清洁效应使水滴难以在表面停留,从而缩短了水与表面的接触时间;对于浸没于水环境的超疏水表面来说,微观结构所捕获的气体形成气膜,也在一定程度上增加了超疏水表面结构对水等腐蚀性介质的物理屏障作用,如图 13 所示[54—56]。

张盾等人进一步研究发现,当水穿透气体屏障以后,Cassie 态接触变为 Wenzel 态接触,超疏水结构的防腐性能下降[57—60]。另外,这些结构大多致密性较差,难以形成持久的物理屏障,水分一旦穿透气膜,渗入这些微米、纳米多孔结构中,就会导致金属基体迅速腐蚀[61—62]。Yu 等人对比了具有一般疏水性和超疏水性的 TiO_2/ZnO 结构,发现超疏水 TiO_2/ZnO 结构

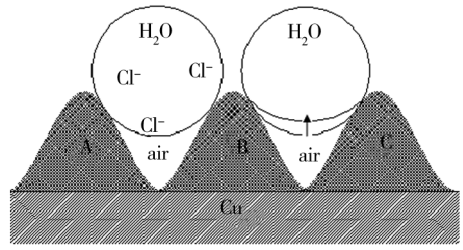


图 13 超疏水表面的防腐机理

Fig. 13 The anticorrosive mechanism of a superhydrophobic surface

由于孔隙率较高,其自清洁性较好,在大气环境下防腐能力较强[62],但是在浸没环境下,超疏水结构的孔隙更易于水的入侵,其防腐性能反而比一般疏水涂层更差。图 14 对比了这种超疏水结构在水滴实验和浸没实验下的电化学阻抗谱,水滴实验装置如图 15 所示。结果证明,超疏水涂层只有在保持液滴滚动特点时才会体现出高于一般疏水性表面的耐蚀性,在浸没环境中并不一定能够体现出高的耐蚀性。此外,目前超疏水防腐表面的制备方法大多难以实现精确调控表面粗糙度,对粗糙度及其对应的疏水性在防腐作用中的重要性还有待进一步研究[63—64]。

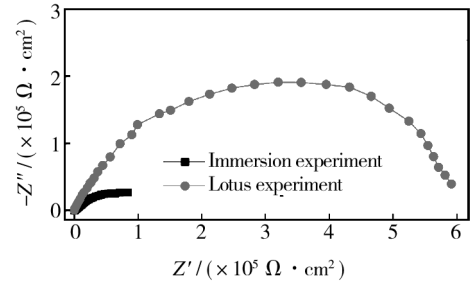


图 14 TiO_2/ZnO 超疏水结构经过 72 h 水滴实验和浸泡实验后的阻抗图

Fig. 14 Nyquist plots of the superhydrophobic TiO_2/ZnO surface after 72 h lotus experiment and immersion test

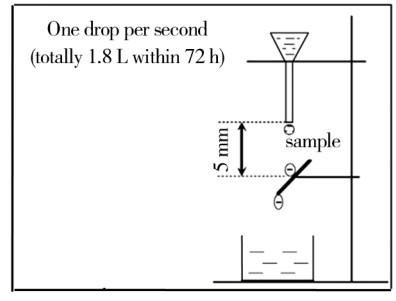


图 15 水滴实验示意

Fig. 15 Scheme of the instrument for lotus experiment

3　超疏水表面防腐技术未来的发展方向

3.1　提高超疏水防腐结构的机械强度及化学稳定性

目前已有的超疏水表面大多机械强度不高,在受到外力作用破坏时,其表面疏水性能下降,内部完整性遭到损伤,产生裂口等缺陷,防护能力随之降低。另外,这些涂层的化学稳定性较差,在紫外光照、酸、碱等苛刻条件下易被破坏。因此,提高机械强度及化学稳定性成为发展长效、耐久超疏水表面防腐技术的关键。Dennis 等人证明[65],具有微米、纳米二级结构的超疏水表面耐磨性能要好于单纯由纳米或微米结构组成的超疏水表面。Cohen 等人[66]通过水热法处理层层自组装法构建的聚合物/纳米粒子超疏水涂层,使涂层的机械耐磨性显著提高。Xu 等人[ ]以丝网为模板,压在低密度聚乙烯上,冷却后去除模板,聚乙烯表面形成了排列有序的三维阵列结构(图 16),不需经过化学修饰即可形成超疏水膜。以 8 cm/s 的速度反复研磨 5500 次后,聚乙烯表面仍然能够保持良好的超疏水性。Chen 等人采用盐酸多巴胺溶液和溶有 1-正十二硫醇的二氯甲烷溶液,在铜板表面形成一层多巴胺/1-正十二硫醇膜。电化学实验结果表明,该涂层具有良好的耐蚀性,在海水中浸泡 20 天后接触角变化很小,进一步说明其化学稳定性优异[68]。Ma 等人[69]通过热塑成型的过程,利用氧化铝模板和硅模板分别在金属玻璃表面构建微米、纳米二级结构,不经低表面能物质修饰即达到了超疏水。反复研磨实验和酸碱浸泡实验结果表明,该超疏水结构具有良好的机械强度和化学稳定性。

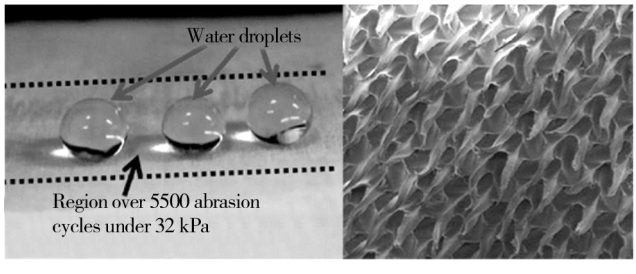


图 16　低密度聚乙烯超疏水表面

Fig. 16 Superhydrophobic low-density polyethylene surface

3.2　提高超疏水防腐结构的自修复能力

自修复材料指在破损时具有自修复功能,或者在热、光等外界刺激下自行修复的一种新兴智能材料,在腐蚀防护领域具有极为广泛的应用前景。将超疏水结构与自修复能力相结合,是综合提升材料表面防腐性能的一个理想手段[70]。对于超疏水表面,其疏水能力的自修复主要通过恢复低表面能物质来实现。例如,孙俊奇等人利用气相沉积法,在具有微观粗糙结构的多孔层层自组装涂层表面和内部沉积大量全氟辛基三甲氧基硅烷,制备了超疏水涂层。当疏水功能受损时,涂层微孔内储存的氟硅烷自行释放到涂层表面,实现超疏水性能的修复(图 17)[71]。利用相同的原理,介孔二氧化硅微米颗粒被用来存储低表面能十八烷基胺分子,组成具有自修复能力的超疏水涂层[72]。

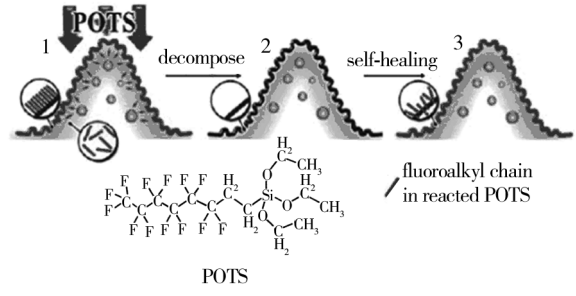


图 17　超疏水涂层自修复过程

Fig. 17 The self-healing process of a superhydrophobic coating

与恢复低表面能物质相比,通过恢复涂层表面粗糙微观结构实现超疏水性自修复的难度更大[72—74]。Manna 等人在化学交联聚乙烯亚胺-聚乙烯基二甲基恶唑啉酮层层自组装结构的基础上,结合正癸胺分子低表面能修饰,制备了具有微米、纳米多孔结构的超疏水涂层。当该涂层受到外力挤压失去表面微观结构时,涂层疏水性能下降,而水、酸等液体可通过对涂层的溶胀作用恢复这种结构,使其重新具有超疏水性能[74]。

4　结语

超疏水表面技术对于腐蚀防护领域的发展意义非凡。理解并运用超疏水表面的防护机制,能够推动超疏水表面技术在腐蚀防护领域中的广泛应用。探究提升超疏水表面机械强度与化学稳定性,并使超疏水表面在破损后迅速恢复原有防腐性能的有效途径,为开发长效智能防腐表面技术提供了新的思路,具有重要科学意义和实用价值。

参考文献

[1]　SΦRENSEN P A,Kiil S,DAM-JOHANSEN K,et al. Anticor-

rosive Coatings:A Review[J]. Journal of Coatings Technology and Research,2009,6:135—176.

[2] ZHANG J T,HU J M,ZHANG J Q,et al. Studies of Impedance Models and Water Transport Behaviors of Polypropylene Coated Metals in NaCl Solution[J]. Progress in Organic Coatings,2004,49:293—301.

[3] TAN Y. An Overview of Techniques for Characterizing Inhomogeneities in Organic Surface Films and Underfilm Localized Corrosion[J]. Progress in Organic Coatings,2013,76:791—803.

[4] 顾惕人,朱步瑶,马季铭. 表面化学[M]. 北京:科学出版社,2001.
GU T R,ZHU B Y,MA J M. Surface Chemistry[M]. Beijing:Science Publishing,2001.

[5] LI X M,REINHOUDT D,CREGO-CALAMA M. What do We Need for a Superhydrophobic Surface? A Review on the Recent Progress in the Preparation of Superhydrophobic Surfaces[J]. Chemical Society Reviews,2007,36(8):1350—1368.

[6] 赵宁,卢晓英,张晓艳,等. 超疏水表面的研究进展[J]. 化学进展,2007,19(6):860—871.
ZHAO N,LU X Y,ZHANG X Y,et al. Progress in Superhydrophobic Surfaces[J]. Progress in Chemistry,2007,19(6):860—871.

[7] BARTHLOTT W,NEINHUIS C. Purity of the Sacred Lotus,or Escape from Contamination in Biological Surfaces[J]. Planta,1997,202:1—8.

[8] FENG L,LI S,LI Y,et al. Super-hydrophobic Surfaces:From Natural to Artificial[J]. Advanced Materials,2002,14(24):1857—1860.

[9] YOUNG T. An Essay on the Cohesion of Fluids[J]. Philosophical Transactions of the Royal Society of London,1805,95:65—87.

[10] 柯清平,李广录,郝天歌,等. 超疏水模型及其机理[J]. 化学进展,2010,22(2):284—290.
KE Q P,LI G L,HAO T G,et al. Superhydrophobicity:Theoretical Models and Mechanism[J]. Progress in Chemistry,2010,22(2):284—290.

[11] 刘胭芝,李鸿岩,费明. 有机硅化学改性环氧树脂的研究进展[J]. 包装学报,2012,4(4):31—37.
LIU Y Z,LI H Y,FEI M. Research Progress of Chemical Modification of Epoxy Resin with Organic Silicon[J]. Packaging Journal,2012,4(4):31—37.

[12] 张斌,刘伟区. 有机硅改性环氧树脂[J]. 化工新型材料,2001,29(8):12—17.
ZHANG B,LIU W Q. Epoxy Resin Modified by Organic Silicon[J]. New Chemical Materials,2001,29(8):12—17.

[13] 郑黎俊,乌学东,楼增. 表面微细结构制备超疏水表面[J]. 科学通报,2004,49(17):1691—1699.
ZHENG L J,WU X D,LOU Z. Surface Preparation of Superhydrophobic Surface Microstructure[J]. Chinese Science Bulletin,2004,49(17):1691—1699.

[14] LIU K,TIAN Y,JIANG L. Bio-inspired Superoleophobic and Smart Materials:Design,Fabrication,and Application[J]. Progress in Materials Science,2013,58:503—564.

[15] 张成. 金属基超疏水表面的一步法制备及耐蚀性研究[D]. 大连:大连理工大学,2013.
ZHANG C. Corrosion Resistance of Super-hydrophobic Film Fabricated by One-step Method on Metal Substrate[D]. Dalian:Dalian University of Technology,2013.

[16] ADEL M A,MOHAMED,ABOUBAKR M,et al. Corrosion Behavior of Superhydrophobic Surfaces:A Review[J]. Arabian Journal of Chemistry,2014:1—17.

[17] SHON M,KWON H. Comparison of Surface Modification with Amino Terminated Polydimethylsiloxane and Amino Branched Polydimethylsiloxane on the Corrosion Protection of Epoxy Coating[J]. Corrosion Science,2009,51:650—657.

[18] 张冰,刘香鸾,黄英. 氨基聚硅氧烷对改性环氧树脂的形态与性能的影响[J]. 功能高分子学报,2000,13:69—72.
ZHANG B,LIU X L,HUANG Y. Effects of the Amino Group Content of Polydimethylsiloxane Bearing Pendant Amino Groups on the Morphology and Properties of Modified Epoxy Resin[J]. Journal of Functional Polymers,2000,13:69—72.

[19] CUI X,GAO Y,ZHONG S,et al. Synthesis and Surface Properties of Semi-interpenetrating Fluorine-containing Polyacrylate and Epoxy Resin Networks[J]. Journal of Po-lymer Research,2012,19:1—7.

[20] 朱晓明,周学杰,纪方奇,等. 氟碳涂层体系在严酷自然环境中的腐蚀行为[J]. 涂料技术,2012,33:32—39.
ZHU X M,ZHOU X J,JI F Q,et al. Anticorrosion Performance of Fluorocarbon Coatings System in Severe Natural Environment[J]. Coatings Technology,2012,33:32—39.

[21] YUAN S J. Superhydrophobic Fluoropolymer-modified Copper Surface via Surface Graft Polymerisation for Corrosion Protection[J]. Corrosion Science,2011,53(9):2738—2747.

[22] 刘涛. 金属基体超疏水表面的制备及其海洋防腐防污功能的研究[D]. 青岛:中国海洋大学,2009.
LIU T. Fabrication of Super-hydrophobic Surfaces on Metallic Substrates and Research on Anti-corrosion and Anti-biofilm Properties[D]. Qingdao:Ocean University of China,2009.

[23] DIAZ I,CHICO B,DE LA FUENTE D,et al. Corrosion Re-

sistance of New Epoxy-Siloxane Hybrid Coatings[J]. Alaboratory Study Progress in Organic Coatings,2010,69:278—286.

[24] CHEN X Y,YUAN J H,HUANG J,et al. Large-scale Fabrication of Superhydrophobic Polyurethane/Nano-Al_2O_3 Coatings by Suspension Flame Spraying for Anti-corrosion Applications[J]. Applied Surface Science,2014,311:864—869.

[25] WANG P,ZHANG D,QIU R,et al. Green Approach to Fabrication of a Super-hydrophobic Film on Copper and the Consequent Corrosion Resistance[J]. Corrosion Science,2014,80:366—373.

[26] FAN Y H,CHEN Z J,LIANG J,et al. Preparation of Superhydrophobic Films on Copper Substrate for Corrosion Protection[J]. Surface & Coatings Technology,2014,244:1—8.

[27] PHILIP M B,PRATIK B S,ERIK B W,et al. Corrosion Inhibition Using Superhydrophobic Films[J]. Corrosion Science,2008,50:897—902.

[28] BOINOVICH L B,GNEDENKOV S V,ALPYSBAEVA D A. Corrosion Resistance of Composite Coatings on Low-carbon Steel Containing Hydrophobic and Superhydrophobic Layers in Combination with Oxide Sublayers[J]. Corrosion Science,2012,55:238—245.

[29] ISIMJAN T T,WANG T Y,ROHANI S. A Novel Method to Prepare Superhydrophobic, UV Resistance and Anti-corrosion Steel Surface[J]. Chemical Engineering Journal,2012,210:182—187.

[30] GIVENCHY EPT De,AMIGONI S,MARTIN C,et al. Fabrication of Superhydrophobic PDMS Surfaces by Combining Acidic Treatment and Perfluorinated Monolayers[J]. Langmuir,2009,25(11):6448—6453.

[31] LIU T,YIN Y,CHEN S,et al. Super-hydrophobic Surfaces Improve Corrosion Resistance of Copper in Seawater[J]. Electrochimica Acta,2007,52:3709—3713.

[32] ISHIZAKI T,MASUDA Y,SAKAMOTO M. Corrosion Resistance and Durability of Superhydrophobic Surface Formed on Magnesium Alloy Coated with Nanostructured Cerium Oxide Film and Fluoroalkylsilane Molecules in Corrosive NaCl Aqueous Solution[J]. Langmuir, 2011, 27: 4780—4788.

[33] HE T,WANG Y C,ZHANG Y J,et al. Super-hydrophobic Surface Treatment as Corrosion Protection for Aluminum in Seawater[J]. Corrosion Science,2009,51:1757—1761.

[34] ZHAO L, LIU Q, GAO R, et al. One-step Method for the Fabrication of Superhydrophobic Surface on Magnesium Alloy and Its Corrosion Protection, Antifouling Performance [J]. Corrosion Science,2014,80:177—183.

[35] ZHANG F,CHEN S G,DONG L H,et al. Preparation of Superhydrophobic Films on Titanium as Effective Corrosion Barriers[J]. Applied Surface Science, 2011, 257: 2587—2591.

[36] WANG P,QIU R,ZHANG D,et al. Fabricated Super-hydrophobic Film with Potentiostatic Electrolysis Method on Copper for Corrosion Protection[J]. Electrochimica Acta,2010,56:517—522.

[37] 孙佳. AZ31 镁合金表面超疏水膜层制备及耐蚀性能研究[D]. 哈尔滨:哈尔滨工业大学,2013.
SUN J. Superhydrophobic Coating Prepared and Study on Corrosion Resistance of AZ31 Magnesium Alloy[D]. Harbin:Harbin Engineering University,2013.

[38] 苏东. 改性环氧树脂超疏水涂层的制备、结构与性能研究[D]. 广州:华南理工大学,2012.
SU D. Studys on Fabrication,Structure and Properties of Superhydrophobic Film Modified with Epoxy Resin[D]. Guangzhou:South China University of Technology,2012.

[39] LIANG J,HU Y C,WU Y Q,et al. Fabrication and Corrosion Resistance of Superhydrophobic Hydroxide Zinc Carbonate Film on Aluminum Substrates[J]. Journal of Nanomaterials,2013:1—6.

[40] FENG L,ZHANG H,WANG Z,et al. Superhydrophobic Aluminum Alloy Surface:Fabrication,Structure,and Corrosion Resistance[J]. Colloids and Surfaces A:Physicochemical and Engineering Aspects,2014,441:319—325.

[41] LIU K S,ZHANG M L,ZHAI J,et al. Bioinspired Construction of Mg-Li Alloys Surfaces with Stable Superhydrophobicity and Improved Corrosion Resistance[J]. Applied Physics Letters,2008,92:183103-1—3.

[42] 王青芬,陈吕,龙鑫远. 基于水热处理的镁合金超疏水表面制备及其腐蚀防护性能研究[J]. 江西化工,2013(1):66—71.
WANG Q F,CHEN L,LONG X Y. Fabrication of Superhydrophobic Surfaces on Magnesium Alloy Substrates by Hydrothermal Treatment and Its Corrosion Resistance[J]. Jiangxi Chemical Industry,2013(1):66—71.

[43] OU J,HU W,XUE M,et al. Superhydrophobic Surfaces on Light Alloy Substrates Fabricated by a Versatile Process and Their Corrosion Protection[J]. ACS Applied Materials & Interfaces,2013,5:3101—3107.

[44] 徐建海,李梅,赵燕. 具有微纳米结构超疏水表面润湿性的研究[J]. 化学进展,2006,18(11):1425—1433.
XU J H,LI M,ZHAO Y. Advance of Wetting Behavior Research on the Superhydrophobic Surface with Micro- and Nano-structures[J]. Progress in Chemistry,2006,18(11):1425—1433.

[45] LIN Y C,HSU S H,CHUNG Y C. Thermal Imprint Techniques for Preparation of Superhydrophobic Polymer Coa-

tings[J]. Surface & Coatings Technology, 2013, 231: 501—506.

[46] 谢永元,周勇亮,俞小春. 以砂纸为模板制作聚合物超疏水表面[J]. 高等学校化学学报, 2007(8): 1577—1580.
XIE Y Y, ZHOU Y L, YU X C. Replication of Superhydrophobic Surfaces of Polymer from Abrasive Papers [J]. Chemical Journal of Chinese Universities, 2007(8): 1577—1580.

[47] CHANG C H, HSU M H, WENG C J, et al. 3D-bioprinting Approach to Fabricate Superhydrophobic Epoxy/Organophilic Clay as an Advanced Anticorrosive Coating with the Synergistic Effect of Superhydrophobicity and Gas Barrier Properties [J]. Journal of Materials Chemistry A, 2013, 1: 13869—13877.

[48] CHANG K C, HSU M H, LU H I, et al. Room-temperature Cured Hydrophobic Epoxy/Graphene Composites as Corrosion Inhibitor for Cold-rolled Steel [J]. Carbon, 2014, 66: 144—153.

[49] LI S M, WANG Y G, LIU J H, et al. Preparation of Superhydrophobic Coating on Aluminum Alloy with Its Anti-corrosion Property [J]. Physico-Chimica Sinica, 2007, 23(10): 1631—1636.

[50] SU F H, YAO K. Facile Fabrication of Superhydrophobic Surface with Excellent Mechanical Abrasion and Corrosion Resistance on Copper Substrate by a Novel Method [J]. ACS Applied Materials & Interfaces, 2014, 6: 8762—8770.

[51] RAO A V, SANJAY S L, SATISH A M. Mechanically Stable and Corrosion Resistant Superhydrophobic Sol-Gel Coatings on Copper Substrate [J]. Applied Surface Science, 2011, 257: 5772—5776.

[52] WANG P, ZHANG D, QIU R. Liquid/Solid Contact Mode of Super-hydrophobic Film in Aqueous Solution and Its Effect on Corrosion Resistance [J]. Corrosion Science, 2012, 54: 77—84.

[53] 张泓筠. 超疏水表面微结构对其疏水性能的影响及应用[D]. 湘潭: 湘潭大学, 2013.
ZHANG H J. Influence of Microstructure for Superhydrophobic Surfaces on Superhydrophobicity and Its Application [D]. Xiangtan: Xiangtan University, 2013.

[54] YIN Y S. Structure Stability and Corrosion Inhibition of Super-hydrophobic Film on Aluminum in Seawater [J]. Applied Surface Science, 2008, 255(5): 2978—2984.

[55] HUANG Y, SARKAR D K, GALLANT D, et al. Corrosion Resistance Properties of Superhydrophobic Copper Surfaces Fabricated by One-step Electrochemical Modification Process [J]. Applied Surface Science, 2013, 282: 689—694.

[56] EJENSTAM L, OVASKAINENC L, RODRIGUEZ-MEIZOSO I, et al. The Effect of Superhydrophobic Wetting State on Corrosion Protection——The AKD Example [J]. Journal of Colloid and Interface Science, 2013, 412: 56—64.

[57] SONG J L, XU W J, LU Y, et al. Fabrication of Superhydrophobic Surfaces on Mg Alloy Substrates Via Primary Cell Corrosion and Fluoroalkylsilane Modification [J]. Materials and Corrosion, 2013, 64(11): 979—987.

[58] WANG P, ZHANG D, QIU R, et al. Super-hydrophobic Film Prepared on Zinc and Its Effect on Corrosion in Simulated Marine Atmosphere [J]. Corrosion Science, 2013, 69: 23—30.

[58] WANG C Q, XIAO J Y, ZENG J C. A Novel Method to Prepare a Microflower-like Superhydrophobic Epoxy Resin Surface [J]. Materials Chemistry and Physics, 2012, 135: 10—15.

[60] 刘明芝. 超疏水表面制备及其在海水中的腐蚀行为研究[D]. 南昌: 南昌航空大学, 2012.
LIU M Z. Fabrication of Superhydrophobic Surface and Its Corrosion Behaviors in Seawater [D]. Nanchang: Nanchang Aeronautical University, 2012.

[61] QIU R, ZHANG D, WANG P. Superhydrophobic-Carbon Fibre Growth on a Zinc Surface for Corrosion Inhibition [J]. Corrosion Science, 2013, 66: 350—359.

[62] YU D, TIAN J. Superhydrophobicity: Is It Really Better than Hydrophobicity on Anti-corrosion? [J]. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2014, 445: 75—78.

[63] 曲爱兰,文秀芳,皮丕辉. 超疏水涂膜的研究进展[J]. 化学进展, 2006, 18(11): 1434—1439.
QU A L, WEN X F, PI P H. Studies on Super-hydrophobic Films [J]. Progress in Chemistry, 2006, 18(11): 1434—1439.

[64] 潘光,黄桥高,胡海豹. 超疏水表面的润湿性及其应用研究[J]. 材料导报, 2009, 23(11): 64—67.
PAN G, HUANG Q G, HU H B. Study Wettability of Superhydrophobic Surface and Its Application [J]. Material Review, 2009, 23(11): 64—67.

[65] XIU Y, LIU Y, HESS D W, et al. Mechanically Robust Superhydrophobicity on Hierarchically Structured Si Surfaces [J]. Nanotechnology, 2010, 21(15): 155705—155709.

[66] ZEKERIYYA G, HIROOMI S, COHEN R E, et al. Hydrothermal Treatment of Nanoparticle Thin Films for Enhanced Mechanical Durability [J]. Langmuir, 2008, 24(5): 2168—2177.

[67] XU Q F, MONDAL B, LYONS A M. Fabricating Superhydrophobic Polymer Surfaces with Excellent Abrasion Resistance by a Simple Lamination Templating Method [J]. ACS Applied Materials & Interfaces, 2011, 3(9): 3508—3514.

(下转第 30 页)

234.

[7] ZENG D Z, CHEN R, ZHANG Z, et al. Research on Stress Corrosion Sensitivity of C110 Casing in Wellbore Protection Fluid[J]. Energy Procedia, 2012, 16: 816—821.

[8] ABAYARATHNA D, NARAGHI A, WANG S H. The Effect of Surface Films on Corrosion of Carbon Steel in a CO_2-H_2S-H_2O System[C]//Corrosion 2005. Houston: NACE, 2005: 05624.

[9] LI W F, ZHOU Y J, XUE Y. Corrosion Behavior of 110S Tube Steel in Environments of High H_2S and CO_2 Content [J]. Journal of Iron and Steel Research, International, 2012, 12(19): 59—65.

[10] YIN Z F, ZHAO W Z, BAI Z Q, et al. Corrosion Behavior of SM 80SS Tube Steel in Stimulant Solution Containing H_2S and CO_2[J]. Electrochimica Acta, 2008, 53(10): 3690—3700.

[11] APISPEC 5CT. Specification for Casing and Tubing[S].

[12] GB/T 15970.6—1998. Corrosion of Metals and Alloys—Stress Corrosion Testing—Part 6: Preparation and Use of Precracked Specimens for Tests Under Constant Load or Constant Displacement[S].

[13] WU Y M. Applying Process Modeling to Screen Refining Equipment for Wet Hydrogen Sulfide Service[J]. Corrosion, 1998, 54(2): 169—173.

[14] HEUER J K, STUBBINS J F. An XPS Characterization of $FeCO_3$ Films from CO_2 Corrosion[J]. Corrosion Science, 1999(41): 1231—1243.

[15] MA H Y, CHENG X L, LI G Q, et al. The Influence of Hydrogen Sulfide on Corrosion of Iron under Different Conditions[J]. Corrosion, 2000(42): 1669—1683.

[16] KITTEL J, ROPITAL F, GROSJEAN F, et al. Corrosion Mechanisms in Aqueous Solutions Containing Dissolved H_2S. Part 1: Characterization of H_2S Reduction on a 316L Rotating Disc Electrode[J]. Corrosion Science, 2013, 66: 324—329.

[17] FRAGIEL A, SEMA S, PEREZ R. Electrochemical Study of Two Micro-alloyed Pipeline Steels in H_2S Environments [J]. International Journal of Hydrogen Energy, 2005, 30: 1303.

[18] LIU Z Y, DONG C F, LI X G. Stress Corrosion Cracking of 2205 Duplex Stainless Steel in H_2S-CO_2 Environment[J]. J Mater Sci, 2009, 44: 4228—4234.

[19] DING J H, ZHANG L, LU M X, et al. The Electrochemical Behavior of 316L Austenitic Stainless Steel in Cl^- Containing Environment under Different H_2S Partial Pressures [J]. Applied Surface Science, 2014, 289: 33—41.

[20] BANAS J, LELEK-BORKOWSKA U, MAZURKIEWICZ B, et al. Effect of CO_2 and H_2S on the Composition and Stability of Passive Film on Iron Alloys in Geothermal Water[J]. Electrochimica Acta, 2007, 52(18): 5704—5714.

[21] JEVREMOVIC I, SINGER M, NESIC S, et al. Inhibition Properties of Self-assembled Corrosion Inhibitor Talloil Diethylenetriamine Imidazoline for Mild Steel Corrosion in Chloride Solution Saturated with Carbon Dioxide[J]. Corrosion Science, 2013, 77: 265—272.

(上接第 24 页)

[68] CHEN S J, CHEN Y, LEI Y H, et al. Novel Strategy in Enhancing Stability and Corrosion Resistance for Hydrophobic Functional Films on Copper Surfaces[J]. Electrochemistry Communications, 2009, 11: 1675—1679.

[69] MA J, ZHANG X Y, WANG D P, et al. Superhydrophobic Metallic Glass Surface with Superior Mechanical Stability and Corrosion Resistance[J]. Applied Physics Letters, 2014, 104(173701): 1—5.

[70] ZHENG S X, LI J H. Inorganic-Organic Sol Gel Hybrid Coatings for Corrosion Protection of Metals[J]. Journal of Sol-Gel Science and Technology, 2010, 54: 174—187.

[71] LI Y, LI L, SUN J. Bioinspired Self-healing Superhydrophobic Coatings[J]. Angewandte Chemie, 2010, 122: 6265—6269.

[72] LIU Q, WANG X, YU B, et al. Self-healing Surface Hydrophobicity by Consecutive Release of Hydrophobic Molecules from Mesoporous Silica[J]. Langmuir, 2012, 28: 5845—5849.

[73] XUE C H, MA J Z. Long-lived Superhydrophobic Surfaces [J]. Journal of Materials Chemistry A, 2013, 1: 4146—4161.

[74] CHEN C M, YANG S. Directed Water Shedding on High-aspect-ratio Shape Memory Polymer Micropillar Arrays[J]. Advanced Materials, 2014, 26(8): 1283—1288.