Full Length Article

Evaluating oxidation behavior of amorphous aluminum phosphate coating

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ABSTRACT

The aim of this study was to investigate the oxidation properties of amorphous aluminum phosphate coating. Aluminum phosphate precursor solution was prepared by a sol–gel process and then applied on AISI 304 stainless steel using dip coating technique. To evaluate the oxidation behavior, samples were placed in an electrical furnace upto 1100 °C for 100 h in air with weight measurements performed at regular ten-hour intervals. Phase composition analysis of the coatings before and after cyclic oxidation process were performed by X-ray diffractometer (XRD). The surface and cross-sectional morphology of the coatings were observed using scanning electron microscopy (SEM) analysis equipped with energy dispersive spectroscopy of characteristic X-rays (EDS). The amorphous-nanocrystalline structure and distribution of nanocrystals in the amorphous matrix were studied by transition electron microscopy (TEM). According to SEM images a uniform, continuous and crack-free coating was achieved. XRD analysis as well as TEM observations showed that the amorphous structure of coating remained unchanged after annealing at 500 °C for 15 min however; an amorphous-nanocrystalline structure was obtained after annealing at 1100 °C for 1 h. Weight change measurements after 100 h oxidation test revealed that the trace of weight gain against oxidation time for both coated and un-coated substrates were parabola in nature and the range of the weight change of the bare substrate was about 30 times greater than that of observed for the aluminum phosphate coating. In general, the results showed that the synthesized amorphous aluminum phosphate is capable of surface protecting of metals/alloys against degradation at harsh environments.

1. Introduction

The most significant concerns of degradation of engineering components are surface factors including oxidation, corrosion and wear which may restrict their longevity and use. Therefore, it is essential to protect engineering parts against harsh environments using appropriate protective coatings [1].

One of the compositions with favorable properties which can be considered as a coating is aluminum phosphate ($AlPO_4$). Aluminum phosphate has low density ($2.56 \, g/cm^3$ 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 changes and subsequent stresses caused by the polymorphic transformations (berlinite, tridymite, and cristobalite) [2].

Many efforts have been done in order to synthesize aluminum phosphate with amorphous structure to improve oxidation resistance

and thermal stability over the past few years. Most of them considered amorphous to crystalline transition below 1000 °C. For instance, Wang et al [2] synthesized amorphous aluminum phosphate coating using ethanol, aluminum nitrate nonahydrate ($Al(NO_3)_3 \cdot 9H_2O$) and phosphorus pentoxide (P_2O_5). The coating synthesized by Wang et al started to crystallize at 900 °C. Li et al [3] synthesized amorphous aluminum phosphate using the same precursors which remained amorphous up to 900 °C.

An amorphous aluminum phosphate composition with low oxygen diffusivity and desirable corrosion resistance over 1000 °C has been recently developed by Sambasivan et al. which may provide oxidation protection for metal substrates when deposited as a coating [4,5].

Stainless steels have good strength and good resistance to corrosion and oxidation at elevated temperatures. Intermittent service temperature for stainless steel 304 is around 850 °C. Among various applications, stainless steels are nowadays widely used in exhaust pipes to improve the service life of their components, especially the upstream part of the exhaust line (manifold, down-pipe, converter shell), where temperature can reach 1100 °C [6,7].

The aim of the present study was to develop a non-stoichiometric,

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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	< 0.050	0.164	0.0705	0.0145	0.0537

amorphous aluminum phosphate coating by the simple and low-cost sol-gel process to increase the working temperature or extend the longevity of stainless steel 304 as an inexpensive substrate. Amorphous structures can provide oxidation and corrosion resistance. By controlling the stoichiometry, metastable structures with high thermal stability can be produced that delays crystallization up to high temperatures or long times. It is expected that this coating can provide adequate protection to metal, alloy and ceramic surfaces against degradation at high temperatures over 1000 °C.

2. Materials and methods

2.1. Substrate preparation

A 1 mm thick AISI 304 stainless steel sheet was cut into samples of $20 \times 20 \, mm^2$ using a spark wire machine. The chemical composition of substrates is given in Table 1. The samples were grounded to 4000 grit SiC paper followed by polishing using 0.3 μm alumina slurry. The samples 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%) and H_3PO_4 (85%) mixed in equal volume fractions for 5 min in order to create micro roughness and improve wettability of the surface. All raw chemical was purchased from Sigma-Aldrich.

2.2. Coating preparation

Non-stoichiometric amorphous aluminum phosphate precursor solution was synthesized by sol-gel process. 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 certain amount of $Al(NO_3)_3 \cdot 9H_2O$ and P_2O_5 were dissolved in ethanol. The two solutions were mixed together and allowed to stir for several minutes. Polyvinylpyrrolidone (PVP, Sigma-Aldrich, molecular weight = 10,000) was added to the above solution (a 0.5 M PVP concentration) with stirring until complete dissolution. The resulting solution was then applied on the stainless steel substrates by dip coating process with a constant withdrawal rate of 15 mm·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. Oxidation resistance

Investigation of the oxidation behavior of the coated and un-coated samples were carried out in an electrical furnace at 1100 °C for 100 h in air with weight measurements of both the sample and the spalls performed at regular ten-hour intervals. The samples were placed in Al_2O_3 crucibles, oxidized at desired temperature in ambient air, and cooled to room temperature. The weight change of samples after each thermal cycle was measured by an electrical balance with a sensitivity of ± 0.1 mg. The weight gain per unit area ($\Delta W/A$, mg·cm^{-2}) was calculated by Eq. (1).

$$\Delta W/A = (W_i - W_0)/A \tag{1}$$

where W_i (mg) was the weight of the sample after each cycle, W_0 (mg) was the initial weight of the sample before oxidation test, and A (cm^2) was the surface area of the specimen exposed to oxidizing atmosphere.

2.3.2. XRD analysis

Phase composition analysis of the synthesized powder, coatings and oxidized samples were performed by an X-ray diffractometer (XRD, Philips PW1830) using Ni filtered Cu Ka (lCu Ka = 0.154 nm, radiation at 40 kV and 40 mA) over the 2θ range of 10–90° (time per step: 1.25 s and step size: 0.051). The Grazing Incidence XRD (GIXRD) scan was collected with a grazing incidence angle of 0.8° for the coated samples to produce an intense signal from the film and not the substrate. XRD spectra were compared to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCDPS).

2.3.3. SEM, EDS and GDOES investigations

The Surface and cross section morphologies of the coatings and the oxidized samples were observed using scanning electron microscopy (SEM, using either a Zeiss EVO 50 EP equipped with energy dispersive X-ray spectrometer (EDS) or 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 powder and distribution of nanocrystals in the amorphous matrix were studied by TEM (Philips-CM200 FE) technique. 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.

3. Results and discussion

3.1. Synthesized powder characterization

3.1.1. Phase composition analysis

The XRD patterns of the synthesized powder after drying at 65 °C for 2 h, annealing at two different temperatures, namely, 500 °C for 15 min and 1100 °C for 1 h, are shown in Fig. 1.

It is seen that the structure of the synthesized powder evolves by heat treatment. The as-synthesized dried gel does not show any crystalline feature and is characterized by a broad hump at low 2θs (between 20° and 30°), indicative of amorphous nature. Whereas calcination at 500 °C does not remarkably modify the pattern except appearance of minor crystalline diffractions around 26°, 37° and 46°, calcination at 1100 °C however clearly promotes the crystallization of the sample as demonstrated by $AlPO_4$ and Al_2O_3 peaks, supposedly embedded in the parent amorphous aluminum phosphate matrix. The initial hump at low 2θs has not disappeared however, that along with low intensity crystalline peaks, suggest a mixed amorphous-nanocrystalline structure.

3.1.2. TEM investigations

TEM bright field images and selected area electron diffraction (SAED) patterns of aluminum phosphate gel dried at 65 °C for 2 h,