Comparison study of aqueous binder systems for slurry-based processing

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Abstract

The use of environmentally friendly alternatives, such as water, to replace volatile and toxic solvents for material forming applications has been gaining increased attention from industry in recent years. This study provides the groundwork for selecting water-compatible binders for clean slurry-based processing based on the relative performance of binders. In particular, the study examines the influence of various binders, including thermoplastic starch, polyvinyl alcohol, styrene–butadiene latex, and acrylic latex, on the properties of aqueous-based powder suspensions and pre-fired multilayer laminates fabricated using a modified dip coating process. Tungsten (W)/aluminum oxide (Al_2O_3), a common metal–ceramic system used in various slurry-based processes and applications, is selected as a representative material system for the study. Through the characterizations of physical properties and microstructures of the materials, the application-specific property optimization of each binder system is determined and discussed. Latexes and cross-liked PVA are found feasible for water-based processing, provided that there is proper control of processing parameters.

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1. Introduction

Slurry-based processing has been employed extensively in various types of material forming techniques including tape casting [1,2], three-dimensional printing [3,4], slip casting [5], and dip coating [6]. Slurries typically comprise ceramic or metallic powders, solvents, binders, and other additives such as dispersant, surfactant and anti-foaming agents. Traditionally, organic solvents, such as alcohols, ketones, and hydrocarbons, are used as liquid carriers for powders as they dry relatively quickly and exhibit good compatibility with other materials in the system [7]. Due to their toxicity, inflammability and volatile nature, however, organic solvents usually pose health and environmental hazard problems. Consequently, materials processing industries are currently moving towards the use of more environmentally friendly solvents, namely water, and studies are being conducted within the research area to better understand water-based systems [8].

To effectively employ water-based slurries in material forming processes, it is important to develop binder systems that are compatible with water and provide desired properties of the intermediate and final products as specified by particular applications. Some common criteria include: (i) stability, (ii) appropriate viscosity of a powder suspension, and (ii) sufficient green strength of the as-dried products. In the past decade, water-based colloidal binders, particularly latexes [9–14] and water-soluble binders, namely cellulose ether [8,15,16] and polyvinyl alcohol (PVA) [17,18], were investigated for the process of tape casting. Powder materials that have been studied include Al_2O_3 [10,12,13], Y_2O_3-stabilized ZrO_2 [14,17], cordierite-based glass ceramic [9], and lanthanum-modified lead zirconate titanate [18]. By controlling the rheological properties of the suspensions, prepared with the aforementioned aqueous-compatible binders and through careful adjustments of dispersant content, the use of these binders was found feasible for tape casting applications. In addition, because slurries containing a high concentration of water-soluble binder generally have a higher viscosity of slip that is hard to tape cast [13], they are less attractive than latex binders for this application.

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While an increasing number of studies on aqueous-based binders are focused on tape casting applications, studies of water-based binders for other material forming techniques have not been documented. Moreover, other techniques may pose different or further requirements for slurries and final product properties. For instance, in the dip coating process, which involves a series of submersions and withdrawals of a substrate from a powder suspension, the production of multilayer components is complicated by additional requirements beyond (i)–(iii) above. These may include (iv) good wettability of slurry between various coating layers, (v) non-dissolution of the as-dried coating layers when exposed to water, and (vi) uniformity of the coating layer in the presence of aggregates along coating interfaces. It should be noted also that prior research that is aimed to compare the performance of different types of aqueous-based binders is rather limited [8,19,20]. The process of materials selection, which is useful during the early stages of development for aqueous processing, may be conducted if various binders of different natures are investigated in tandem under similar processing conditions.

In this paper, a comparison study that entails the development and relative performance of various types of binders for aqueous processing, including thermoplastic starch, PVA, cross-linked PVA, styrene–butadiene latex, and acrylic latex is presented. The focus is made on the influence of binders on the properties of suspensions and pre-fired laminates (i.e., (i)–(vi)), which were fabricated using a modified dip coating process. While the study was solely conducted on W/Al$_2$O$_3$ multilayer laminates, the knowledge gained from the study may be extended to different materials systems and applications.

2. Experimental

2.1. Materials

2.1.1. Powders

W and Al$_2$O$_3$ were chosen as representative powder materials for the study because, first, W and Al$_2$O$_3$ powders are not reactive in the presence of water, and thus they are suitable for aqueous processing. Second, W/Al$_2$O$_3$ is a metal–ceramic system used to a great extent, especially for electronic packaging and metal brazing applications [21,22]. Developments of water-based processing technology for this material system would pose a significant impact for the industry. W (Alldyne Powder Technologies, Huntsville, Alabama) and Al$_2$O$_3$ powders (Remet Corp., Utica, NY) used in the study had mean particle sizes of 1 and 4 μm, respectively.

2.1.2. Binders

W/Al$_2$O$_3$ multilayer dip-coat laminates were formed using various types of binder systems; details of the specimen fabrication process are discussed in Section 2.2. For Al$_2$O$_3$ dip-coat layers, a single type of binder, namely water-based colloidal silica binder (28 wt.% SiO$_2$), was used to prepare all specimens in this work. Colloidal silica is a common type of binder used for the forming of Al$_2$O$_3$ powder [4,23]. Spherical, sub-micron, amorphous silica particles that are dispersed in the binder provide

green strength to Al$_2$O$_3$ via gellation upon drying of the solvent, and also help enhance the sintering kinetics of Al$_2$O$_3$ upon firing. SiO$_2$ and/or its derivatives will, however, remain in the final products, which may not be desirable for some applications.

Several binder systems for the W layer were examined. The description of each material is presented below:

- *Thermoplastic starch*: starch is an environmentally friendly, biodegradable, and readily available biopolymer consisting of condensed glucose units. Due to its gelling properties [24], the material has been used as a binder for gel-casting processes [25] and as a binder and pore former for the fabrication of porous ceramics [26,27]. In this work, a modified thermoplastic starch binder that exhibited a minimal dissolution when exposed to water, based on a formulation proposed by E.S. Stevens [28] was prepared. The mixture was comprised of cornstarch and NaCl in 1% glycerol solution (6.5 g of starch:50 mg NaCl:200 mL of 1% glycerol solution). The solution was continuously stirred while heating to the boiling point, after which the product was covered and allowed to cool to room temperature. Heating to the boiling point is critical because it allows the starch biopolymer chains to fully react with the glycerol. If sufficient heat is not provided to the mixture, the resulting thermoplastic film (without the addition of W) readily disintegrates when exposed to water.

- *Latex*: a latex is a stable colloidal dispersion of a polymeric sub-micron particles in water [8]. During evaporation of the solvent, these particles coalesce and form a polymeric network, providing green strength to the dried product. Two commercial latex binders were examined in the study: (i) LATRIX 6300, a styrene–butadiene latex, which was supplied by Ondeo Nalco (Naperville, IL) and (ii) UCAR DT211, an acrylic latex supplied by Dow Chemical (Midland, MI). For convenience, the latex binder materials are labeled Latex I and Latex II, respectively. To aid in suspension of W in Latex II, a calcium neutralized naphthalene sulfonate dispersion agent, Daxad 19LCA (Dow Chemical), was added to the binder solution. De-ionized water was added to both latexes to achieve the composition of 47.6 wt.% as-received latex and 47.6 wt.% water and 4.8 wt.% Daxad.

- *Polyvinyl alcohol*: polyvinyl alcohol (PVA) is a thermoplastic polymer that is water-soluble, exhibits good flexibility, and dries quickly [8]. In this study, Evanol 52-22 L10, a partially hydrolyzed commercial PVA (DuPont Corp., Deepwater, NJ) was used. De-ionized water was added to the as-received PVA to give the final binder solution composition of 50 wt.% PVA and 50 wt.% water.

- *Cross-linked PVA*: In order to help impede dissolution of the PVA binder in water, cross-linking of PVA to form a polymeric network was promoted through the use of a cross-linking agent. Tyzor LA, an aqueous titanium lactate cross-linking agent supplied by DuPont Corp. was chosen for the investigation. A preliminary study was carried out to determine the optimum amount of cross-linking agent to be added to the binder solution based on measured viscosity of the solution and insolubility of the dried film. Addition of the cross-linking agent was carried out in ambient conditions, and mixed for

20 min. The composition of the binder solution chosen for the fabrication of test specimens was 49.4 wt.% PVA, and 49.4 wt.% water, and 1.2 wt.% cross-linking agent. Based upon a visually observable increase in viscosity, cross-linking of PVA appeared to occur upon mixing the solution [29]. Furthermore, cross-linking additions greater than 1.5 wt.% caused the solution to gel and no longer flow, thus becoming unusable as a binder.

2.1.3. Aggregates

Sand aggregate is often applied between coating layers, particularly in dip coating process, to provide mechanical interlocking between layers, to facilitate wetting of the subsequent coating layer, and to aid in a rapid increase in thickness of the final multi-layer composite [30]. In this study, we examined how different aqueous binders interact with sand aggregates. Two types of stucco sand were employed in the production of W/Al$_2$O$_3$ laminar specimens—(1) CaO-partially stabilized ZrO$_2$ sand ($\sim$300 μm), and (2) Al$_2$O$_3$ sand ($\sim$500 μm) (Remet Corp., Utica, NY). The use of these aggregates is further discussed in Section 2.2.

2.2. Processing

The processing method employed to fabricate the W/Al$_2$O$_3$ laminar specimens was similar to the standard multiple dip coating technique [6]. Moreover, dip coating was chosen because it has been widely used in various industrial and engineering applications, including the manufacture of investment casting moulds [31], piezoelectronic materials [32], cutting tools [33] and bone implants [34]. First an Al$_2$O$_3$ slurry and five different sets of W slurries were prepared by mechanically mixing together the powders and appropriate binder solutions, discussed in Section 2.1.2. The Al$_2$O$_3$ solid loading content in the slurry was maintained for all samples at 48 vol.%. Because of its strong influence on slurry viscosity, the solid loading content for W was individually determined for each binder system to provide optimal coating characteristics. To improve wetting properties of the W slurries, 0.02 wt.% of Victawet-12 (SPI Supplies West Chester, PA), a nonionic complex phosphate ester surfactant, was added to each slurry during mixing.

After the W slurries had been mixed for 1 h, they were poured onto coating substrates made of paraffin wax pieces cut to the size of 5 cm × 2.5 cm × 0.8 cm. The same pouring rate and pouring angles were maintained for all prepared specimens. Excess slurry was allowed to drip off for approximately 5 min and the specimens were subsequently sprinkled with calcia-stabilized zirconia stucco sand. The specimens were then dried for 24 h and then dipped into the Al$_2$O$_3$ slurry. Again, dipping angles and withdrawal rates were carefully controlled for all cases. To improve the green strength of the structures and to suppress the formation of drying cracks, alumina sand was uniformly applied onto a wet Al$_2$O$_3$ dipcoat layer. After drying for 48 h, removal of the wax substrate (i.e. de-waxing) was conducted in a high pressure steam environment using a lab-scale autoclave with a 10 min ramp to 3 min of soaking at 106 °C and 40 psi. The resulting W/Al$_2$O$_3$ laminar specimens were allowed to dry for

another 24 h before characterization. All drying stages took place in laboratory air with a temperature of 23 ± 2 °C and 54 ± 7% humidity.

2.3. Characterization

Several modes of characterization were conducted to assess the properties of W suspensions as well as the quality of fabricated green products. The viscosity for each W slurry was determined using a viscometer (Brookfield LVT) with a shear rate of 2 s^{-1}. To determine the most appropriate solid loading content for each binder system, preliminary viscosity measurements were performed to examine the viscosity of the suspensions as a function of solid loading. To evaluate stability of the W slurries, sedimentation tests were carried out by placing each slurry into a standing test tube and then measuring the W-fallout level after 10 min, 1 h, 3 h, and 1 day. Additionally, the packing fraction of the materials, which describes the degree of coagulation of W powders in slurries, was measured by centrifuging the W suspensions at the rate of 3400 rpm for 30 min. The packing fraction (PF) was determined from:

$$\text{PF} = \frac{V_p}{V_a} = \frac{\text{SL} \times (V_p + V_b)}{V_a} \qquad (1)$$

where V_p and V_a are the actual volume of W powder added in binder solution and the apparent volume of settled W agglomerates, respectively. The volume of binder solution is represented by V_b. SL is the solid loading of powder, which, by definition, equals to a ratio of V_p and the total volume of powder suspension ($V_p + V_b$).

A dissolution test was performed by placing wax pieces, which had been coated by a single layer of W slurries and dried for 1 day, into a bath of distilled water for 5 min. After 1-day of drying, the difference of the weight before and after water submersion of the coated wax specimens was calculated. To test for absorption of water by the W layer, 1 cc of water was dripped onto a W-layer coated wax samples inclined at 45°. Inclination of the sample provided drainage so that water could flow over the W-layer. The weight of the sample after the absorption test was then compared with the original weight. Finally, the integrity, surface quality, and the thickness of W layers of all de-waxed W/Al$_2$O$_3$ laminar specimens were evaluated using optical and scanning electron microscopy techniques.

3. Results

3.1. Properties of W suspensions

From preliminary viscosity measurements, it was observed that the viscosity of W powder suspensions prepared with different binder systems all increased exponentially with W solid loading content. The optimum W solid loading content based on the viscosity measurement is reported in Table 1 for each binder system examined. Also shown in Table 1 is the corresponding viscosity for each suspension. While the optimum W solid loading content for Latex I and Latex II was approximately 50%, that of PVA, cross-linked PVA, and starch was 30%

Table 1
The characteristics of W slurries prepared by various binder systems

Binder system	Solid loading (vol.%)	Viscosity (cP)	Packing fraction	Stability
Starch	20	18,520	0.39	Excellent
PVA	30	760	0.5	Relatively poor
Cross-linked PVA	30	1,096	0.47	Relatively poor
Latex I	50	326	0.69	Relatively poor
Latex II	55	1,250	0.62	Excellent
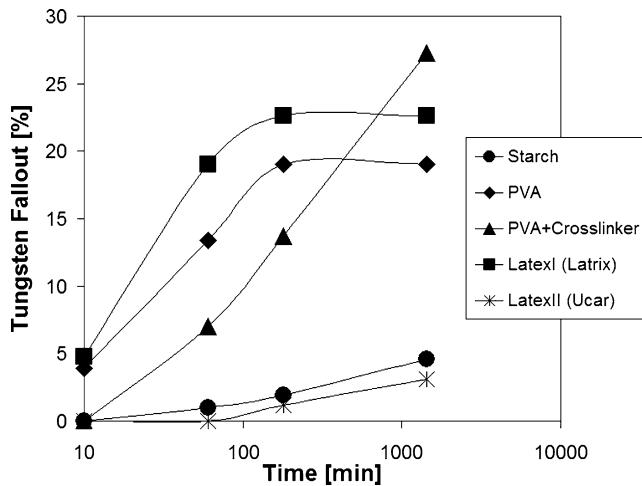
Fig. 1. The trends of slurry sedimentation as observed in various sets of W slurries that contain different types of binders.

and below. In the case of starch, for example, solid loading of merely 20% resulted in a relatively high suspension viscosity of 1.85×10^4 cP. In agreement with what has been observed in prior studies [8], suspensions of water-based colloidal binders exhibited lower viscosity than those with water soluble binders.

Results from the stability test, presented in Fig. 1, show that W suspensions with starch and Latex II were relatively stable, with less than 5% W fallout after settling for 1 day. For PVA, cross-linked PVA, and Latex I systems, the stability of the suspensions was relatively poor. However, a notable improvement in suspension stability was observed when PVA was modified with a cross-linking agent. A wide range of packing fractions, from 39 to 69%, were achieved when different binder systems were employed, as reported in Table 1. Relatively high packing fractions, which suggest that W particles were well-deflocculated in the suspension, were found in the systems containing latexes.

Moderate and the low packing fractions were observed for the PVA and starch systems, respectively.

Specimens prepared for the dissolution and absorption tests exhibited good quality following the coating and drying steps. Specifically, all of the W slurry systems appeared to wet the paraffin wax well, and were homogeneously distributed without the presence of microvoids on the surface. Table 2 presents the results obtained from the dissolution test. It was observed that W layers using starch and the two latex binders remained intact on their respective wax surface with negligible amount of W dissolved in water. Without a cross-linking additive, the W layer prepared with PVA readily disintegrated when submerged in water. The test also showed that the use of a controlled amount of the cross-linking agent in PVA helped enhance the water resistance of the PVA binder system. After a few minutes of being immersed in water, however, the modified PVA W layer swelled and peeled away from the wax surfaces in one single piece.

Also shown in Table 2 are the results obtained from the absorption test. Comparing the percent weight increase due to water absorption of different specimen sets, it appeared that the two latex systems exhibited a relatively low degree of water uptake. Additionally, no changes in film characteristics were observed for samples of these systems. In the case of the starch, PVA, and modified PVA samples, a significant amount of water was absorbed. While the PVA samples distributed the water throughout a flat W-layer, the W films of modified PVA and starch samples wrinkled upon water absorption.

3.2. Properties of pre-fired W/Al₂O₃ laminates

Following the de-waxing step, W/Al_2O_3 laminate specimens produced from each of the binder systems were intact without the presence of interfacial delamination or surface cracks. Optical micrographs presented in Fig. 2a–e show the surface quality of a W layer for post-autoclave W/Al_2O_3 laminates. Examination of the starch binder samples (Fig. 2a) reveals that their W

Table 2
Results obtained from the dissolution and absorption tests in comparison to the characteristics of the respective W/Al₂O₃ laminate

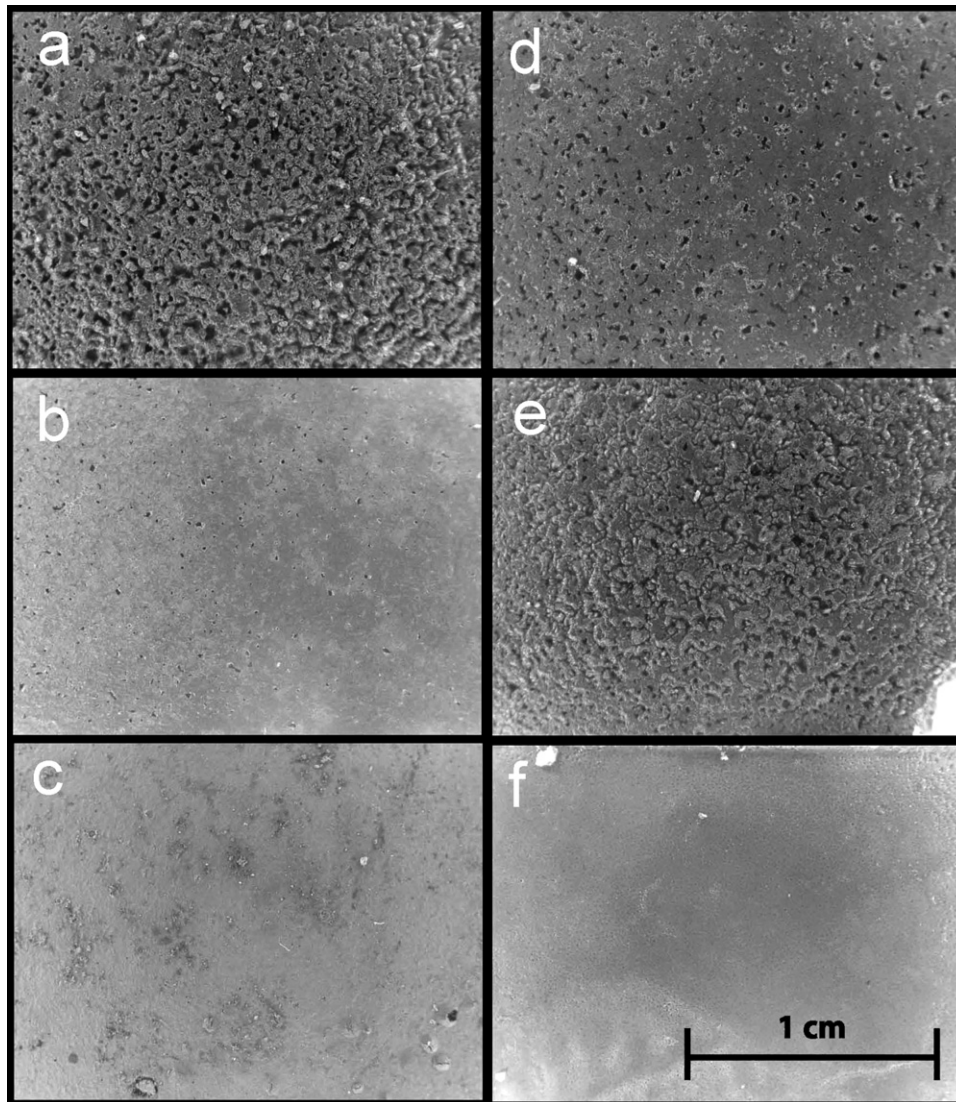| Binder System	W/wax specimen		W/Al₂O₃ laminate	
	Dissolution (%)	Absorption (%)	Surface quality	W layer thickness (μm)
Starch	0.1	0.9	Poor	300
PVA	12.9	1.1	Acceptable	280
Cross-linked PVA	1.8	0.7	Poor	250
Latex I	0	0.2	Excellent	30
Latex II	0.2	0.2	Excellent	130

Fig. 2. Optical micrographs showing the morphology of the W surfaces prepared by slurries that contained: (a) starch, (b) Latex I (LATRIX), (c) Latex II (UCAR), (d) PVA, and (e and f) PVA + cross-linker, as a binder. Specimens (a–e) contained zirconia sand between the W and Al_2O_3 layers, excepts for that shown in (f) which did not have stucco applied.

layer exhibited a relatively high degree of surface roughness and small pores, comparable in size to the zirconia stucco sand, were visible throughout the surface. On the other hand, a high quality surface finish was observed for the samples prepared using Latex I and Latex II, as shown in Fig. 2b and c, respectively. Particularly, specimens of these two sets had uniform W coating layers and minimal porosity on the W surfaces. For the case of PVA, the W surface appeared to be uniform, however it contained a large amount of porosity as depicted in Fig. 2d. Interestingly, with the addition of the cross-linking agent to PVA, the quality of the resulting W layer deteriorated (Fig. 2e), exhibiting very rough surface morphology and containing small pores throughout the surface in a manner similar to what was observed with starch.

Fig. 3a–e shows cross-sectional micrographs of laminate specimens from the various sets. It is observed that the specimens prepared with either Latex I or Latex II exhibit a uniform thickness of W coating layers. The thickness of the W layer for

each of the specimens was measured and is reported in Table 2. A wide range of W coating layer thicknesses, from approximately $30\,\mu m$ (Latex I) to $300\,\mu m$ (starch), were obtained. Most importantly, the thickness of a coating layer is considered a critical parameter because it affects the physical and mechanical properties of multi-layered laminate structures. Thickness of the W coating layer is also directly proportional to production costs. Therefore, knowledge of the relationship between processing variables and resulting thickness is crucial in actual applications.

4. Discussion

Based upon a variety of quantitative and qualitative properties, water-soluble latexes (i.e., Latex I and Latex II) exhibited superior performance, resulting in W layers that were strongly water resistant and had exceptional surface finish. The Latex II suspension, in particular, was also stable. This characteristic can be attributed to the use of a controlled amount of disper-
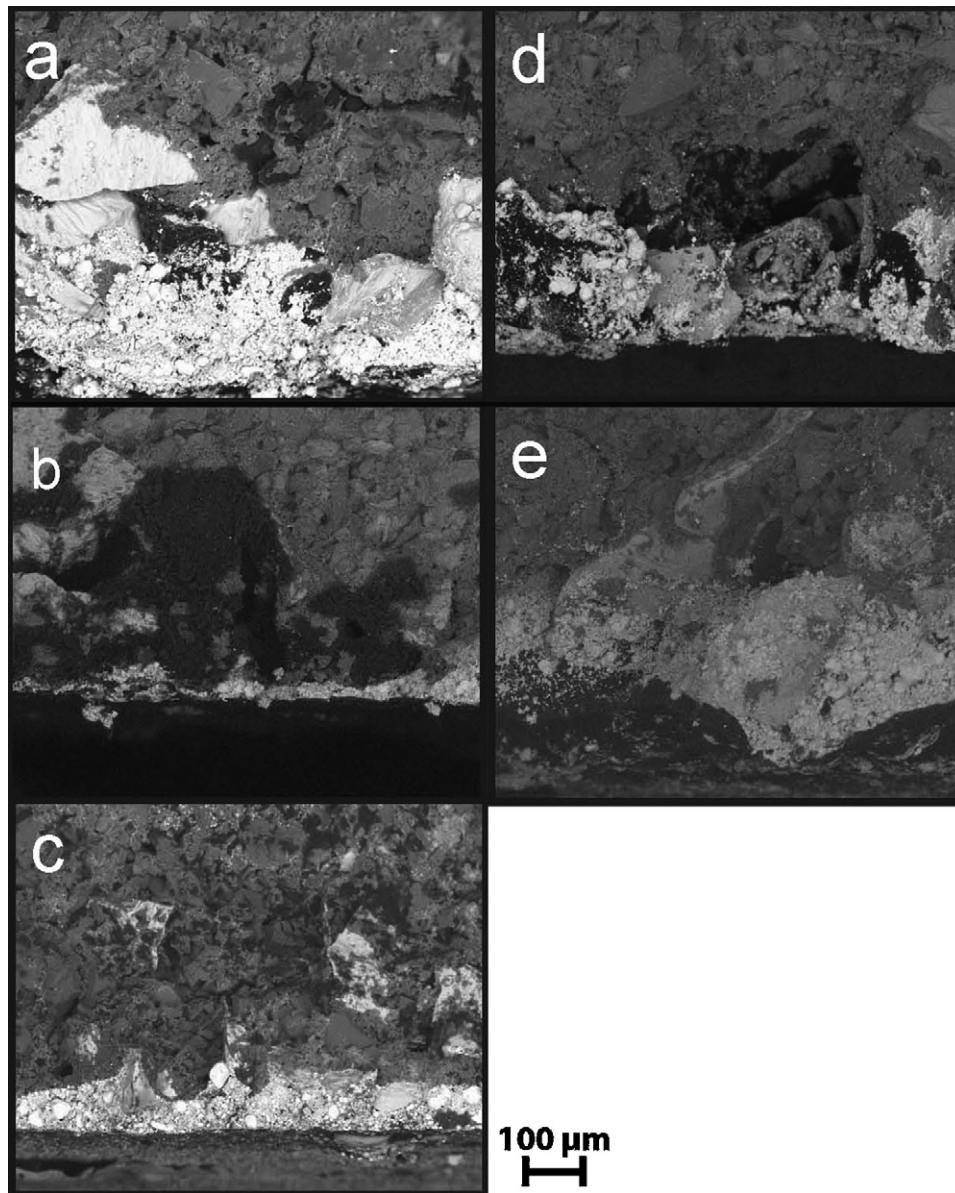
Fig. 3. Cross-sectional SEM micrographs showing the specimens prepared by slurries that contained: (a) starch, (b) Latex I (LATRIX), (c) Latex II (UCAR), (d) PVA, and (e) PVA + cross-linker, as a binder. All specimens (a–e) contained zirconia sand between the W (bottom) and Al_2O_3 (top) layers.

sant, which affects the density of surface charges, altering the electrostatic forces of repulsion between W particles. Because of the relatively high packing fractions, when W particles were added to the two latex binder systems, low viscosity and high slurry density were achieved in the suspensions. Correspondingly, these qualities gave rise to relatively thin and uniform W layers [35] as is evident in Fig. 3b and c and Table 2.

Using the values of packing fraction and W layer thickness presented in Tables 1 and 2, it can be estimated that the weight per unit area of the W layer prepared with Latex I is approximately four times smaller than that of the W layer prepared with Latex II. Latex I is therefore more attractive from the economics standpoint, as a lesser amount of powder material is required to produce a layer of coating. However, Latex II could be more desirable for applications that require a thick coating, such as reaction barriers and thermal barriers [36]. Additionally, com-

pared to a case of very thin coating, a thicker coating could provide relatively low level of deformation and residual stress in as-fired products [37].

With a flat and relatively uniform W coating layer that contained pores throughout the surface, the laminates prepared with the PVA system appeared to have an intermediate quality. Owing to PVA's poor resistance to water absorption and dissolution (Table 2), it is most likely that the formation of defects observed on the W surface was a result of thinning the PVA W layer through dissolution during the autoclave operation. The addition of a controlled amount of a cross-linking additive had resulted in the improvements of suspension stability and, most importantly, resistance to dissolving in water. Yet, when the modified PVA was employed, a poor surface finish was obtained.

Compared to the cross-linked PVA, the starch binder exhibited several comparable properties, including moderately high

water absorption but with minimal dissolution in water. Most likely due to steric effects, cross-linked PVA and starch provided reasonably stable W suspensions. W surfaces with rough and sponge-liked morphology were also obtained in the laminates of both binder systems (cf. Fig. 2a and e). The formation of such defects in the W layers could be due to water absorption in the binders, causing swelling to occur. The expanding W films may swell into the recesses between the grains of stucco sand located along the W/Al_2O_3 interface and/or adversely interact with the sand, resulting in the irregularity of the W surfaces.

To assess the influence of stucco particles on the W layer quality for films with relatively high degree of water absorbance, an additional set of specimens were fabricated following the same procedure employed for the production of W/Al_2O_3 laminates with the cross-linked PVA system. However, zirconia stucco sand was not applied along the W/Al_2O_3 interface. The resulting W layer surface quality of a specimen from this set is shown in Fig. 2f. In comparison to the counterpart specimen that contained sand (Fig. 2e), the removal of the sand produced very smooth and uniform surfaces. In fact, without a trace of micropores on the surface, the surface quality of these specimens even surpassed that obtained from latex binder samples. The results obtained from this observation therefore indicate that sand along the interface of coating layers can detrimentally affect coating quality of materials in pre-fired stage. For coating layers prepared with cross-linked PVA, which exhibited a high degree of water uptake, it appears that the presence of stucco sand facilitates the process of film spallation induced by moisture absorption of the coating layers during the de-waxing process.

5. Conclusions

The use of different binder systems, namely thermoplastic starch, styrene–butadiene latex, acrylic latex, PVA, and cross-linked PVA, in the production of W/Al_2O_3 laminates provided powder slurries and green materials with very distinct properties. Most notably, viscosity of the powder suspension at a specific solid loading content, disintegration of the coating layers in the presence of water or steam environments, and uniformity and thickness of a coating layer provide a means to evaluate the performance of each binder. Binder systems that incorporated latex particles produced W/Al_2O_3 laminar specimens with exceptional coating quality. On the other hand, while the thermoplastic starch system is the most environmentally benign, the poor surface quality of the post-autoclave W layer must be further explored before this clean alternative can be utilized. In light of its rapid dissolution property in the presence of water, PVA by itself is a poor candidate for use as a binder in processing that involves multiple coatings or that is performed in a steam environment. Once combined with a cross-linking agent, PVA became insoluble in water, but still absorbed water and resulted in a final film quality similar to starch. For coating layers that exhibit a high degree of water uptake, poor surface quality of the final laminate was found to relate to the presence of stucco sand. With the absence of aggregate, the use of cross-linked PVA as a binder becomes more viable. However, the use of stucco sand might be required in some applications. For instance, the

ability for multi-layer composites in the post-fired condition to effectively withstand residual and external stresses that arise in service can be greatly enhanced by aggregates. As a result, it is important that the application of sand aggregate be carefully controlled and properly adjusted when different types of binders are used.

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