



Synthesis and characterization of sol-gel derived non-stoichiometric aluminum phosphate coating



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ABSTRACT

The aim of this study was to synthesize a non-stoichiometric aluminum phosphate coating with high thermal stability. The aluminum phosphate precursor solution, in the presence of polyvinylpyrrolidone (PVP) as a crack-limiting agent was prepared by a sol-gel process and then applied on AISI 304 stainless steel substrate using the dip coating technique. Phase composition analysis of the coating material was performed by X-ray diffraction (XRD). The surface and cross sectional morphology of the coating after annealing at 500 °C for 15 min were observed using scanning electron microscopy (SEM). Topography and roughness of coated surface were investigated by atomic force microscopy (AFM). The amorphous-nanocrystalline structure and distribution of nanocrystals in the amorphous matrix were studied by transition electron microscopy (TEM). Thermal analysis and study of amorphous to crystalline transformation were investigated by thermal-gravimetric and differential scanning calorimetry (TG-DSC). Molecular spectroscopy of the synthesized powder was studied by Raman spectroscopy. According to SEM and AFM images a smooth, uniform, continuous and crack-free coating with 6.7 nm surface roughness was achieved. XRD analysis showed that the amorphous structure of the coating remained almost unchanged after annealing at 500 °C for 15 min. Conversely, an amorphous-nanocrystalline structure was obtained after air annealing at 1100 °C for 1 h. Also, oxide peaks number and intensity after oxidation at 1100 °C for 10 h were remarkably less in the coated sample than the bare one indicating the surface protection of aluminum phosphate coating against oxidation. The presence of graphitic and amorphous carbon ($I_D:I_G = 0.97$) in the coating structure was confirmed by Raman spectroscopy. TEM observations also confirmed the amorphous structure of the coating after annealing at 500 °C for 15 min and the partial transformation into a mixed amorphous-nanocrystalline structure after annealing at 1100 °C for 1 h. Accordingly, the thermal analysis of the coating material showed that the onset temperature of the amorphous to crystalline transformation was around 1050 °C, a value higher compared to previous reports (below 1000 °C) for the same material.

1. Introduction

Surface protection of engineering parts against oxidation is a key factor to prolong their longevity. In this regard, using a material that is chemically inert with low oxygen permeability and good compatibility with several metals, alloys, and ceramics at high temperatures offers an excellent opportunity [1–3]. One of the compositions having the desired properties of a protective coating is aluminum phosphate ($AlPO_4$). Aluminum phosphate has low density ($2.56 \text{ g}\cdot\text{cm}^{-3}$ for berlinite), high melting temperature (1800 °C) and high hardness (6.5 Mohs). It is also stable at high temperatures; as well being chemically compatible with many metals and most widely used ceramic materials including silicon carbide, alumina, and silica over a moderate range of temperatures. However, it is unsuitable to be used as a high temperature ceramic

material due to the large volume change and subsequent stresses induced by the polymorphic transformations (berlinite, tridymite, and cristobalite) [4].

Many efforts have been done over the past few years to synthesize aluminum phosphate with amorphous structure via sol-gel process in order to improve oxidation resistance and thermal stability. Most of them have revealed an amorphous to crystalline transition below 1000 °C. For instance, Campelo et al. [5] synthesized amorphous aluminum phosphate using ammonium dihydrogen phosphate ($NH_4H_2PO_4$) (which was fully crystallized at 1000 °C. Liu et al. [6] synthesized aluminum phosphate using aluminum nitrate, phosphoric acid and citric acid ($C_6H_8O_7$) which remained amorphous up to 900 °C. Wang et al. [4] synthesized amorphous aluminum phosphate coating using ethanol, aluminum nitrate nonahydrate ($Al(NO_3)_3\cdot 9H_2O$) and

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phosphorus pentoxide (P_2O_5). The coating synthesized by Wang et al. started to crystallize at 900 °C.

An amorphous aluminum phosphate composition which is stable over 1000 °C has been developed by Sambasivan et al. [1] with low oxygen diffusivity and desirable corrosion resistance at elevated temperatures, which may provide oxidation protection for metal substrates when deposited as a coating [1, 2].

There are several advantages in using sol-gel method to form thin films. However, the crack formation due to shrinkage during drying and annealing stages and corresponding stress development between the coating and the substrate, sets serious limits to the facile applicability of this approach. To overcome this drawback, using an additive could be helpful. The additives decelerate the condensation reaction and facilitate structural relaxation in the coating. Polyvinylpyrrolidone (PVP, $(C_6H_9NO)_n$) can be considered as an effective additive to restrict the crack formation [7–9]. PVP belongs to organic polymers with amide groups which can hybridize with metaloxane polymers in molecular scale through strong hydrogen bonding between the C=O groups of the PVP and the OH groups of the metaloxane polymers. Such C=O groups can be considered as the capping agent for the OH groups of the metaloxane polymers hindering the condensation reaction and facilitating the structural relaxation [9]. PVP with C=O groups can coordinate metal atoms, offering homogeneity in metal atom distribution in sols and gel films [7].

The aim of the present study was to develop a non-stoichiometric amorphous-nanocrystalline aluminum phosphate coating in the presence of PVP as a crack-limiting agent to achieve minimum cracks and maximum uniformity and oxidation resistance by the simple and low-cost sol-gel process. By controlling the stoichiometry and using a suitable surfactant, a metastable structure with high thermal stability was produced [3].

2. Material and methods

2.1. Substrate preparation

A 1 mm thick AISI 304 stainless steel sheet was cut into samples of $20 \times 20 \text{ mm}^2$ using a spark wire machine. The chemical composition of the steel substrate is given in Table 1. The samples were ground to 4000 grit SiC abrasive paper followed by polishing using 0.3 μm alumina slurry. The samples were then degreased ultrasonically in acetone, ethanol and distilled water for 10 min. The substrates were chemically etched in a concentrated acid solution of HCl (37%, Sigma-Aldrich) and H_3PO_4 (85%, Sigma-Aldrich) mixed in equal volume fractions for 5 min in order to create surface micro roughness and improve adhesion of the coating to the substrate.

2.2. Coating preparation

The precursor solution for the synthesis of non-stoichiometric amorphous-nanocrystalline aluminum phosphate coating was prepared by sol-gel method. Aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$, Merck, 98.5% purity), phosphorus pentoxide (P_2O_5 , Merck, 98% purity) and ethanol (C_2H_5OH , Merck, 99.8% purity) were the starting materials. To synthesize the precursor solution, a specified proportion of $Al(NO_3)_3 \cdot 9H_2O$ and P_2O_5 were dissolved in ethanol. The two solutions were mixed together and stirred for several minutes. Polyvinylpyrrolidone (PVP, Sigma-Aldrich, molecular weight = 10,000) was added to the above solution (a 0.5 M PVP

concentration) under stirring until complete dissolution. The resulting solution was then used to coat the stainless steel substrates using a lab-made dip coater at the constant withdrawal rate of $15 \text{ mm} \cdot \text{min}^{-1}$. The coated samples were dried in an oven at 65 °C and then annealed in air at 500 °C for 15 min. In addition to the coated samples, a separate batch of the prepared gel was dried at 65 °C for 2 h for complete dehydration, which resulted in a light yellow, fluffy gel. Finally, samples of the dried gel were subjected to annealing in air at 500 °C for 15 min or 1100 °C for 1 h, and collected at the end of the treatment for subsequent characterization.

2.3. Coating characterization

2.3.1. XRD analysis

Phase structure analysis of the synthesized powder and coatings were performed by an X-ray diffractometer (XRD, Philips PW1830) using Ni filtered Cu Ka ($1Cu \text{ Ka} = 0.154 \text{ nm}$, radiation at 40 kV and 40 mA) over the 2θ range of 10° – 90° (time per step: 0.50 s and step size: 0.02°). Grazing Incidence XRD (GIXRD) scans of the coated samples were collected with a grazing incidence angle of 0.8° . XRD spectra were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCDPS).

2.3.2. AFM studies

Topographic studies on the polished, etched and coated surfaces were carried out by atomic force microscopy (AFM, NT-MDT Solver Pro-M) using silicon cantilevers (CSG 10) with tip radius of 10 nm curvature in contact mode and analyzed by Nova RC1 (1.0.26.1138) and WSxM 5.0 Develop 9.1 software [10]. Evaluation of the surface micro-features was performed based on the deflection related signal images of the AFM. Roughness derived from AFM topographic images was calculated over the sample area of $50 \mu\text{m} \times 50 \mu\text{m}$.

2.3.3. SEM and GDOES investigations

The Surface and cross sectional morphologies of the coating after annealing at 500 °C for 15 min was studied by scanning electron microscopy (SEM), using a Stereoscan 360 Cambridge instrument. Glow discharge optical emission spectrometry (GDOES, GDA 750 HR) technique operated at 700 V and regulated pressure of 2.3 hPa was performed to assess the composition and thickness of the coating.

2.3.4. TEM studies

The amorphous-nanocrystalline structure of the synthesized powders was studied by transmission electron microscopy (TEM) using a Philips CM200 FEG TEM instrument. The powder sample for TEM observation was prepared by dispersing the powder in methanol and adding a few drops of the suspension on carbon coated TEM grid. Complementary processing of images was carried out by ImageJ where needed.

2.3.5. Thermal analysis

Thermal stability and phase transformations of the dried gel were investigated using a thermo-gravimetric differential scanning calorimetry analyzer (TG-DSC, SETARAM) in the range of 30–1200 °C at a heating rate of $10^\circ \text{C} \cdot \text{min}^{-1}$ in air.

2.3.6. Raman spectroscopy

Raman spectroscopy (Horiba Jobin-Yvon LabRam HR-800) was used to study the presence of carbonaceous phases in the synthesized

Table 1
Chemical composition of substrate in terms of weight percent of the elements.

Element	Fe	C	Si	S	P	Mn	Ni	Cr	Mo	Cu	Nb	Ti	V
Wt%	70.52	0.0455	0.295	< 0.030	< 0.007	1.52	11.3	16.0	< 0.050	0.164	0.0705	0.0145	0.0537

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