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Electroless Generation of Phosphate Films on Metals from Zinc Dialkyldithiophosphates

M. L. Suominen Fuller, K. L. De Jong, M. Kasrai,* and G. M. Bancroft

Department of Chemistry, University of Western Ontario, London, Ontario, N6A 5B7

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An electroless (solution growth) technique based on the thermooxidative decomposition of zinc dialkyldithiophosphates (ZDDPs) in solution, has been developed for the deposition of thin phosphate films on a wide variety of metals including gold and silver. An additional annealing step in air results in a uniform, sturdy, and well-adhering film, consisting of small (submicrometer) intergrown particles bonded to the metal surface. The coating process is very simple and well controlled. Any shape can be coated. Films ranging in thickness from 10s to 1000s of angstroms can be generated reproducibly, depending on the solution temperature and time of heating. These films are very hard, have excellent mechanical stability and reasonable chemical stability, and should be useful for many protective purposes.

Introduction

An electroless (solution growth) technique based on the thermooxidative decomposition of zinc dialkyldithiophosphates (ZDDPs), followed by an annealing step in air, has been developed for the deposition of sturdy, well-adhering, thin phosphate films on a wide range of metals. ZDDPs are dual-functional antiwear and antioxidant additives that have been used extensively in engine oil formulations for over 50 years.[1] ZDDPs act as antiwear agents by decomposing at the rubbing surfaces to form a protective phosphate film, containing a small amount of sulfur. A vast amount of literature exists, exploring the mechanism of film formation from ZDDPs. Although the rubbing or tribological process is extremely important in forming an effective antiwear film, the thermooxidative decomposition of ZDDP is also believed to play a major role. A few studies have therefore focused, not only on the chemical characterization of antiwear films formed under various conditions, but also on the thermooxidative decomposition of ZDDPs. As a result, a few researchers have looked at films formed by the static immersion of metal substrates in heated ZDDP oil solutions,[2−9] but none have explored these immersion films as viable protective coatings. These studies have focused on determining the mechanism by which antiwear films are formed, rather than on the properties and morphology of the thermooxidative films.

Galvin and Bird[2] used X-ray photoelectron spectroscopy (XPS) to show that antiwear and thermooxidatively deposited immersion films (referred to hereafter as thermal films) generated from ZDDPs are chemically similar. Barcroft et al.[4] reported the formation of P- and S-containing films on steel and bronze as well as on such unreactive materials as gold, platinum, and stainless steels using the hot wire method, at temperatures from ambient to above 1000 °C. However, the chemical species constituting the film were not determined and the film properties were not studied. X-ray absorption near-edge structure (XANES) spectroscopy, a sensitive technique for characterizing the chemical environment around the absorbing atom, has been recently used to characterize the P and S environments in antiwear[6−10] and thermal films[6−9] generated from ZDDPs on steels and aluminum alloys. Here we present the electroless generation and characterization of thin annealed phosphate films (thermal films) from heated ZDDP oil solutions on a wide range of metals including steel, aluminum alloys, silver, and gold. Thermal annealing of the generated coatings yields films with quite remarkable protective properties.

Experimental Section

Film Preparation. Metal substrates were polished and cleaned prior to film generation. Steel (AISI-52100) coupons of Vickers Hardness 870 were polished with 3 μm diamond

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* To whom correspondence should be addressed. E-mail: mkasrai@uwo.ca. Phone: 519-661-2111, ext. 6332. Fax: 519-661-3022.

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paste. Steel coupons were then washed with a mild dish detergent, rinsed with distilled water, and sonicated in methanol and then in hexane. Al(Si) alloy coupons were polished with 320, followed by 600 grade alumina paper. Al alloy coupons were sonicated in methanol and then in hexane. The pure silver was immersed in 70% nitric acid for a few minutes and then rinsed well with distilled water. Following this procedure, the silver was polished with an abrasive pad, rinsed in methanol, and allowed to air-dry. Pure gold foil was dipped into 5% nitric acid and rinsed well with distilled water, then methanol, and finally hexane.

A commercial ZDDP, consisting of 85% secondary (C-4) and 15% primary (C-8) (referred to as ZDDP), was used for this study. ZDDP oil solutions, 0.1% or 0.5 wt % in P, were prepared by mixing the appropriate amount of ZDDP concentrate in MCT-10 base oil, by stirring at 50−60 °C for 15 min. Thermal films were generated from ZDDP on steel, aluminum alloy, and pure silver and gold foils by immersion in a heated ZDDP oil solution for various lengths of time from the initiation of solution heating. The ZDDP oil solution heating temperature was set above the thermal decomposition temperature of the ZDDP. It is the nature of the ZDDP organic substituents that determines the ZDDP decomposition temperature[11,12] and rate of ZDDP decomposition. Heating temperatures from 150 to 200 °C have been explored for this commercial ZDDP, but 150 °C was used for this study as it gives the best control.

After removal from solution, the metal coupons were rinsed well with hexanes to remove any residual oil. The films were then hardened by annealing at 250 °C (well above the thermooxidative decomposition temperature of the ZDDP), in a furnace in air.

Data Acquisition and Analysis. Phosphorus and sulfur K- and L-edge X-ray absorption spectra were obtained at the 1 GeV Aladdin storage ring, University of Wisconsin, Madison. The K-edge spectra were obtained on the double crystal monochromator (DCM) beamline, covering the photon region of 1500−4000 eV. The Grasshopper beamline was used to obtain the L-edge spectra, in which the X-ray beam is monochromatized by an 1800 g/mm grating and covers the photon region of 70−900 eV. The photon resolution at the P L-edge and P K-edge were <0.2 and <0.8 eV, respectively.

The photoabsorption spectra were recorded in the total electron yield (TEY) and fluorescence yield (FY) modes. The maximum analysis depths are ~50 Å for TEY at the L-edge, ~500 Å for FY at the L-edge and TEY at the K-edge.[13] The attenuation length has been calculated to be ~1 μm for FY at the P K-edge for $Zn_2P_2O_7$. For the L-edge and K-edge spectra, a single scan, with good signal-to-noise ratio could be accomplished. However, in most cases at least three scans were digitally combined and after normalization, a background was removed.

Scanning electron microscopy was performed on a Hitachi s-4500 series Field Emission Microscope at Surface Science Western.

Results and Discussion

P L-Edge XANES. X-ray absorption near-edge structure (XANES) spectroscopy using synchrotron radiation has been proven to be a sensitive technique for the speciation of the chemical nature of P and S in antiwear and thermooxidative (immersion) films generated from ZDDPs on steel surfaces.[6−10,17] XANES is very sensitive to small atomic displacements, bond angles, and relative atomic positions in the environment of the absorbing atom. Thus, to identify the chemical nature of the absorbing atom in complex matrixes, it is essential to compare XANES spectra of the films with those of different model compounds in which the local chemical environments of the absorbing atom are known.

The P L-edge X-ray absorption near edge structure (XANES) spectra of the thermal films, before and after annealing are shown in Figure 1, along with model compound spectra. The immersion times are indicated in the figure. The P L-edge spectra shown in Figure 1 were collected in the total electron yield mode (TEY). The sampling depth at the P L-edge in the TEY mode is predicted to be ~50 Å[13] and is therefore indicative of the near surface chemistry of the thermal films. As is indicated in Figure 1, the thermal film spectra are quite different from that of the starting material, the ZDDP (lines A and G), indicating that the ZDDP has decomposed to form the thermal films. The film spectra most closely resemble the polyphosphate spectra (lines B and H), with variations in peaks a and b intensity, reflecting differences in chain length.[10,14] The greater the intensity of peak a and b relative to peak c, the longer the polyphosphate chain length. As well, an intermediate species is indicated by the presence of intensity in peak position 3. This intermediate species is believed to be a rearranged ZDDP,[9] referred to as linkage isomer ZDDP (LI-ZDDP), in which the alkyl groups have migrated to the S atoms, and the O atoms are now linked to the Zn. Suominen Fuller et al.[9] identified the LI-ZDDP in a ZDDP solution decomposition study. The chemistry of antiwear and thermal films is governed by the ZDDP oil solution chemistry (i.e., the extent of ZDDP decomposition in solution). A previous antiwear film formation mechanism by Yin et al.[10] was revised as a result of these studies.[9] Thermal film formation is believed to follow a similar mechanism; ZDDP rearranges to LI-ZDDP, and then decomposes to a long-chain polyphosphate by release of alkyl sulfides, followed by reaction with residual water in the oil to form short-chain polyphosphate.

There is more LI-ZDDP in the films removed from solution at 6 h of heating (steel, line C, and gold, line E). It is interesting that the spectra for steel and gold are similar. Barcroft et al.[4] found that tenacious films were formed on gold and platinum, just as readily as on steel and bronze. We believe that a Au−S bond, or in the case of silver, a Ag−S bond, is formed at the metal−film interface, providing a strong link between the metal and the film. Equation 1 illustrates what is believed to occur in film formation on nonoxidizing surfaces, such as gold and platinum:

$$\mathrm{Zn[(RO)_2PS_2]_2 \text{ or } Zn[O_2P\,(SR)_2]_2 \text{ (adsorbed)} + O_2 \text{ (oil)} \Rightarrow Zn(PSO_2)_2 + \text{sulfur species}} \quad (1)$$

In this case, it can be seen that not all of the sulfur groups are lost to solution but rather are retained in the zinc thiophosphate. The presence of the sulfur in

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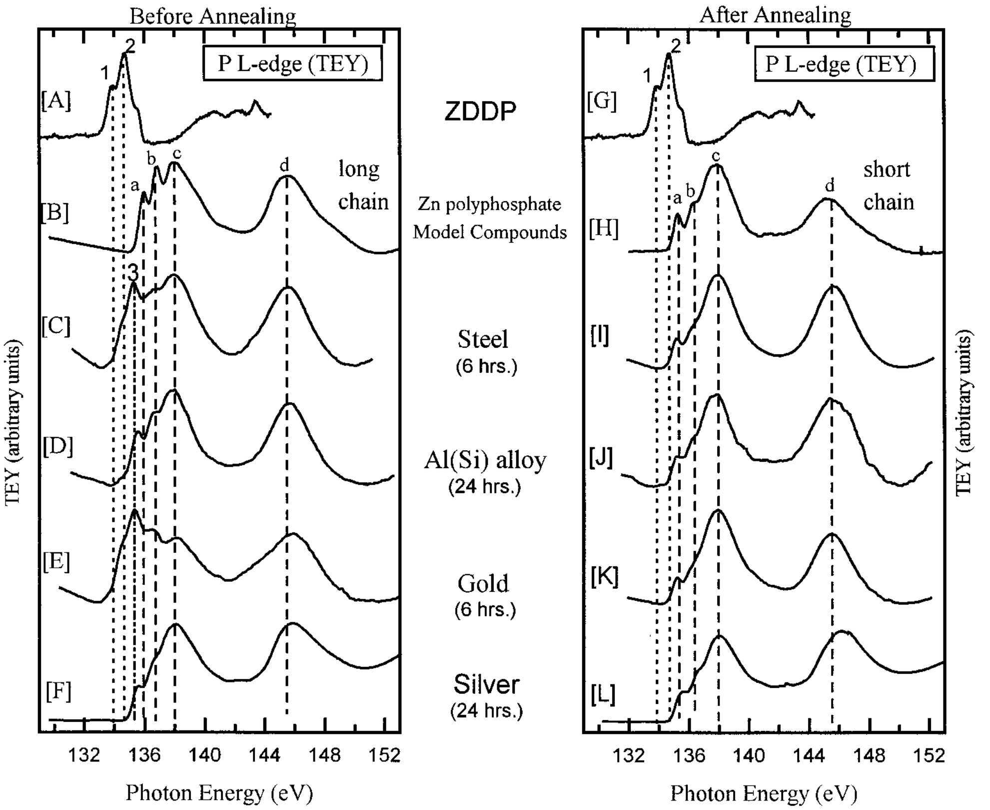

Figure 1. P L-edge (TEY) XANES spectra of thermal films generated from ZDDP on steel, Al(Si) alloy, pure gold and silver, before and after annealing. Immersion/heating times are indicated in the brackets under the respective metal labels.

this complex gives rise to covalent bonds between the sulfur and gold in this case. This covalent bond is believed to be sufficient to provide a suitable adhesion between the film and the substrate. For example, a Au−S bond is much stronger than a Au−O bond.[15] Much literature exists regarding alkane thiol self-assembled monolayers (SAMs) on gold surfaces. Siqueira Petri et al.[16] used XPS to study the immobilization of a cellulose thiosulfate on gold surfaces. Results indicate that the thiosulfato groups are homolytically cleaved, and the resulting cellulose-thio radicals bind covalently to the gold substrate.

The P L-edge TEY spectra of the films on Al(Si) alloy (line D) and silver (line F) both indicate a short to midchain polyphosphate (compare line B to line H). These results are also in agreement with the results of Suominen Fuller et al.[9] in that after 24 h of heating at 150 °C, very little ZDDP remains. The films consist of shorter chain polyphosphates, consistent with the mechanism of Suominen Fuller et al.[9]

The P L-edge TEY spectra of the films after annealing are also presented in Figure 1. All film spectra after annealing are consistent with a short-chain polyphosphate structure. Longer chain polyphosphate, as in the case of the 24 h films on Al(Si) alloy (line D) and silver (line F), is converted to short-chain polyphosphate through annealing (lines J and L, respectively). Also, unreacted ZDDP or LI-ZDDP, as seen in the 6 h films on steel (line C) and gold (line E), is converted to short chain polyphosphate (lines I and K, respectively).

P L-edge XANES spectra of the films were also collected in the fluorescence yield (FY) mode (not shown) with a sampling depth of ~500 Å.[13] Differences in the near surface and bulk film structure are indicated by the TEY and FY P L-edge XANES film spectra before annealing, with longer chain polyphosphate and unreacted ZDDP or LI-ZDDP on the surface, and shorter chain polyphosphate in the bulk, depending on the conditions. The annealed films, on the other hand, are more homogeneous in composition, manifesting a short-chain polyphosphate structure.

The decomposition of ZDDP or LI-ZDDP at the high annealing temperatures is believed to be due to an intermolecular decomposition reaction rather than the thermooxidative mechanism of Suominen Fuller et al.[9] Spedding and Watkins[18] investigated the thermal decomposition of a pure ZDDP in oil, under a nitrogen atmosphere. A number of volatile P/S compounds, as well as alkyl sulfides were identified using ^{31}P NMR, proton NMR, infrared spectroscopy, and mass spectroscopy. One possible mechanism for the intermolecular decomposition reaction of ZDDP, consistent with the results of Spedding and Watkins,[18] is

$$2Zn[(RO)_2PS_2]_2 \Rightarrow Zn_2P_2O_7 + (RS)_3PO + (RS)_3PS + RSR \quad (2)$$

The result is the formation of the short-chain polyphosphate, $Zn_2P_2O_7$, with the release of volatile P/S compounds and alkyl sulfides. The loss of S is reflected in the S L-edge TEY film spectra (not shown). The S L-edge TEY spectra of the same films, before annealing, indicate the presence of sulfide species, along with some oxidized S in the form of sulfate. The sulfide content is very small or absent in the films after annealing, indicating that LI-ZDDP decomposition has resulted in

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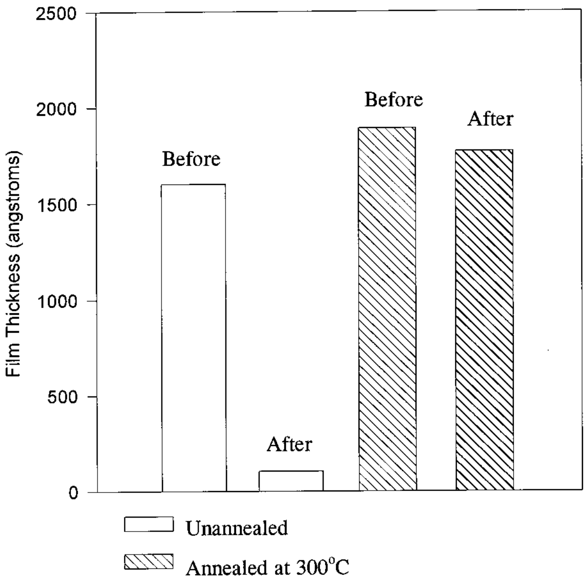

Figure 2. Phosphate film thickness[17] of the unannealed and annealed thermal films on gold, before and after treatment consisting of liberal spraying with a "household" cleaner, followed by wiping 10 times with a tissue.

the release of volatile S compounds. Although the S content is reduced through annealing, it is believed that S remains bonded to the gold or silver substrate at the film–substrate interface. This small amount of S may not be detectable by the XANES spectroscopy in films of 50 Å or greater thickness. In the case of steel and Al alloy, reaction of the ZDDP with the metal oxide layer results in a chemical bond at the phosphate–metal interface, thereby providing good adherence.

Annealing not only reduces the film S content, but also results in a harder, sturdier film. Films on pure gold foil, before and after annealing, were tested by spraying liberally with a household cleaner (DowBrands "Fantastik" All Purpose Cleaner), followed by "wiping" with a tissue 10 times. Film thickness, before and after testing, was determined using P K-edge XANES spectroscopy,[17] and the results are shown in Figure 2. The edge jump amplitude in the XANES spectrum is proportional to the number of absorbing atoms.[19] White line (1s → np) areas and intensities have also been used in quantitative determinations.[17,20–21] In this case, the white line intensities (peak heights) of P K-edge spectra of a set of thermal films of varying thickness were measured. The mass thickness of each of these calibration films was also measured using the particle-induced X-ray emission (PIXE) technique. A calibration curve relating P K-edge white line peak height to P areal density (mass thickness), with a correlation coefficient of 0.997, was constructed. Mass thickness of an unknown film was extrapolated from the calibration curve. Mass thickness was converted to a physical film thickness assuming a Zn pyrophosphate film composition. Film composition after annealing, as revealed by P L-edge XANES spectroscopy (Figure 1), is consistent with a short chain polyphosphate structure.

Film thickness results presented in Figure 2 show that the film that was not annealed is much less stable to the testing or treatment than its annealed counterpart. Most of the film (not annealed) was wiped away, while there was very little change in the thickness of the annealed film.

Adhesion of the film to the steel substrate was investigated using the tape test. A 1000 Å film on 52100 steel, annealed at 250 °C for 1 h, was tested using adhesive Cu tape (type used in electron microscopy). P K-edge XANES spectroscopy of the film and tape, before and after testing, revealed that very little film had been removed by the tape, indicating excellent film adhesion to the substrate. Scratch testing of the thermal films on steel, to be described in a later publication,[22] has also demonstrated the excellent adhesion of the film to the steel substrate.

Scanning Electron Microscopy. Film morphology was examined using scanning electron microscopy (SEM). Representative film SEMs are presented in Figure 3. The SEM shown in panel a is of a thermal film on steel prepared by immersion in a ZDDP solution (0.5 wt % P) for 3 h, heated at 150 °C. Film thickness was determined to be ~70 Å.[17] Comparison with a steel blank (not shown) reveals that a film composed of submicrometer size (a few hundred angstroms) nodules is growing on the metal surface. The SEM shown in panel b is of a film grown on pure silver during 24 h of immersion in a ZDDP solution (0.1 wt % P), heated at 150 °C. The film particles are larger, densely packed, and intergrown. The thickness of the film in panel b was determined to be ~2500 Å.[17] The lower magnification SEMs shown in panels c and d are of a films generated from a 0.1 wt % P ZDDP solution on the Al-(Si) alloy, before (c) and after (d) annealing. The SEMs (panels c and d) are remarkable similar, indicating that annealing has not affected the appearance of the film. While a fairly uniform submicrometer phosphate film has been generated on the metal surface (regions 2), consistent with the film structure described in panel b, some large phosphate particles have also been deposited on the film surface during film generation (e.g., regions 1). The presence of the large phosphate particles is believed to be due to the deposition of colloidal polyphosphate material from solution in which the ZDDP has decomposed. These findings are in agreement with the mechanism proposed by Suominen Fuller et al.,[9] and also parallels the mechanism by which thin films of II-V and IV-VI compound semiconductors are deposited by a controlled homogeneous precipitation technique.[23–24] Kaur, Pandy, and Chopra[24] found that growth of CdS films takes place either by ion-by-ion condensation of Cd^{2+} and S^{2-}, or by the adsorption of colloidal particles of CdS formed in solution, depending on the various deposition parameters and the method of preparation. In our case, ZDDP decomposition, and hence, film

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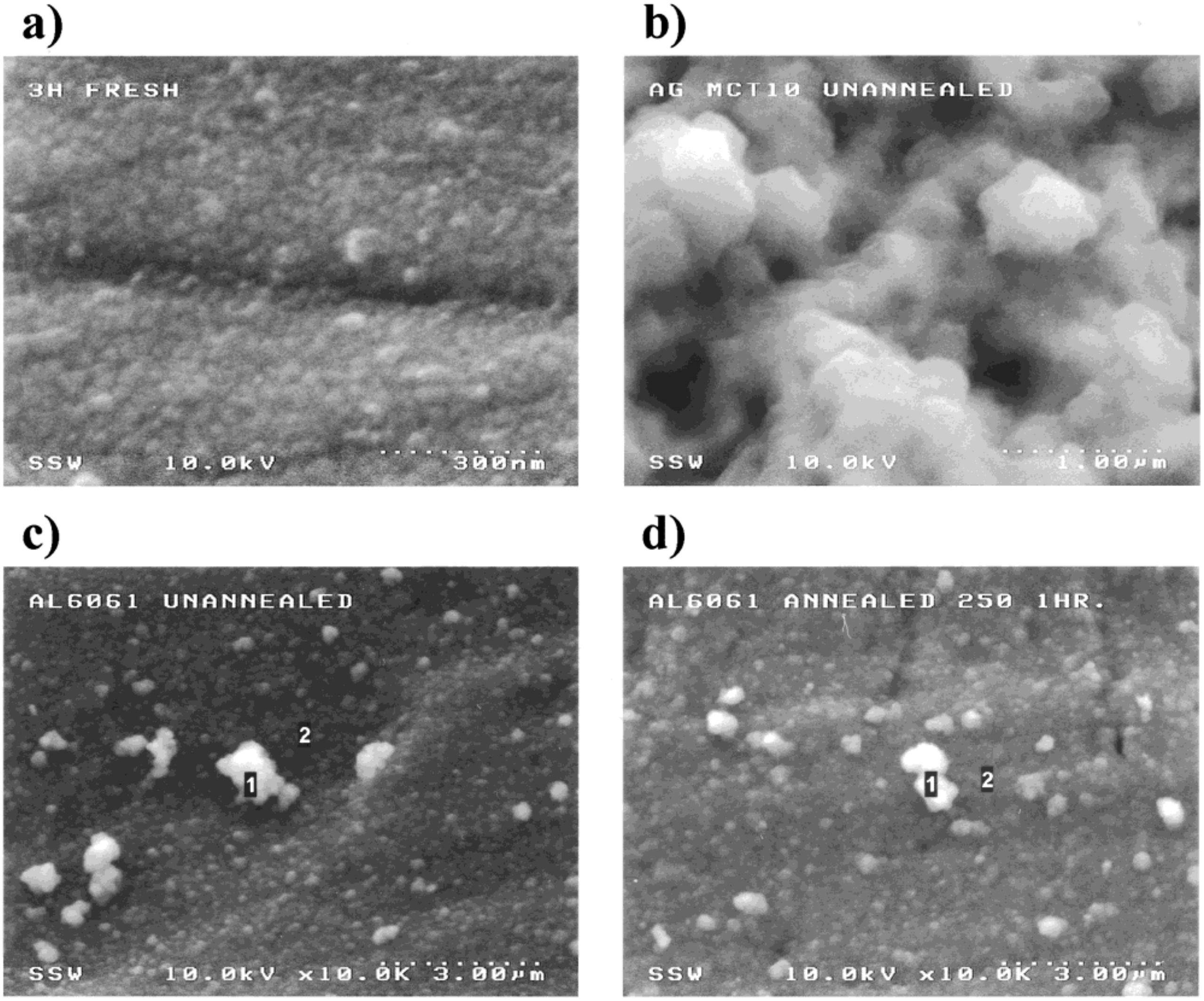

Figure 3. Scanning electron micrographs (SEMs) showing the morphology of (a) a thermal film on steel prepared by immersion in a ZDDP solution (0.5 wt % P) for 3 h, heated at 150 °C; (b) a film grown on pure silver during 24 h of immersion in a ZDDP solution (0.1 wt % P), heated at 150 °C; (c and d) films generated from a 0.1 wt % P ZDDP solution on the Al(Si) alloy, before (c) and after (d) annealing.

growth, are not linear.[9] There is an induction period during heating while the ZDDP rearranges, followed by rapid reaction and precipitation of an oil insoluble Zn polyphosphate. Even so, this film growth process is well controlled. Films ranging in thickness from 10s to 1000s of angstroms can be generated, depending on the temperature and time of heating.

In summary, thin phosphate films have been generated from ZDDPs on a wide variety of metals including gold and silver, by an electroless (solution growth) technique. An additional annealing step in air results in a uniform, sturdy, well-adhering film which should be useful for many protective purposes.

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