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Andressa Trentin

PhD Thesis

Structure and electrochemical properties of PMMA-silica hybrid coatings modified with cerium and lithium ions

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Structure and electrochemical properties of PMMA-silica hybrid coatings modified with cerium and lithium ions

Thesis in a Joint PhD submitted in fulfillment of the requirements for the degree of Doctor in Chemistry

Supervisors: Prof. Dr. Peter Hammer
Prof. Dr. ir. Tom Hauffman

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Structure and electrochemical properties of PMMA-silica hybrid coatings modified with cerium and lithium ions

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CONFERENCES AND PRESENTATIONS

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European Technical Coatings Congress, ETCC 2018. Amsterdam, The Netherlands, June 26th – 29th 2018.

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Smart Coatings 2017. Orlando, USA, February 22th – 24th 2017.

XVI Brazilian Materials Research Society meeting, XVI SBPMat. Gramado, Brazil, September 10th – 14th 2017.

European Corrosion Congress, EUROCORR 2016. Montpellier, France, September 11th – 15th 2016.

XV Brazilian Materials Research Society meeting, XV SBPMat. 2016. Campinas, Brazil, September 25th – 29th 2016.

Brazilian Chemistry Society annual meeting, XXXVIII RASBQ. Águas de Lindóia, Brasil, May 25th – 28th 2015.

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Best Young Scientist Contribution at the European Technical Coatings Congress (ETCC 2018 - Amsterdam, The Netherlands) by the presentation “Increased durability and corrosion protection of PMMA-siloxane hybrid coatings modified with cerium and lithium”.

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ABSTRACT

This work reports on a detailed investigation of the structural and electrochemical properties of poly(methyl methacrylate) (PMMA)-silica coatings. Raman spectroscopy and thermal analysis showed that the fine-tuning of the benzoyl peroxide (BPO) amount, as a critical synthesis parameter, improves the polymerization efficiency of methyl methacrylate (MMA), leading to a highly cross-linked hybrid structure. Electrochemical impedance spectroscopy (EIS) showed for coatings deposited on carbon steel (A1020) and Al alloy (AA7075) a quasi-ideal capacitive impedance response, maintaining the low frequency impedance modulus of up to 10 GΩ cm^2 essentially unchanged during 19 months of immersion in 3.5% NaCl. Although high performance passive coatings have been developed, pitting can significantly affect their durability. Hence, active corrosion inhibition induced by lithium and cerium ions in PMMA-silica sol-gel coatings was investigated. The addition of lithium carbonate yielded coatings with improved connectivity of nanometric silica cross-link nodes and stronger adhesion to the aluminum substrate. EIS results showed that higher lithium concentrations result in an increased impedance modulus and induce the self-healing ability, extending significantly the service life of the coatings. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) suggest that the regeneration process occurs by means of lithium ions leaching from the adjacent coating towards the corrosion spot, which is restored by a protective layer of Li containing aluminum hydroxide species. Finally, coatings loaded with Ce(III) and Ce(IV) provided long term protection for aluminum alloy, however only Ce(IV) imparts active inhibition due to the passivation of cathodic sites by forming highly insoluble Ce oxides and hydroxides. Intermediate Ce(IV) concentrations proved to be more effective in improving the barrier property combined with active protection of intact and damaged coatings over immersion time. In brief, this study found a close relationship between optimized structure, anticorrosive effectiveness and self-healing activity induced by lithium and cerium ions in PMMA-silica coatings, highlighting their high potential of the material for the effective protection of metallic surface.

Keywords: Organic-inorganic coatings, PMMA-silica hybrid, lithium carbonate, Ce(IV), Ce(III), self-healing

RESUMO

Este trabalho relata uma investigação detalhada das propriedades estruturais e eletroquímicas de revestimentos de polimetilmetacrilato (PMMA)-sílica. Espectroscopia Raman e análise térmica mostraram que o ajuste da quantidade de peróxido de benzoíla (BPO), como um parâmetro crítico de síntese, melhora a eficiência de polimerização do metilmetacrilato (MMA), levando a uma estrutura híbrida altamente reticulada. A espectroscopia de impedância eletroquímica (EIS) mostrou para revestimentos depositados sobre aço carbono (A1020) e liga de Al (AA7075) uma resposta de impedância capacitiva quase ideal, mantendo o módulo de impedância de baixa frequência de até 10 GΩ cm^2 essencialmente inalterado durante 19 meses de imersão em NaCl 3,5%. Embora revestimentos passivos de alto desempenho tenham sido desenvolvidos, pites de corrosão podem afetar significativamente sua durabilidade. Assim, a inibição da corrosão ativa induzida por íons lítio e cério em revestimentos de sílica sol-gel de PMMA foi investigada. A adição de carbonato de lítio produziu revestimentos com melhor conectividade dos nós de sílica nanométricos e forte adesão ao substrato de alumínio. Os resultados de EIS mostraram que as concentrações de lítio mais altas resultam em um aumento no módulo de impedância e induzem a autorregeneração que aumenta significativamente sua vida útil dos revestimentos. *Time-of-flight* secondary ion mass spectrometry (ToF-SIMS) e a espectroscopia de fotoelétrons excitados por raios-X (XPS) sugerem que o processo de regeneração ocorre por meio de íons lítio lixiviados do revestimento adjacente em direção ao pite de corrosão, que é restaurado por uma camada de espécies de hidróxidos de alumínio contendo Li. Finalmente, os revestimentos contendo Ce(III) e Ce(IV) forneceram proteção de longo prazo para a liga de alumínio, porém somente Ce(IV) confere inibição ativa devido à passivação de sítios catódicos pela formação de óxidos e hidróxidos de Ce altamente insolúveis. As concentrações intermediárias de Ce(IV) mostraram-se mais eficazes para melhorar a propriedade de barreira combinada à proteção ativa de revestimentos intactos e danificados durante o tempo de imersão. Em resumo, este estudo encontrou uma relação íntima entre estrutura otimizada, eficácia anticorrosiva e atividade de *self-healing* induzida por íons lítio e cério em revestimentos PMMA-sílica, demostrando o alto potencial do material para eficiente proteção de superfícies metálicas.

Palavras-chave: Revestimentos orgânico-inorgânicos, híbrido PMMA-sílica, carbonato de lítio, Ce(IV), Ce(III), *self-healing*.

SAMENVATTING

In dit werk worden de structurele en elektrochemische eigenschappen van PMMA-silica coatings gedetailleerd bestudeerd. Raman spectroscopie en thermische analyses toonden aan dat door de fine-tuning van het gehalte aan de kritische synthese parameter BPO, de polymerisatie efficiëntie van MMA werd verbeterd. Dit leidde tot sterk vernette hybride structuren. Elektrochemische impedantie spectroscopie (EIS) toonde een quasi-ideale capacitieve impedantie respons aan, waarbij de laagfrequentie impedantie modulus van 10 GΩ cm^2 onveranderd bleef gedurende 19 maanden onderdompeling in 3.5% NaCl. Hoewel hoog performante passiverende coatings ontwikkeld werden, kan pitting hun duurzaamheid drastisch beïnvloeden. Het toevoegen van lithium carbonaat resulteerde in coatings met verbeterde connecties tussen de nanometer geschaalde, vernette silica nodules en een verbeterde adhesie met het aluminium substraat. EIS toonde aan dat hogere lithium concentraties leidden tot een verhoogde impedantie modulus en dat de lithium geïnduceerde zelf-herstelling op een significante wijze de levensduur van de gecoate substraten verlengde. Time-of-flight secundaire ionen mass spectrometrie (ToF-SIMS) en X-stralen foto-elektronen spectroscopie (XPS) wijzen erop het regeneratieproces gebeurt door dat de lithium ionen uitlogen vanuit de naburige coating naar de corrosie plaats, die op zijn beurt dan hersteld wordt door de vorming van een beschermende laag bestaande uit Li bevattende aluminium hydroxide bestanddelen. Tenslotte hebben ook de Ce(III) en Ce(IV) bevattende coatings een langetermijns bescherming voor de aluminium legering iopgeleverd. Echter, alleen Ce(IV) resulteerde in een actieve inhibitie door passivatie van de kathodische sites door de vorming van onoplosbare oxides en hydroxides na migratie van Ce ionen vanuit de coating. Gemiddelde concentraties aan Ce(IV) bewezen meer effectief te zijn in het verbeteren van de barrière eigenschappen gecombineerd met actieve bescherming van intacte en beschadigde coatings gedurende de onderdompelingstijd. Kortom, deze studie vond een hechte relatie tussen geoptimaliseerde structuur, anti-corrosie effectiviteit en zelf-herstellings activititeit van lithium en cerium ionen in PMMA-silica coatings.

Sleutelwoorden: Organisch-anorganische hybride coatings, lithiumcarbonaat, Ce (IV) en Ce (III), zelfherstellend.

FIGURES

TABLES

Abbreviations and symbols

AA	Aluminum alloy
AFM	Atomic force microscopy
at.%	Atomic concentration
BE	Binding energy
BPO	Benzoyl peroxide
Ce(III)	Cerium nitrate hexahydrate ($Ce(NO_3)_3.6H_2O$)
Ce(IV)	Cerium ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$)
CPE	Constant phase element
Cr(VI)	Hexavalent chromium
DTA	Differential thermal analysis
DTG	Derivative of the thermogravimetry
EIS	Electrochemical impedance spectroscopy
EEC	Electrical equivalent circuit
EDS	Energy dispersive X-ray spectroscopy
FWHM	Full-width at half-maximum
GDP	Gross Domestic Product
Li	Lithium
LNLS	National Synchrotron Light Laboratory
Li-PB	Lithium intercalated pseudo boehmite
MMA	Methyl methacrylate
MPTS	3-methacryloxy propyltrimethoxysilane
NACE	National Association of Corrosion Engineers
NaCl	Sodium chloride
NMR	Nuclear magnetic resonance
NSS	Neutral salt spray test
OCP	Open circuit potential
ORR	Oxygen reduction reaction
PMMA	Poly(methyl methacrylate)
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RMS	Root mean square
SAXS	Small angle X-ray scattering
SEM	Scanning electron microscopy
SiO_2	Silica oxide

STEM	Scanning transmission electron microscopy
TEM	Transmission electron microscopy
TEOS	Tetraethyl orthosilicate
TG	Thermogravimetry
ToF SIMS	Time-of-flight secondary ion mass spectrometry
Wt %	Weight percent
XPS	X-ray photoelectron spectroscopy
α	Porod exponent
C_d	Degree of condensation
C_f	Film capacitance
d	Average distance between particles
δ	Inner layer thickness
E_c	Corrosion potential
E_{SHE}	Standard hydrogen electrode potential
ε_0	Permittivity of vacuum
ε_w	Permittivity in the wet zone
i_c	current density
$I(q)$	Scattering intensity
κ_f	Conductivity at the metal/coating interface
λ	Sharpness of the conductivity decay
R_f	Film resistance
R_g	Radius of gyration
R_s	Electrolyte resistance
P	Porosity
ρ_b	Bulk density
ρ_s	Skeletal density
θ	Scattering angle
τ	Time-constant
Z_Y	Young impedance

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RESUMO EXPANDIDO

Atualmente, a proteção contra corrosão de ligas de aço e alumínio é obtida principalmente pela anodização em combinação com o processo de conversão de cromo hexavalente. Esse método, amplamente aplicado na indústria aeroespacial, está sendo banido por regulamentações dos EUA e da União Européia, como REACH (Registro, Avaliação, Autorização e Restrição de Produtos Químicos) devido aos altos riscos da exposição laboral ao tóxico cromo hexavalente e sua liberação no meio ambiente. Nesse contexto várias estratégias alternativas foram desenvolvidas para substituir os revestimentos de conversão de cromato como proteção contra corrosão de componentes metálicos. Uma das alternativas mais promissoras é a utilização de barreiras físicas de difusão na forma de revestimentos que dificultam a permeação de espécies agressivas.

Os revestimentos híbridos orgânico-inorgânicos são considerados muito promissores para cumprir o papel de proteção contra corrosão eficiente, econômica e ambientalmente compatível. Poucos micrômetros de revestimentos híbridos apresentam desempenho comparável ou até melhor do que os sistemas convencionais combinando primer e acabamento. Quando adequadamente preparado, o material híbrido exibe forte sinergismo entre as fases como consequência do ajuste cuidadoso da composição, proporções e tipo de interação destas. Mais especificamente, nanocompósitos híbridos combinam propriedades como processabilidade, flexibilidade e hidrofobicidade de polímeros com alta estabilidade térmica, química e mecânica de materiais cerâmicos. Esses materiais multifuncionais são de particular interesse para o desenvolvimento de revestimentos anticorrosivos de alto desempenho devido à possibilidade de sintetizar uma rede interconectada, ligando covalentemente ambas as fases na escala molecular e assim formando uma barreira de difusão eficiente.

Estudos recentes sobre a estrutura do sistema híbrido PMMA-sílica mostraram que a fase inorgânica em forma de nódulos nanométricos de sílica-siloxano tem o importante papel de aumentar a estabilidade térmica e mecânica, promover forte adesão ao substrato metálico e principalmente contrair as cadeias de PMMA covalentemente reticuladas as quais vedam hermeticamente a estrutura e, assim,

promovem a formação de revestimentos densos e homogêneos que proporcionam proteção eficiente a longo prazo de superfícies metálicas em contato com ambientes salinos e salinos/ácidos.

Para avaliar a eficiência da proteção contra corrosão de um revestimento, a espectroscopia de impedância eletroquímica (EIS) é a técnica mais aplicada, fornecendo informações detalhadas sobre a evolução sistema eletroquímico eletrólito/revestimento/metal durante a permeação do eletrólito. Na análise padrão dos dados de EIS, um revestimento que sofre absorção de água em contato com uma solução agressiva pode ser descrito por um circuito elétrico equivalente (EEC) composto por uma combinação paralela de resistência e capacitância do filme combinada com uma resistência de transferência de carga e capacitância da dupla camada elétrica na interface revestimento/metal, definindo assim duas constantes de tempo.

No entanto, no estágio inicial de imersão de revestimentos altamente resistivos, as quantidades elétricas da camada não são constantes ao longo da direção normal à superfície. Essa característica leva a um desvio de um comportamento simples do circuito RC devido a uma distribuição contínua de constantes de tempo, resultando em características de ângulo de fase capacitivo na faixa de frequência média e alta. Este comportamento pseudo capacitivo é em geral considerado substituindo o capacitor por um elemento de fase constante (CPE), amplamente utilizado na modelagem EEC para levar em conta a não-idealidade do capacitor. Embora a modelagem de curvas EIS pelo uso de CPE forneça, na maioria dos casos, uma excelente concordância com os dados experimentais, é difícil estabelecer uma relação entre CPE e as propriedades físicas do filme durante a permeação, ou seja, a variação de resistividade e constante dielétrica ao longo a espessura do filme pela absorção não homogênea do eletrólito.

Assim, para fornecer um modelo eficaz que identifique de forma confiável os perfis dos parâmetros físicos e sua evolução durante a progressão dos eletrólitos, alguns autores propuseram um sistema de duas camadas usando o modelo de Young. Essa abordagem é baseada em uma camada externa na interface eletrólito/ revestimento mostrando uma absorção de eletrólitos não homogênea, levando à uma

queda exponencial da condutividade em relação ao volume, dada pelo termo Young, e uma camada de alta impedância essencialmente não afetada na interface metal/revestimento. O ajuste dos dados do EIS, de acordo com este modelo, fornece perfis de parâmetros físicos e sua evolução temporal e, assim, permite uma visão mais profunda do processo de permeação e sua relação com as propriedades estruturais do revestimento.

Na primeira etapa da investigação, foi estudada a influência da estrutura de híbridos de PMMA-sílica modificada por uma variação sistemática do iniciador térmico de polimerização (peróxido de benzoíla) nas propriedades de barreira a longo prazo do aço carbono revestido em contato com o ambiente salino. A alta estabilidade eletroquímica dos revestimentos, investigada por EIS, foi modelada de acordo com o modelo CPE e comparado com a abordagem de duas camadas de Young, esta última envolvendo uma zona de permeação em expansão com condutividade decaindo exponencialmente, a qual explica o desvio das curvas EIS do comportamento capacitivo quase ideal.

Embora revestimentos híbridos de alta-proteção passiva tenham sido desenvolvidos, em caso de danos mecânicos ou corrosivos da camada protetora, o ataque na área afetada leva à perda rápida da integridade estrutural do componente metálico, eventualmente com consequências drásticas. A incorporação de inibidores de corrosão pode melhorar a eficiência de proteção dos revestimentos retardando ou, em alguns casos, até mesmo interrompendo o processo de corrosão pela formação de uma camada inerte na zona defeituosa. Essa inibição de corrosão ativa é capaz de restaurar as áreas danificadas e, assim, reduzir efetivamente o acesso de espécies agressivas na interface revestimento/metal.

Com esse propósito, foi investigado o potencial inibidor do lítio nas propriedades estruturais e a inibição ativa da corrosão de revestimentos de PMMA-sílica modificados com diferentes quantidades de carbonato de lítio. Os resultados demonstram uma melhora significativa na vida útil do revestimento induzida pela lixiviação preferencial do Li em locais afetados pela corrosão, proporcionando melhor proteção ao substrato. Ambas, a estrutura híbrida densa com distribuição homogênea de nanopartículas de sílica altamente reticulados na matriz de PMMA formadas na

presença de lítio e a formação de uma camada protetora induzida por íons de lítio após falha local (pite) e cortes artificiais contribuem para as notáveis propriedades de barreira dos revestimentos. Com base nos resultados de análises estruturais e eletroquímicas, é proposto um mecanismo para a autorregeneração (*self-healing*) induzida pelo lítio.

Entre os inibidores de corrosão inorgânicos, os sais de cério têm sido relatados como os mais eficientes quando adicionados em soluções aquosas. Os íons de cério adicionados no material, incorporados em reservatórios ou diretamente em soluções agem como inibidores catódicos através da precipitação de óxidos e hidróxidos insolúveis em áreas defeituosas. Embora os mecanismos e as mudanças estruturais por cério em revestimentos sol-gel tenham sido amplamente discutidos, uma comparação entre nitrato de amônio cério (Ce(IV)) e nitrato de cério hexahidratado (Ce(III)) na estrutura de revestimentos híbridos de PMMA-sílica depositados em AA7075 ainda não foi realizada.

Os estudos de híbridos modificados com lítio e cério foram realizados por espalhamento de raios-X a baixo ângulo (SAXS), microscopia de força atômica (AFM) e análise termogravimétrica (TGA). Após deposição em alumínio, a atividade dos íons de Li, Ce(III) e Ce(IV) nos revestimentos foi investigada por EIS e teste de névoa salina (revestimentos riscados). O mecanismo inibidor foi estudado usando espectrômetro de massa de íon secundário (SIMS) em um pite de corrosão e microscopia eletrônica de varredura com espectroscopia de energia dispersiva de raios-X (SEM-EDX) para defeitos artificiais. Os resultados revelaram que os íon de Li e Ce(IV) são mais eficiente que o Ce(III) como inibidor de corrosão, conferindo proteção ativa para a liga de alumínio.

3.3 Conclusions

The addition of Ce(III) and Ce(IV) into PMMA-silica hybrids increased the thermal stability up to 247 °C along with a gradual reduction of unsaturated PMMA terminations by enhancing the PMMA chain growth, as found by TGA. SAXS results showed more significant changes in the hybrid structure for higher cerium content (≥3000 ppm), explained by an excess of cerium salts which aggregate in the hybrid network, leading to a decrease of adhesion to the substrate and coating durability. Hence, intermediate cerium loading (500 – 1000 ppm) provides an optimized structure resulting in an excellent passive protection of the aluminum surface.

All hybrid coatings presented high anticorrosive performance, with impedance modulus up to 7.1 GΩ cm^2 μm^{-1}, nonetheless only the addition of Ce(IV) provided active protection for AA7075. This partial regeneration effect of the PMMA-silica-Ce(IV) coating was is explained by the redox activity of Ce(IV) ions leached from adjacent coating walls into the damaged zone and the subsequent formation of insoluble oxide and hydroxide phases that block corrosive process. The beneficial effect provided by intermediate Ce(IV) loadings on the structure and active corrosion inhibition properties of PMMA-silica coatings makes this material a potential candidate for the development of low-cost, high-performance and active chromium-free coatings.

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