第 33 卷　第 2 期
2014 年 2 月

中国材料进展
MATERIALS CHINA

Vol. 33　No. 2
Feb. 2014

特约专栏

有机硅溶胶 – 凝胶防腐蚀涂层研究进展

彭叔森，曾志翔，韩　金，陈建敏，乌学东
（中国科学院宁波材料技术与工程研究所 中国科学院海洋新材料与应用技术重点实验室
浙江省海洋材料与防护技术重点实验室，浙江 宁波 315201）

摘　要：有机硅溶胶 – 凝胶涂层是指以烷基烷氧基硅烷为前驱体通过溶胶 – 凝胶技术制备的涂层。有机硅是分子水平上的有机 – 无机杂化分子，因此有机硅溶胶 – 凝胶涂层兼具了有机材料和无机材料的性能，并且能通过合理的调控有机和无机成分来获得所需的性能。其热稳定、耐刮擦性与无机材料的结合性能明显高于普通的有机材料，柔韧性与有机材料的结合性能明显高于一般的无机涂层。近年来，这种新型的、具有特殊性能的涂层被广泛研究用来保护金属材料（如铝、铁、镁、铜基材料）。介绍了有机硅溶胶 – 凝胶涂层涉及的基本反应、硅烷在金属表面上的成键机理以及在不同金属上的应用等方面的研究进展，并展望了有机硅溶胶 – 凝胶涂层应用前景及未来的研究方向。

关键词：防腐蚀；溶胶 – 凝胶；有机硅；涂层

中图分类号：TM207　　**文献标识码**：A　　**文章编号**：1674 – 3962(2014)02 – 0077 – 09

Progress of Anticorrosion of Silane Based Sol-Gel Coating

PENG Shusen, ZENG Zhixiang, HAN Jin, CHEN Jianmin, WU Xuedong
(Key Laboratory of Marine Materials and Related Technologies, Zhejiang Key Laboratory of Marine Materials and Protective Technologies, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China)

Abstract: Silane based sol-gel coating refers to coating material prepared by sol-gel technique using alkyl alkoxy silane as precursor. Silane is a molecular level organic-inorganic hybrid molecule, therefore silane based sol-gel coating combines the properties of organic materials and inorganic materials, and can achieve desired properties through controlling organic and inorganic components. Its thermal stability, scratching resistant and adhesion to inorganic material are significantly higher than organic coating, its flexibility and adhesion to organic materials are remarkably higher than inorganic coating. Recently, this novel and special coating is widely used to protect metal materials such as aluminum, iron, magnesium and copper-based metals. The basic reactions in sol-gel process, the bond mechanism between silane and metal surface and application of silane based sol-gel coating on various metals are introduced. Recent research and future applications of the coating are discussed too.

Key words: anticorrosion; sol-gel; organic silane; coating

1　前　言

溶胶 – 凝胶技术是一种由金属有机化合物、金属无机化合物或它们的混合物经水解缩合过程，逐渐凝胶化及进行相应后处理，而获得氧化物或其它化合物的工艺。现代溶胶 – 凝胶技术的历史可以追溯到 1846 年，法国科学家 Ebelmen 发现 $SiCl_4$ 与乙醇混合后在湿空气中会水解形成凝胶[1]。经过近两个世纪的发展，溶胶 – 凝胶技术已被广泛的用于制备体材料、纤维材料、薄膜材料及纳米粉体等[2]。早期用于金属表面上的溶胶 – 凝胶涂层从其作用上可以分为抗氧化涂层、耐蚀涂层、附着促进层、耐刮擦涂层及绝缘涂。Guglielmi[3] 于 1997 年撰文总结了用于金属表面的溶胶 – 凝胶涂层的工作，从该文献可知涂层材料多为无机材料。无机溶胶 – 凝胶涂层的优点是具有高的热稳定性及在金属上有好的附着性能，其优异的附着性能也使得溶胶 – 凝胶涂层作为一种取代铬钝化和磷化膜的技术而被广泛研究。不过，尽管无机溶胶 – 凝胶涂层能够提供很好的腐蚀保护效果，然而其应用受限于：①无机氧化物涂层的高内应力、高

收稿日期：2013 – 11 – 01
基金项目：国家自然科学青年基金资助项目(51303192)；国家自然科学基金资助项目(51335010)
第一作者：彭叔森，男，1985 年生，博士后
通讯作者：乌学东，男，1972 年生，研究员，博士生导师，Email：xdwu@ nimte. ac. cn
DOI：10. 7502/j. issn. 1674 – 3962. 2014. 02. 02

脆性使得难以获得无裂痕的厚膜(>1 μm); ②需要相对的高温(400 ~800 ℃)才能获得较好的性能[4]。

有机 - 无机杂化材料兼具了有机材料和无机材料的特性，而成为新材料的研发热点[6]。通过改变无机、有机组分可以连续的改变材料的性质而获得所需的性能。无机成分可以获得好的耐刮擦、耐久性能及在金属上优异的附着性能；而有机组份提高材料的致密性、韧性以及带官能基团等。溶胶 - 凝胶技术是一种制备有机 - 无机杂化材料的优异的手段，关于这方面的工作可以参阅 Wilkes 等人的综述文章[7-8]。为了解决纯无机溶胶 - 凝胶涂层的高脆性、降低其成膜温度，有机成分被添加到体系中以来获得优异的性能。目前主要有 3 种途径获得有机 - 无机杂化溶胶 - 凝胶涂层[9]：简单混合有机组分和无机溶胶 - 凝胶，两成分间无化学键作用(图 1a)；利用有机聚合物/低聚物中的官能团与无机前驱体反应，两者间通过化学键连结(图 1b)；使用烷基烷氧基硅烷作为溶胶 - 凝胶前躯体或与金属醇盐、$Si(OR)_4$ 一起作为起溶胶 - 凝胶的前躯体，所得的主链为无机 Si - O - Si 或 Si - O - M(M 为 Zr 或 Ti)结构，有机成份为侧基悬挂在硅原子上(图 1c)。在这 3 种途径中，以有机硅为前驱体的方法使用最为广泛。这是因为烷基烷氧基硅烷的有机活性基团多种多样、Si - OR 水解反应温和、多数烷基烷氧基硅烷为商业化、批量生化产的产品。近年来，有机硅溶胶 - 凝胶防腐蚀涂层已成为防腐蚀材料领域的研究热点。本文从有机硅溶胶的制备的基本反应、硅烷在金属表面上的成膜机理以及在不同金属上的应用等方面进行介绍。

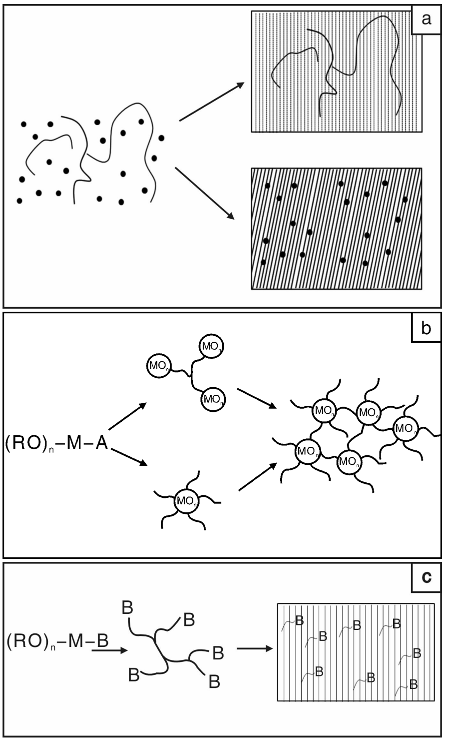

图 1 溶胶 - 凝胶技术制备有机 - 无机杂化材料的结构示意图[5]

Fig. 1 Structural models of different classes of organic-inorganic hybrid materials formed by the sol-gel process[5]

2 有机硅溶胶 - 凝胶涂层

有机硅溶胶 - 凝胶涂层是指以烷基烷氧基硅烷为前驱体通过溶胶 - 凝胶技术制备的涂层。烷基烷氧基硅烷是一类天然的有机 - 无机杂化分子：一端是可水解的Si - OR基团；另一端是各种有机基团如氨基、环氧、巯基、双键、异氰基官能等。这类有机硅化合物作为偶联剂而广泛应用于有机聚合物复合材料的制备、高分子化合物改性以及有机 - 无机杂化材料的合成等领域。图 2 给出了一些常见的

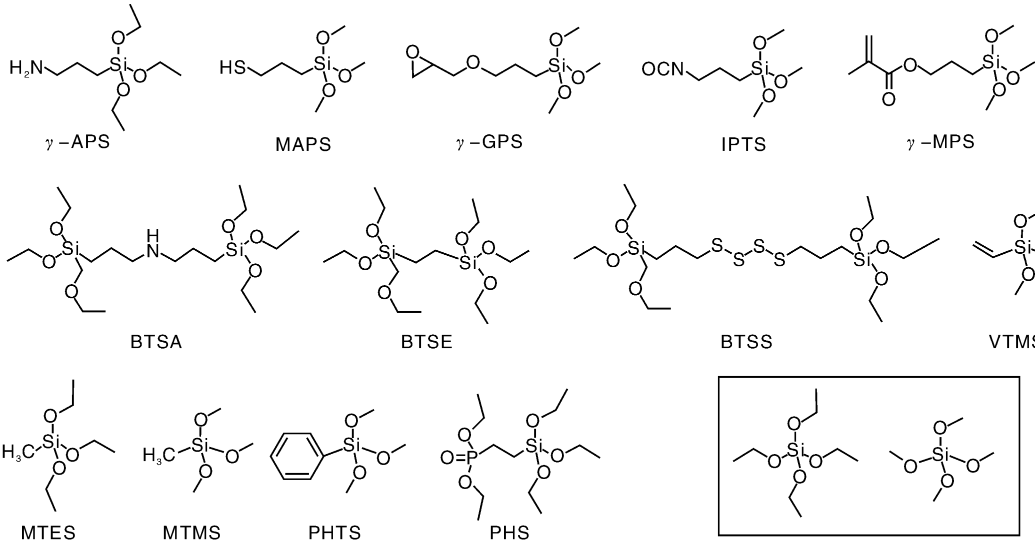

图 2 一些常见烷基烷氧基硅烷和烷氧基硅烷的分子结构

Fig. 2 Molecular structure of alkylalkoxysilanes and alkoxysilanes

烷基烷氧基硅烷和烷氧基硅烷的分子结构示意图。有机硅分子在溶胶－凝胶过程中主要涉及 Si－OR 的水解及 Si－OH 的缩合反应，下面专门进行介绍。

2.1　烷氧基硅烷和烷基烷氧基硅烷的反应

烷氧基硅烷在含水溶液中最为重要的反应是水解和缩合反应[10]。这两个反应会影响硅烷分子的溶解性、硅烷溶液的稳定性[11]、反应活性以及所得产物的结构，因此已有大量关于其反应机理的研究。第一篇相关的研究报道见于 1844 年，Ebelmen 研究了四乙氧基硅烷(TEOS)的水解和缩合反应[12]，并发现缩聚反应伴随水解反应的进行而进行。Konrad[13]系统的研究了水在四甲氧基硅烷(TMOS)水解中起到的作用，其结果显示当水量少于可水解基团的时，产物更偏向形成线性分子，而当水过量时产物偏向形成三维网状结构。Schmidt[14]撰文这方面的工作进行了详细的综述。

对烷基烷氧基硅烷的水解－缩合的研究也有不少的报道，如已有报道研究了甲基三乙氧基(MTES)[15]，乙烯基三甲氧基硅烷(VTMS)和乙烯基三乙氧基硅烷(VTES)[15]，3－缩水甘油氧基丙基三甲氧基硅烷(γ－GPS)[16]，γ－GPS 和胺丙基三乙基硅烷(γ－APS)混合体系[17]，γ－UPS[17]，甲基丙烯酰氧基丙基三甲氧基硅烷(γ－MPS)[18]，苯基三乙氧基硅烷(PHTS)[19]，胺丙基三乙氧基硅烷(γ－APS)，1，2－二(三乙氧基硅基)乙烷(BTSE)[20]，1，2－二(3－三甲氧基甲硅烷基丙基)胺(BTSA)和乙烯基三乙酰氧基(VTSA)的混合体系[21]，VTSA[22]，丙基三甲氧基硅烷(PTS)[23]的水解－缩合反应。研究手段多为 IR，Raman，1H－NMR，29Si－NMR 等。总的来说，影响烷基烷氧基硅烷的反应活性的因素[24]主要有烷氧基的体积效应[25]、连接在硅原子上的烷基、有机溶剂、溶液浓度、pH 值及温度。

2.2　硅烷在金属表面上的成键机理

硅烷在金属表面的成键机理一般认为是硅醇能和金属表面上的羟基通过脱水反应形成 Si－O－Me 键，其反应如图 3 所示。该机理由 Plueddemann[26]提出，也为已有的一些研究所证实。如 Getting 等[27]利用 SIMS 和 XPS 研究了 γ－GPS 在钢材上形成薄膜。SIMS 结果显示在硅烷处理过的钢材上得到 $Fe－O－Si^+$ 峰，因此他们称硅烷在钢上形成 Si－O－Fe 键而结合到铁基体上。Watts 等[28]用 SIMS 和 XPS 研究了 γ－GPS 在铁基体上形成的硅烷薄膜，同样发现 $Fe－O－Si^+$ 的存在。在 γ－GPS 处理过的铝合金表面上，Leung 等[29]通过 XPS 分析得到了 Si－O－Al 的信号。Teo 等[30]用 SIMS 研究了经 BTSE 处理的铝表面发现了 $Al－O－Si^+$ 的峰。Fang 等[31]用 SIMS 和 XPS 研究了 γ－GPS 处理过的铝合金表面，获得了 $Al－O－Si^+$ 的信息。从文献报道来看，关于硅烷在金属表面上的成键机理还需进一步的研究，还需要更多的数据支持。

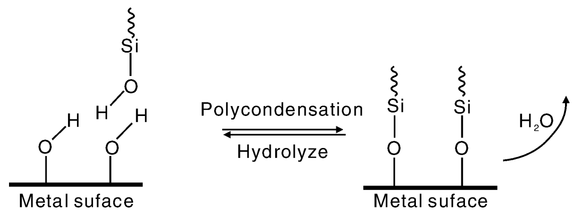

图 3　硅羟基和金属表面上的羟基的反应示意图

Fig. 3　Schematic representation of condensation of silanol with hydroxyl groups on the metal surface

2.3　有机硅溶胶-凝胶涂层在不同金属上的应用

Schmidt 等[32]在 1994 年撰文介绍了有机－无机杂化溶胶－凝胶涂层在不同场合下的应用，其中提到有机硅溶胶－凝胶涂层用作金属防腐涂层。1997 年，Pilz 等[33]采用多种硅烷制备了用于青铜户外保护的溶胶－凝胶涂层。1998 年，Langenfeld 等[34]研究了基于 γ－GPS 的溶胶－凝胶涂层对镁、铝、锌、黄铜的保护。1999 年，Metroke 等[35]以 γ－GPS 和 TEOS 为前驱体制备了杂化溶胶－凝胶涂层，并用盐雾测试评估了该涂层对铝合金的保护效果。进入 2000 年后，有机硅溶胶－凝胶涂层也得到了飞速发展。表 1 给出了常用硅烷及其它前驱体的缩写及化学名称。

表 2 总结了 2000 年后有关于有机硅溶胶－凝胶防腐蚀涂层的文献报道。文献按照金属基体进行了分类并列出了所用的前驱体(缩写及化学名称见表 1)及添加物。从金属基体看有机硅溶胶－凝胶防腐蚀涂层主要应用于铝基、铁基、铜基及镁基材料。其中在铝基材料研究最多，在纯铝及各种型号的铝合金上都有相关的研究。铁基材料除纯铁外，还涉及碳钢、不锈钢及镀锌铁。在铜基材料上主要为紫铜。随着近年来镁合金的应用推广，利用有机硅溶胶－凝胶涂层对镁合金的防护研究也日趋增多。研究报道的多少在一定程度上也反映了有机硅溶胶－凝胶涂层在该金属基材料上应用情况。从应用上看，在铝合金最为成功，国外已有取代铬钝化的应用，在铜上的效果较差。这是因为涂层的保护性能取决于涂层在金属表面上的附着性能，而有机硅溶胶－凝胶涂层与金属间的附着取决于是否易形成 Si－O－Metal 键。已有的研究证实 Si－O－Al 易形成[31]，而 Si－O－Cu 是难以形成的[36]。

从有机基团的角度可以将有机硅溶胶－凝胶涂层分为以下几大类：①有机基团为非活性基团的甲基、苯基，如以 MTMS[37]，PhTS[38]为前驱体制备的涂层等；②有机活性基团带有环氧基团，烷基烷氧基硅烷多为

表1 常用硅烷及其它前驱体的缩写及化学名称

Table 1 Abbreviation and chemical name of some used precursors

Abbreviation	Chemical name
γ－AAPS	[3－(2－Aminoethyl) aminopropyl] trimethoxysilane
γ－APS	3－Aminopropyltriethoxysilane
BTSA	Bis－[trimethoxysitylpropyl] amine
BTSE	1，2－Bis[tfiethoxysilyl] ethane
BTSS	Bis－[3－(triethoxysilyl) propyl] tetrasulfide
DMDES	Dimethyldiethoxysilane
DMDMS	Dimethyldimethoxysilane
DTMS	Dodecyltrimethoxysilane
IPTS	3－Isocyanatopropyltriethoxysilane
γ－GPS	3－Glycidyloxypropyltrimethoxysilane
MAPS	(3－Mercaptopropyl) triethoxysilane (3－Mercaptopropyl) trimethoxysilane
γ－MPS	Metacryloxypropylmethoxysilane
MTMS	Methyltrimethoxysilane
TEOS	Tetraethoxysilane
TMOS	Tetramethoxysilane
TPOT	Titanium tetra-propoxide
TPOZ	Zirconium tetra-propoxide
PHS	Diethylphosphonatoethyltriethoxysilane
PHTS	Phenyltrimethoxysilane
PTS	Propyltrimethoxysilane
γ－UPS	Ureidopropyltrimethoxysilane
VTES	Vinyltriethoxysilane
VTMS	Vinyltrimethoxysilane
VTSA	Vinyltriacetoxysilane

γ－GPS；③有机活性基团带有双键，烷基烷氧基硅烷多为γ－MPS或VTMS；④有机活性基团带有氨基，如以γ－APS为前驱体[39]。第一类适合作为单独的保护涂层，如MTES/TEOS的溶胶－凝胶涂层具有优异的耐高温特性[40]。而带有环氧、双键、氨基的涂层，能够和有机涂层通过这些基团形成化学键，因此除作为单独的保护涂层，还适合作为有机涂层的打底涂层提高有机涂层在金属上的附着性能。除这些基团，一些含有特殊基团的涂层也被设计。如Khramov等[41]以PHS和TEOS为前躯体制备了含有膦基的涂层，该涂层可以通过膦基和镁合金形成化学键；含巯基的涂层被用来获得在铜上有好的性能的[42－44]基于巯基可以和铜形成Cu－S－C键。

为了进一步提高有机硅溶胶－凝胶涂层的防腐蚀性能有机和无机缓蚀剂[45－46]被添加到涂层中。缓蚀剂的浓度在一定的范围内可以有效的增强涂层的性能，但是当浓度过高时会破坏溶胶－凝胶涂层的结构而降低性能[47]。一些报道还研究了微米、纳米颗粒对涂层性能的影响[48－49]。

2.4 有机硅溶胶-凝胶涂层在海洋防腐蚀的应用

尽管目前有关于有机硅溶胶－凝胶涂层的报道还集中于涂层的设计及对不同金属的保护效果的评价，直接针对海洋相关领域的应用研究还非常少见。但有机硅溶胶－凝胶涂层优异的耐热、力学性能、耐腐蚀、附着性

表2 不同金属表面上的有机硅溶胶－凝胶防蚀腐涂层

Table 2 Corrosion protective silane based sol-gel coatings on metal surface

Metal	Precursors	Additives and References
Al based material		
	MAPS + BTSE	[42]
	PTMS + BTSE	[50]
	γ－GPS + MTMS	γ－AAPS[51]
	γ－GPS + TMOS	[52－53]，DETA[54]
	γ－GPS + TEOS	BPA[55]
	γ－GPS + TPOZ	[56]
	γ－GPS + TEOS	[57－59]，Ce[60]，organic inhibitor[61－63]，EDA[64]，DETA[65－66]，TEPA[67－68]
	γ－GPS + TMOS	[69]，AEP[70]，γ－APS[71]，EDA[70]，DETA[70－73]，organic inhibitor[74－76]
	γ－GPS + TPOZ	Ce[76]
	DTMS	TiO_2[77]
	MTES	$Mg(NO_3)_2$[78]
	γ－MPS + TEOS	BPO[64]，SiO_2[48]
	γ－MPS + VTMS + TMOS	[79]
	γ－MPS + VTMS + TMOS + MAPS	Micron particle[49]
	γ－MPS + VTMS + TEOS	[80]
	γ－MPS + PHTS + TEOS	Inhibitor[45]
	γ－MPS + TPOZ	[81－82]
	VTMS + TEOS	BPO[64]
3005	MTES + TESO	Ce[37]
5050	MTES + TEOS + PhTS	[83]
	PhTS + TEOS	Phenylphosphonic acid[38]
6061	γ－GPS + TEOS	HDA + γ－APS[84]，HDA[84]
6082	γ－GPS + TEOS	Inhibitor[85]
Fe based material		
ADI	MTES + TEOS	[86]
Mild steel	γ－GPS + TPOZ	Photo initiator[87]，propargyl alcohol[88]
	γ－GPS + TEOS	TiO_2[89]
Carbon steel	MAPS + TEOS	[90]
	γ－MPS + TEOS	Phyllosilicates[91－92]
	MTES + TEOS	[93－94]，$AlCl_3$ + Ce[95] Silica + Ce[95]
Steel	MTES + TEOS	[96]
HDG	γ－GPS + MTES	Montmorillonite[97]
GS	MTES + TEOS	Sodium silicate[98]

（接下表）

（续表）

Metal	Precursors	Additives and References
304	γ－MPS＋TMOS	[99]
	γ－MPS＋TEOS	[100]
	MTES＋ TEOS	Ce[101]
	PEG＋ IPTS	[102]
316L	γ－MPS＋TMOS	[99]
	γ－MPS＋TEOS	[103]，[100]，BPO[104－105]，HEMA[106－107]
	MTES＋TEOS	[40，103]，HEMA[106－107]
	MTMS＋TEOS	[108]，$NaO \cdot CaO \cdot SiO_2$[109]
	MTMS＋TBOT	[110]
Cu based material		
Brass Bronze	γ－GPS＋MTMS	SiO_2[111]
Copper	BTSE＋MAPS	[42]
	BTSE＋PTMS	[50]
	γ－GPS＋MAPS	Curing agent＋SiO_2[43]
	γ－GPS＋TEOS	DETA[36，112]，EDA[112]，TUA[36]，organic inhibitor[113]
	γ－MPS＋MAPS	Fumed silica[44]
Mg based material		
	γ－GPS＋TPOZ	tTMSPh[114]，8－Hydroxyquinolin[115]
	γ－GPS＋TEOS	TETA[116]，PANI[117]，
	PHS＋TEOS	[41]
	γ－GPS＋TEOS	[118－119]，organic inhibitor[120]
	MTES	Ce[47]
	MTES＋TEOS	[121]
	PhTMS＋TPOZ	[122]
	VTES＋TEOS	[123]
	VTMS＋TEOS	[118]

能以及灵活的施工手段使得其在一些特殊的场合有大的应用前景。如对耐热、耐刮擦有一定要求，但一般有机涂层无法满足要求的场合，或者其它保护如喷涂技术无法施工的地方。当然，有机硅溶胶－凝胶涂层在海洋相关领域的应用还需结合实际情况具体分析和探讨。

3　结　语

有机硅溶胶－凝胶涂层因其特殊的性能而广泛用于金属材料的防腐蚀，应用前景非常广阔。目前，市面上已有些商业化的产品。但有机硅溶胶－凝胶涂层也面临一些亟需解决问题及值得继续研究的方向：

（1）多数有机硅溶胶－凝胶涂层体系含有大量醇，醇的来源有两类：一是作为溶剂额外添加的，二是前驱体水解反应产生的。大量醇的存在不但会带来安全隐患，还面临 VOC 排放的问题。因此，开发水基/低 VOC 有机硅溶胶－凝胶涂层非常有意义。

（2）借鉴有机缓蚀剂在金属表面上化学吸附的工作原理，设计含有特殊官能基团的有机硅溶胶－凝胶涂层，通过有机基团和金属的相互作用增强涂层在金属表面（特别是铜）上的附着能力以及具有“自修复”功能的涂层，扩大有机硅溶胶－凝胶涂层的适用范围及提升其保护效果。

参考文献　References

[1] Brinker C J，Scherer G W. *Sol-Gel Science：the Physics and Chemistry of Sol-Gel Processing* [M]. New York：Academic Press，1990.

[2] Huang Jianfeng（黄剑锋）. *Principle and Technology of Sol-Gel*（溶胶－凝胶原理与技术）[M]. Beijing：Chemical Industry Press，2005.

[3] Guglielmi M. Sol-Gel Coatings on Metals [J]. *Journal of Sol-Gel Science and Technology*，1997，8（1－3）：443－449.

[4] Wang D，Bierwagen G R. Sol-Gel Coatings on Metals for Corrosion Protection [J]. *Progress in Organic Coatings*，2009，64（4）：327－338.

[5] Zheludkevich M L，Salvado I M，Ferreira M G S. Sol-Gel Coatings for Corrosion Protection of Metals [J]. *Journal of Materials Chemistry*，2005，15（48）：5 099－5 111.

[6] Sanchez C，Soler-Illia G J D A，Ribot F，*et al*. Designed Hybrid Organic-Inorganic Nanocomposites from Functional Nanobuilding Blocks [J]. *Chemistry of Materials*，2001，13（10）：3 061－3 083.

[7] Wen J Y，Wilkes G L. Organic/Inorganic Hybrid Network Materials by the Sol-Gel Approach [J]. *Chemistry of Materials*，1996，8（8）：1 667－1 681.

[8] Schottner G. Hybrid Sol-Gel-Derived Polymers：Applications of Multifunctional Materials [J]. *Chemistry of Materials*，2001，13（10）：3 422－3 435.

[9] Mammeri F，Bourhis E L，Rozes L，*et al*. Mechanical Properties of Hybrid Organic-Inorganic Materials [J]. *Journal of Materials Chemistry*，2005，15（35－36）：3 787－3 811.

[10] Osterholtz F D，Pohl E R. Kinetics of the Hydrolysis and Condensation of Organofunctional Alkoxysilanes：a Review [J]. *Journal of Adhesion Science and Technology*，1992，6（1）：127－149.

[11] Arkles B，Steinmetz J R，Zazyczny J，*et al*. Factors Contributing to the Stability of Alkoxysilanes in Aqueous-Solution [J]. *Journal of Adhesion Science and Technology*，1992，6（1）：193－206.

[12] Ebelmen. Untersuchungen ber Die Verbindungen Der Borsäure Und Kieselsäure Mit Aether [J]. *Justus Liebigs Annalen der Chemie*，1846，57（3）：319－355.

[13] Konrad E，Bächle O，Signer R. ber Polymere Kieselsäureester. 19. Mitteilung ber Hochpolymere Verbindungen [J]. *Justus Liebigs Annalen der Chemie*，1929，474（1）：276－295.

[14] Schmidt H，Scholze H，Kaiser A. Principles of Hydrolysis and

Condensation Reaction of Alkoxysilanes [J]. *Journal of Non-Crystalline Solids*, 1984, 63 (1-2): 1-11.

[15] Brunet F. Polymerization Reactions in Methyltriethoxysilane Studied through Si-29 Nmr with Polarization Transfer [J]. *Journal of Non-Crystalline Solids*, 1998, 231 (1-2): 58-77.

[16] Premachandra J K, Van Ooij W J, Mark J E. Reaction Kinetics of Gamma-Ureidopropyltrimethoxysilane in the Water-Methanol System Studied by Ftir Spectroscopy [J]. *Journal of Adhesion Science and Technology*, 1998, 12 (12): 1 361-1 376.

[17] Riegel B, Blittersdorf S, Kiefer W, *et al*. Kinetic Investigations of Hydrolysis and Condensation of the Glycidoxypropyltrimethoxysilane/Aminopropyltriethoxy-Silane System by Means of Ft-Raman Spectroscopy I [J]. *Journal of Non-Crystalline Solids*, 1998, 226 (1-2): 76-84.

[18] Pantoja M, Velasco F, Broekema D, *et al*. The Influence of Ph on the Hydrolysis Process of Gamma-Methacryloxypropyltrimethoxysilane, Analyzed by Ft-Ir, and the Silanization of Electrogalvanized Steel [J]. *Journal of Adhesion Science and Technology*, 2010, 24 (6): 1 131-1 143.

[19] Kuniyoshi M, Takahashi M, Tokuda Y, *et al*. Hydrolysis and Polycondensation of Acid-Catalyzed Phenyltriethoxysilane (Phtes) [J]. *Journal of Sol-Gel Science and Technology*, 2006, 39 (2): 175-183.

[20] Diaz-Benito B, Velasco F, Martinez F J, *et al*. Hydrolysis Study of Bis-1, 2-(Triethoxysilyl) Ethane Silane by Nmr [J]. *Colloids and Surfaces A-Physicochemical and Engineering Aspects*, 2010, 369 (1-3): 53-56.

[21] Metroke T, Wang Y M, Van Ooij W J, *et al*. Chemistry of Mixtures of Bis-Trimethoxysilylpropyl Amine and Vinyltriacetoxysilane: an Nmr Analysis [J]. *Journal of Sol-Gel Science and Technology*, 2009, 51 (1): 23-31.

[22] Dubitsky Y, Zaopo A, Zannoni G, *et al*. H-1 Nmr Study of the Hydrolysis of Vinyltrialkoxysilanes [J]. *Materials Chemistry and Physics*, 2000, 64 (1): 45-53.

[23] Li Fangwen (李方文), Wu Jianfeng (吴建锋), Xu Xiaohong (徐晓虹), *et al*. 丙基三甲氧基硅烷的水解 [J]. *Chemical Industry and Engineering* (化学工业与工程), 2008, 25 (3): 203-207.

[24] Van Ooij W, Zhu D, Stacy M, *et al*. Corrosion Protection Properties of Organofunctional Silanes——an Overview [J]. *Tsinghua Science & Technology*, 2005, 10 (6): 639-664.

[25] Pohl E R, Chaves A. *Sterically Hindered Silanes for Waterborne Systems: a Model Study of Silane Hydrolysis* [C]. United States: CRC Press, 2004: 3-9.

[26] Pan G, Schaefer D W, Van Ooij W J, *et al*. Morphology and Water Resistance of Mixed Silane Films of Bis 3-(Triethoxysilyl) Propyl Tetrasulfide and Bis-Trimethoxysilylpropyl Amine [J]. *Thin Solid Films*, 2006, 515 (4): 2 771-2 780.

[27] Gettings M, Kinloch A J. Surface Analysis of Polysiloxane Metal Oxide Interfaces [J]. *Journal of Materials Science*, 1977, 12 (12): 2 511-2 518.

[28] Davis S J, Watts J F. Organization of Methoxysilane Molecules on Iron [J]. *International Journal of Adhesion and Adhesives*, 1996, 16 (1): 5-15.

[29] Susac D, Leung C W, Sun X, *et al*. Comparison of a Chromic Acid and a Btse Final Rinse Applied to Phosphated 2024-T3 Aluminum Alloy [J]. *Surface & Coatings Technology*, 2004, 187 (2-3): 216-224.

[30] Teo M, Kim J, Wong P C, *et al*. Pre-Treatments Applied to Oxidized Aluminum Surfaces to Modify the Interfacial Bonding with Bis-1, 2-(Triethoxysilyl) Ethane (Btse)-Part I. High-Purity Al with Native Oxide [J]. *Applied Surface Science*, 2005, 252 (5): 1 293-1 304.

[31] Fang J, Flinn B J, Leung Y L, *et al*. A Characterization of the Gamma-Glycidoxypropyltrimethoxysilane and Aluminium Interface by Sims and Xps [J]. *Journal of Materials Science Letters*, 1997, 16 (20): 1 675-1 676.

[32] Kasemann R, Schmidt H. Coatings for Mechanical and Chemical Protection Based on Organic-Inorganic Sol-Gel Nanocomposites [J]. *New Journal of Chemistry*, 1994, 18 (10): 1 117-1 123.

[33] Pilz M, Romich H. Sol-Gel Derived Coatings for Outdoor Bronze Conservation [J]. *Journal of Sol-Gel Science and Technology*, 1997, 8 (1-3): 1 071-1 075.

[34] Langenfeld S, Jonschker G, Schmidt H. New Sol-Gel Based Coatings as Corrosion-and Wear-Protection on Non-Ferrous Metals [J]. *Materialwissenschaft und Werkstofftechnik*, 1998, 29 (1): 23-29.

[35] Metroke T L, Parkhill R L, Knobbe E T. Synthesis of Hybrid Organic-Inorganic Sol-Gel Coatings for Corrosion Resistance [J]. *Organic/Inorganic Hybrid Materials II*, 1999, 576: 293-298.

[36] Peng S, Zeng Z, Zhao W, *et al*. Synergistic Effect of Thiourea in Epoxy Functionalized Silica Sol-Gel Coating for Copper Protection [J]. *Surface & Coatings Technology*, 2012, 213: 175-192.

[37] Pepe A, Aparicio M, Cere S, *et al*. Preparation and Characterization of Cerium Doped Silica Sol-Gel Coatings on Glass and Aluminum Substrates [J]. *Journal of Non-Crystalline Solids*, 2004, 348: 162-171.

[38] Sheffer M, Groysman A, Starosvetsky D, *et al*. Anion Embedded Sol-Gel Films on Al for Corrosion Protection [J]. *Corrosion Science*, 2004, 46 (12): 2 975-2 985.

[39] Osborne J H, Du Y J, Damron M, *et al*. Inorganic/Organic Hybrid Coatings for Aircraft Aluminum Alloy Substrates [J]. *Progress in Organic Coatings*, 2001, 41 (4): 226-232.

[40] Gallardo J, Duran A, De Damborenea J J. Electrochemical and in Vitro Behaviour of Sol-Gel Coated 316l Stainless Steel [J]. *Corrosion Science*, 2004, 46 (4): 795-806.

[41] Khramov A N, Balbyshev V N, Kasten L S, *et al*. Sol-Gel Coatings with Phosphonate Functionalities for Surface Modification of Magnesium Alloys [J]. *Thin Solid Films*, 2006, 514 (1-2): 174-181.

[42] Li Y S, Lu W, Wang Y, *et al*. Studies of (3-Mercaptopropyl) Trimethoxylsilane and Bis (Trimethoxysilyl) Ethane Sol-Gel

Coating on Copper and Aluminum [J]. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy*, 2009, 73 (5): 922 – 928.

[43] Tan A L K, Soutar A M. Hybrid Sol-Gel Coatings for Corrosion Protection of Copper [J]. *Thin Solid Films*, 2008, 516 (16): 5 706 – 5 709.

[44] Soutar A, Rabaud B, Qian M, *et al*. Mechanical and Electrochemical Properties of Hybrid Sol-Gel Protective Coatings for Copper Substrates [J]. *SIMTech technical reports*, 2005, 6 (1): 50 – 54.

[45] Raps D, Hack T, Wehr J, *et al*. Electrochemical Study of Inhibitor-Containing Organic-Inorganic Hybrid Coatings on Aa2024 [J]. *Corrosion Science*, 2009, 51 (5): 1 012 – 1 021.

[46] Barranco V, Carmona N, Galvan J C, *et al*. Electrochemical Study of Tailored Sol-Gel Thin Films as Pre-Treatment Prior to Organic Coating for Az91 Magnesium Alloy [J]. *Progress in Organic Coatings*, 2010, 68 (4): 347 – 355.

[47] Correa P S, Malfatti C F, Azambuja D S. Corrosion Behavior Study of Az91 Magnesium Alloy Coated with Methyltriethoxysilane Doped with Cerium Ions [J]. *Progress in Organic Coatings*, 2011, 72 (4): 739 – 747.

[48] Rosero-Navarro N C, Pellice S A, Castro Y, *et al*. Improved Corrosion Resistance of Aa2024 Alloys through Hybrid Organic-Inorganic Sol-Gel Coatings Produced from Sols with Controlled Polymerisation [J]. *Surface & Coatings Technology*, 2009, 203 (13): 1 897 – 1 903.

[49] Metroke T L, Kachurina O, Knobbe E T. Particle-Doped Organic-Inorganic Hybrid Coatings as Corrosion Inhibiting Surface Treatments for Aluminum Alloys [J]. *Materials Research Society Symposium Proceedings*, 2002, 726: 395 – 400.

[50] Li Y S, Tran T, Xu Y, *et al*. Spectroscopic Studies of Trimetoxypropylsilane and Bis(Trimethoxysilyl) Ethane Sol-Gel Coatings on Aluminum and Copper [J]. *Spectrochimica Acta Part A-Molecular and Biomolecular Spectroscopy*, 2006, 65 (3 – 4): 779 – 786.

[51] Pathak S S, Khanna A S. Synthesis and Performance Evaluation of Environmentally Compliant Epoxysilane Coatings for Aluminum Alloy [J]. *Progress in Organic Coatings*, 2008, 62 (4): 409 – 416.

[52] Voevodin N, Buhrmaster D, Balbyshev V, *et al*. Nonchromated Coating Systems for Corrosion Protection of Aircraft Aluminum Alloys [J]. *Materials Performance*, 2006, 45 (11): 48 – 51.

[53] Donley M S, Mantz R A, Khramov A N, *et al*. The Self-Assembled Nanophase Particle (Snap) Process: a Nanoscience Approach to Coatings [J]. *Progress in Organic Coatings*, 2003, 47 (3 – 4): 401 – 415.

[54] Kasten L S, Balbyshev V N, Donley M S. Surface Analytical Study of Self-Assembled Nanophase Particle (Snap) Surface Treatments [J]. *Progress in Organic Coatings*, 2003, 47 (3 – 4): 214 – 224.

[55] Zandi-zand R, Ershad-langroudi A, Rahimi A. Silica Based Organic-Inorganic Hybrid Nanocomposite Coatings for Corrosion Protection [J]. *Progress in Organic Coatings*, 2005, 53 (4): 286 – 291.

[56] Feng Z, Liu Y, Thompson G E, *et al*. Sol-Gel Coatings for Corrosion Protection of 1050 Aluminium Alloy [J]. *Electrochimica Acta*, 2010, 55 (10): 3 518 – 3 527.

[57] Parkhill R L, Knobbe E T, Donley M S. Application and Evaluation of Environmentally Compliant Spray-Coated Ormosil Films as Corrosion Resistant Treatments for Aluminum 2024 – T3 [J]. *Progress in Organic Coatings*, 2001, 41 (4): 261 – 265.

[58] Tavandashti N P, Sanjabi S, Hahrabi T S. Corrosion Protection Evaluation of Silica/Epoxy Hybrid Nanocomposite Coatings to Aa2024 [J]. *Progress in Organic Coatings*, 2009, 65 (2): 182 – 186.

[59] Metroke T L, Kachurina O, Knobbe E T. Spectroscopic and Corrosion Resistance Characterization of Glymo-Teos Ormosil Coatings for Aluminum Alloy Corrosion Inhibition [J]. *Progress in Organic Coatings*, 2002, 44 (4): 295 – 305.

[60] Kasten L S, Grant J T, Grebasch N, *et al*. An Xps Study of Cerium Dopants in Sol-Gel Coatings for Aluminum 2024 – T3 [J]. *Surface & Coatings Technology*, 2001, 140 (1): 11 – 15.

[61] Khramov A N, Voevodin N N, Balbyshev V N, *et al*. Hybrid Organo-Ceramic Corrosion Protection Coatings with Encapsulated Organic Corrosion Inhibitors [J]. *Thin Solid Films*, 2004, 447: 549 – 557.

[62] Shi H W, Liu F C, Han E H. Characterization of Self-Assembled Nano-Phase Silane-Based Particle Coating [J]. *Transactions of Nonferrous Metals Society of China*, 2010, 20 (10): 1 928 – 1 935.

[63] Khramov A N, Balbyshev V N, Mantz R A. Protection of Aluminum Alloys via Hybrid Sol-Gel Coatings with Encapsulated Organic Corrosion Inhibitors [J]. *Research through Innovation and Technology*, 2006: 661 – 666.

[64] Liu Y, Sun D Z, You H, *et al*. Corrosion Resistance Properties of Organic-Inorganic Hybrid Coatings on 2024 Aluminum Alloy [J]. *Applied Surface Science*, 2005, 246 (1 – 3): 82 – 89.

[65] Roussi E, Tsetsekou A, Tsiourvas D, *et al*. Novel Hybrid Organo-Silicate Corrosion Resistant Coatings Based on Hyperbranched Polymers [J]. *Surface & Coatings Technology*, 2011, 205 (10): 3 235 – 3 244.

[66] Voevodin N N, Kurdziel J W, Mantz R. Corrosion Protection for Aerospace Aluminum Alloys by Modified Self-Assembled Nanophase Particle (Msnap) Sol-Gel [J]. *Surface & Coatings Technology*, 2006, 201 (3 – 4): 1 080 – 1 084.

[67] Wu K H, Chang T C, Yang C C, *et al*. Dynamics and Corrosion Resistance of Amine-Cured Organically Modified Silicate Coatings on Aluminum Alloys [J]. *Thin Solid Films*, 2006, 513 (1 – 2): 84 – 89.

[68] Wu K H, Li M C, Yang C C, *et al*. Domain Size and Thermal Stability of Amine-Cured Hybrid Films as Corrosion Resistance Treatments for Aluminum Alloy [J]. *Journal of Non-Crystalline Solids*, 2006, 352 (26 – 27): 2 897 – 2 904.

[69] Donley M S, Balbyshev V N, Oevodin N N V. Self-Assembled

Nanophase Particle (Snap) Surface Treatments for Corrosion Protection of Aa2024 – T3 [J]. *Progress in Organic Coatings*, 2005, 52 (1): 34 – 38.

[70] Vreugdenhil A J, Gelling V J, Oods M E W, *et al*. The Role of Crosslinkers in Epoxy-Amine Crosslinked Silicon Sol-Gel Barrier Protection Coatings [J]. *Thin Solid Films*, 2008, 517 (2): 538 – 543.

[71] Khramov A N, Balbyshev V N, Voevodin N N, *et al*. Nanostructured Sol-Gel Derived Conversion Coatings Based on Epoxy- and Amino-Silanes [J]. *Progress in Organic Coatings*, 2003, 47 (3 – 4): 207 – 213.

[72] Vreugdenhil A J, Balbyshev V N, Donley M S. Nanostructured Silicon Sol-Gel Surface Treatments for Al 2024 – T3 Protection [J]. *Journal of Coatings Technology*, 2001, 73 (915): 35 – 43.

[73] Metroke T L, Kachurina O, Knobbe E T. Spectroscopic and Corrosion Resistance Characterization of Amine and Super Acid-Cured Hybrid Organic-Inorganic Thin Films on 2024 – T3 Aluminum Alloy [J]. *Progress in Organic Coatings*, 2002, 44 (3): 185 – 199.

[74] Voevodin N N, Balbyshev V N, Khobaib M, *et al*. Nanostructured Coatings Approach for Corrosion Protection [J]. *Progress in Organic Coatings*, 2003, 47 (3 – 4): 416 – 423.

[75] Khramov A, Voevodin N N, Balbyshev V N, *et al*. Sol-Gel-Derived Corrosion-Protective Coatings with Controllable Release of Incorporated Organic Corrosion Inhibitors [J]. *Thin Solid Films*, 2005, 483 (1 – 2): 191 – 196.

[76] Yasakau K A, Zheludkevich M L, Karavai O V, *et al*. Influence of Inhibitor Addition on the Corrosion Protection Performance of Sol-Gel Coatings on Aa2024 [J]. *Progress in Organic Coatings*, 2008, 63 (3): 352 – 361.

[77] Li M, Yang Y Q, Liu L, *et al*. Electro-Assisted Preparation of Dodecyltrimethoxysilane/Tio(2) Composite Films for Corrosion Protection of Aa2024 – T3 (Aluminum Alloy) [J]. *Electrochimica Acta*, 2010, 55 (8): 3 008 – 3 014.

[78] Varma P C R, Duffy B, Cassidy J. Influence of Magnesium Nitrate on the Corrosion Performance of Sol-Gel Coated Aa2024 – T3 Aluminium Alloy [J]. *Surface & Coatings Technology*, 2009, 204 (3): 277 – 284.

[79] Kachurina O, Metroke T L, Stesikova E, *et al*. Comparison of Single and Multilayer Coatings Based on Ormosil and Conversion Layers for Aluminum Alloy Corrosion Inhibition [J]. *Journal of Coatings Technology*, 2002, 74 (926): 43 – 48.

[80] Metroke T L, Apblett A. Effect of Solvent Dilution on Corrosion Protective Properties of Ormosil Coatings on 2024 – T3 Aluminum Alloy [J]. *Progress in Organic Coatings*, 2004, 51 (1): 36 – 46.

[81] Varma P C R, Colreavy J, Cassidy J, *et al*. Effect of Organic Chelates on the Performance of Hybrid Sol-Gel Coated Aa 2024 – T3 Aluminium Alloys [J]. *Progress in Organic Coatings*, 2009, 66 (4): 406 – 411.

[82] Varma P C R, Colreavy J, Cassidy J, *et al*. Corrosion Protection of Aa 2024 – T3 Aluminium Alloys Using 3, 4 – Diaminobenzoic Acid Chelated Zirconium-Silane Hybrid Sol – Gels [J]. *Thin Solid Films*, 2010, 518 (20): 5 753 – 5 761.

[83] Sheffer M, Groysman A, Mandler D. Electrodeposition of Sol-Gel Films on Al for Corrosion Protection [J]. *Corrosion Science*, 2003, 45 (12): 2 893 – 2 904.

[84] Tiwari A, Zhu J, Hihara L H. The Development of Low-Temperature Hardening Silicone Ceramer Coatings for the Corrosion Protection of Metals [J]. *Surface & Coatings Technology*, 2008, 202 (19): 4 620 – 4 635.

[85] Lampke T, Darwich S, Nickel D, *et al*. Development and Characterization of Sol-Gel Composite Coatings on Aluminum Alloys for Corrosion Protection [J]. *Materialwissenschaft und Werkstofftechnik*, 2008, 39 (12): 914 – 919.

[86] Pepe A, Galliano P, Cere S, *et al*. Hybrid Silica Sol-Gel Coatings on Austempered Ductile Iron (Adi) [J]. *Materials Letters*, 2005, 59 (17): 2 219 – 2 222.

[87] Kiruthika P, Subasri R, Jyothirmayi A, *et al*. Effect of Plasma Surface Treatment on Mechanical and Corrosion Protection Properties of Uv-Curable Sol-Gel Based Gpts-Zro(2) Coatings on Mild Steel [J]. *Surface & Coatings Technology*, 2010, 204 (8): 1 270 – 1 276.

[88] Hosseini S M A, Jafari A H, Amalizadeh E J. Self-Healing Corrosion Protection by Nanostructure Sol-Gel Impregnated with Propargyl Alcohol [J]. *Electrochimica Acta*, 2009, 54 (28): 7 207 – 7 213.

[89] Madani S M, Ehteshamzadeh M, Rafsanjani H H. Investigation of the Microstructure and Corrosion Performance of a Nanostructured Titania-Containing Hybrid Silicate Film on Mild Steel [J]. *Thin Solid Films*, 2010, 519 (1): 145 – 150.

[90] Peng S S, Zhao W J, Zeng Z X, *et al*. Preparation of Anticorrosion Hybrid Silica Sol-Gel Coating Using Ce(No3)(3) as Catalyst [J]. *Journal of Sol-Gel Science and Technology*, 2013, 66 (1): 133 – 138.

[91] Joncoux-Chabrol K, Bonino J P, Gressier M, *et al*. Improvement of Barrier Properties of a Hybrid Sol-Gel Coating by Incorporation of Synthetic Talc-Like Phyllosilicates for Corrosion Protection of a Carbon Steel [J]. *Surface & Coatings Technology*, 2012, 206 (11 – 12): 2 884 – 2 891.

[92] Liu J G, Gong G P, Yan C W. Enhancement of the Erosion-Corrosion Resistance of Dacromet with Hybrid SiO_2 Sol-Gel [J]. *Surface & Coatings Technology*, 2006, 200 (16 – 17): 4 967 – 4 975.

[93] Pepe A, Aparicio M, Cere S, *et al*. Synthesis of Hybrid Silica Sol-Gel Coatings Containing Zn Particles on Carbon Steel and Al/Zn Coated Carbon Steel [J]. *Materials Letters*, 2005, 59 (29 – 30): 3 937 – 3 940.

[94] Pepe A, Galliano P, Aparicio M, *et al*. Sol-Gel Coatings on Carbon Steel: Electrochemical Evaluation [J]. *Surface & Coatings Technology*, 2006, 200 (11): 3 486 – 3 491.

[95] Wang H, Akid R. Encapsulated Cerium Nitrate Inhibitors to Provide High-Performance Anti-Corrosion Sol-Gel Coatings on Mild Steel [J]. *Corrosion Science*, 2008, 50 (4): 1 142-1 148.

[96] Chen Y A, Wu C C, Ding X G, *et al*. Effect of Water Amount

and Teos/Mtes Ratio on Anti-Corrosion Property of Organic-Inorganic Film [J]. *Rare Metal Materials and Engineering*, 2010, 39: 288 - 291.

[97] Olivier M G, Fedel M, Sciamanna V, *et al*. Study of the Effect of Nanoclay Incorporation on the Rheological Properties and Corrosion Protection by a Silane Layer [J]. *Progress in Organic Coatings*, 2011, 72 (1 - 2): 15 - 20.

[98] Conde A, De Damborenea J, Duran A, *et al*. Protective Properties of a Sol-Gel Coating on Zinc Coated Steel [J]. *Journal of Sol-Gel Science and Technology*, 2006, 37 (1): 79 - 85.

[99] Chou T P, Chandrasekaran C, Limmer S, *et al*. Organic-Inorganic Sol-Gel Coating for Corrosion Protection of Stainless Steel [J]. *Journal of Materials Science Letters*, 2002, 21 (3): 251 - 255.

[100] Chou T P, Chandrasekaran C, Cao G Z. Sol-Gel-Derived Hybrid Coatings for Corrosion Protection [J]. *Journal of Sol-Gel Science and Technology*, 2003, 26 (1 - 3): 321 - 327.

[101] Cere S, Pepe A, Aparicio M, *et al*. Cerium Hybrid Silica Coatings on Stainless Steel Aisi 304 Substrate [J]. *Journal of Sol-Gel Science and Technology*, 2006, 39 (2): 131 - 138.

[102] Okner R, Domb A J, Mandler D. Electrochemically Deposited Poly(Ethylene Glycol)-Based Sol-Gel Thin Films on Stainless Steel Stents [J]. *New Journal of Chemistry*, 2009, 33 (7): 1 596 - 1 604.

[103] Ballarre J, Lopez D A, Cavalieri A L. Nano-Indentation of Hybrid Silica Coatings on Surgical Grade Stainless Steel [J]. *Thin Solid Films*, 2008, 516 (6): 1 082 - 1 087.

[104] Hosseinalipour S M, Ershad-Langroudi A, Hayati A N, *et al*. Characterization of Sol-Gel Coated 316l Stainless Steel for Biomedical Applications [J]. *Progress in Organic Coatings*, 2010, 67 (4): 371 - 374.

[105] Sarmento V H V, Schiavetto M G, Hammer P, *et al*. Corrosion Protection of Stainless Steel by Polysiloxane Hybrid Coatings Prepared Using the Sol-Gel Process [J]. *Surface & Coatings Technology*, 2010, 204 (16 - 17): 2 689 - 2 701.

[106] Lopez D A, Rosero-Navarro N C, Ballarre J, *et al*. Multilayer Silica-Methacrylate Hybrid Coatings Prepared by Sol-Gel on Stainless Steel 316l: Electrochemical Evaluation [J]. *Surface & Coatings Technology*, 2008, 202 (10): 2 194 - 2 201.

[107] Ballarre J, Lopez D A, Rosero N C, *et al*. Electrochemical Evaluation of Multilayer Silica-Metacrylate Hybrid Sol-Gel Coatings Containing Bioactive Particles on Surgical Grade Stainless Steel [J]. *Surface & Coatings Technology*, 2008, 203 (1 - 2): 80 - 86.

[108] Ghaffari M, Barzegar A, Janghorban K, *et al*. Investigation of Effective Parameters in Improving Corrosion Resistance of Silica Coated Stainless Steel via Sol-Gel Method [J]. *Corrosion Engineering Science and Technology*, 2011, 46 (5): 605 - 610.

[109] Gallardo J, Duran A, Garcia I, *et al*. Effect of Sintering Temperature on the Corrosion and Wear Behavior of Protective SiO_2-Based Sol-Gel Coatings [J]. *Journal of Sol-Gel Science and Technology*, 2003, 27 (2): 175 - 183.

[110] Yang Y Q, Liu L, Hu J M, *et al*. Improved Barrier Performance of Metal Alkoxide-Modified Methyltrimethoxysilane Films [J]. *Thin Solid Films*, 2012, 520 (6): 2 052 - 2 059.

[111] Bescher E, Mackenzie J D. Sol-Gel Coatings for the Protection of Brass and Bronze [J]. *Journal of Sol-Gel Science and Technology*, 2003, 26 (1 - 3): 1 223 - 1 226.

[112] Vreugdenhil A J, Woods M E. Continuously Responsive Epoxy-Amine Cross-Linked Silicon Sol-Gel Materials [J]. *Journal of Materials Science*, 2006, 41 (22): 7 545 - 7 554.

[113] Peng S S, Zhao W J, Li H, *et al*. The Enhancement of Benzotriazole on Epoxy Functionalized Silica Sol-Gel Coating for Copper Protection [J]. *Applied Surface Science*, 2013, 276: 284 - 290.

[114] Lamaka S V, Montemor M F, Galio A F, *et al*. Novel Hybrid Sol-Gel Coatings for Corrosion Protection of Az31b Magnesium Alloy [J]. *Electrochimica Acta*, 2008, 53 (14): 4 773 - 4 783.

[115] Galio A F, Lamaka S V, Zheludkevich M L, *et al*. Inhibitor-Doped Sol-Gel Coatings for Corrosion Protection of Magnesium Alloy Az31 [J]. *Surface & Coatings Technology*, 2010, 204 (9 - 10): 1 479 - 1 486.

[116] Guo X H, An M Z. Experimental Study of Electrochemical Corrosion Behaviour of Bilayer on Az31b Mg Alloy [J]. *Corrosion Science*, 2010, 52 (12): 4 017 - 4 027.

[117] Wang H M, Akid R, Gobara M. Scratch-Resistant Anticorrosion Sol-Gel Coating for the Protection of Az31 Magnesium Alloy Via a Low Temperature Sol-Gel Route [J]. *Corrosion Science*, 2010, 52 (8): 2 565 - 2 570.

[118] Hu J Y, Li Q, Zhong X K, *et al*. Organic Coatings Silane-Based for Az91d Magnesium Alloy [J]. *Thin Solid Films*, 2010, 519 (4): 1 361 - 1 366.

[119] Hu J Y, Li Q, Zhong X K, *et al*. Fluoride Treatment and Sol Film Composite Technology for Az91d Magnesium Alloy [J]. *Transactions of the Institute of Metal Finishing*, 2010, 88 (1): 41 - 46.

[120] Shi H W, Liu F C, Han E H. Corrosion Protection of Az91d Magnesium Alloy with Sol-Gel Coating Containing 2-Methyl Piperidine [J]. *Progress in Organic Coatings*, 2009, 66 (3): 183 - 191.

[121] Nikrooz B, Zandrahimi M. Optimization of Process Variables and Corrosion Properties of a Multi Layer Silica Sol Gel Coating on Az91d Using the Box-Behnken Design [J]. *Journal of Sol-Gel Science and Technology*, 2011, 59 (3): 640 - 649.

[122] Tamar Y, Mandler D. Corrosion Inhibition of Magnesium by Combined Zirconia Silica Sol-Gel Films [J]. *Electrochimica Acta*, 2008, 53 (16): 5 118 - 5 127.

[123] Hu J, Li Q, Zhong X, *et al*. Novel Anti-Corrosion Silicon Dioxide Coating Prepared by Sol-Gel Method for Az91d Magnesium Alloy [J]. *Progress in Organic Coatings*, 2008, 63 (1): 13 - 17.