

Electrode Powder Dispersion Evaluation

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Abstract

Physical test properties of electrode powders do not alone dictate performance characteristics of electrode pastes and final electrical properties in MLC devices. Frequently, the nature of organic-organic (solvents-resin-surfactants) and organic-inorganic (electrode powder and dielectric material) reactions is largely ignored in conductive paste applications. These competing reactions contribute to electrode powder agglomeration, electrode laydown and roughness, as well as paste stability and printability. In addition to standard fineness of grind (FOG) and low angle light (LAL) tests on electrode pastes, this paper examines optical polarized light microscopy performed to evaluate dispersion characteristics of electrode powders in the 'wet' state, during drying, and dried films. Paste stability is compared for different paste formulations and powder varieties using time dependent turbidity measurements on real systems.

Introduction

Modern multilayer ceramic (MLC) passive electronic components are composites of dissimilar materials, typically comprised of a conducting material, such as silver, silver-palladium alloys, nickel, or copper, and an insulating substance, commonly a metal oxide or glass. MLC device assembly is generally accomplished by printing the electrode layer on green ceramic tape and then hydrostatically pressing the layers together into a green stack.

Aside from standard industry testing procedures, such as particle size distribution, tap density, specific surface area, purity, etc., there is not a method to predict dispersion character from these physical properties. Measured properties, such as surface area and tap density, can be used as guiding parameters, but again, do not dictate how well a powder material will disperse into a given organic system.

Typically, electrode powders are evaluated by paste and part manufacturers by characterizing how well a powder (or series of powders) disperse into the manufacturer's organic vehicle system. These evaluations generally include how well the electrode powder 'wets' (qualitatively) with a solvent of the vehicle system, fineness of grind (FOG) tests, rheology tests, and printed film roughness of the electrode powder and vehicle. An electrode powder is considered 'good' when it easily wets and apparently disperses into the vehicle system, shows low or no scratches by FOG with low main break, exhibits desired viscosity properties (not too thin and not too viscous), and produces a smooth, continuous printed film.

Sophisticated analytical techniques are available to characterize surface properties of electrode powders [1], but without further extensive studies, relating these results to how well an electrode powder will disperse and perform in a given organic system can be inconclusive and elusive. A useful tool to decipher some aspects of inorganic – organic compatibilities (dispersion) is optical microscopy. Three specific optical microscopy techniques are bright field, dark field, and polarized light.

Bright Field, Dark Field, and Polarized Light Microscopy

With conductive paste dispersions, the use of microscopy is typically performed on a printed film specimen. Bright field (BF) microscopy is the most direct, common method of observing specimen. However, BF microscopy generally reveals only information about surface morphology. Combined with Dark Field (DF) microscopy, BF becomes much more useful. The combination of BF and DF can easily resolve such printed film features such as film continuity, film opacity, and homogeneity. In fact, low-angle light (LAL) imagery can be considered a form of DF microscopy since illumination of the specimen surface is performed from an oblique perspective. Figure 1 show the BF, DF, and corresponding LAL image of a dried Ni paste. Figure 1a shows there are rough defects present on the dried film, however, what is not obvious in the BF image is the region indicated by the white arrow. Under DF (Figure 1b), the indicated region in Figure 1a is clearly seen as a discontinuity surrounding an agglomerate. Figure 1c shows an LAL image of the same film at a typical magnification. The LAL image does not show the detail of either BF or DF images of Figure 1. For example, the finer structure of the film discontinuity is clearly seen in the DF image (Figure 1b) and is not readily apparent in the LAL (or high magnification BF).

Direct observation does not necessarily provide definitive information as to organic phase structure, however, observed texture in polarized light is sufficient for this purpose. Although much neglected and undervalued as an investigative tool, polarized light microscopy provides all the benefits of brightfield microscopy and offers additional information, which is not available with any other microscopy techniques. Polarized light microscopy can distinguish between isotropic and anisotropic materials as well as providing information on absorption color and boundaries between materials of differing refractive indices.

Isotropic materials, which include gases, liquids, unstressed glasses and cubic crystals, have the same optical properties in all directions. They have only one refractive index and no restriction on the vibration direction of light passing through them. In contrast, anisotropic materials, which include 90 percent of all solid substances, have optical properties that vary with the orientation of incident light with the crystallographic axes. Anisotropic materials demonstrate a range of refractive indices depending both on the propagation direction of light through the substance and on the vibrational plane coordinates. Further, anisotropic materials act as beam splitters and divide light rays into two.

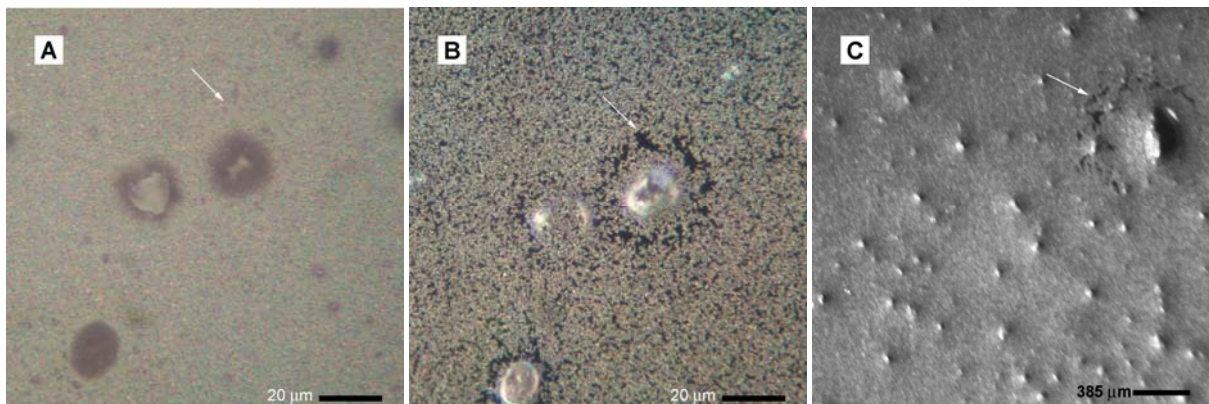


Figure 1. Optical microscopy images of a conductive nickel paste using (A) bright field (BF) microscopy, (B) dark field (DF) microscopy, and (C) low-angle light (LAL). A and B are at higher magnification than the LAL image of C. Each image is captured at 2 micron printed film thickness on glass substrate.

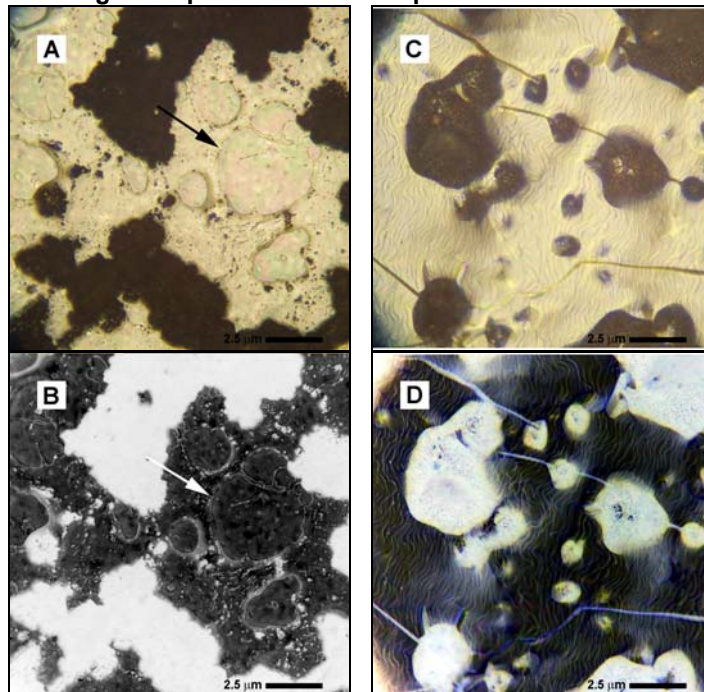


Figure 2. Large lamellar drops in BF (A) and polarized light (B). Striated nematic lamellar in BF (C) and polarized light (D).

Polarizing microscopy can be used both with reflected and transmitted light. Reflected light is useful for the study of opaque materials such as mineral oxides and metals. What becomes apparent using polarized light microscopy are un-desirable organic phases that can arise as a consequence of organic reactions (described below). For example, Figure 2 shows two destabilized organic morphologies of a lamellar nature that originated from printed nickel pastes. Polarized light easily identifies the different optical anisotropies that can arise in organic systems. Well defined anisotropy patterns are used to identify what organic phase or structure the anisotropy is identified with (lamellar, liquid crystal, nematic texture, etc) [2]. In an ideal conductive electrode paste, the organic phase is continuous (optically isotropic, showing no separate phase regions). However, instabilities can arise in the organic phase as a consequence of kinetic components (such as mechanical agitation, printing, drying and binder burn-out, or temperature change) and thermodynamic stability. If the solid components of the dispersion (metal electrode powder, dielectric powder, etc) are not properly charged balanced, kinetic competition can arise which may also destabilize the continuous phase of the organic vehicle system. On the other hand, if the organic phase destabilizes, organic phase separation can occur as well as other dispersion phenomenon, such as flocculation, sedimentation, and creaming. Polarizing microscopy is an effective tool to examine these phenomena.

Organic Reactions

Formulation of electrode pastes comprising solvents, resin, metal powder, and dielectric media are not necessarily straightforward. Design of the electrode pastes considers the solids content, the solids content dispersion stability and quality, rheological properties and printability, shelf life, and thermal characteristics during burn-out. For dispersion purposes, frequently at least one surfactant or dispersant is used to improve the solids suspension. With low-laydown and high layer count parts, the solids content of an electrode paste contains the metal electrode powder and a dielectric material, generally similar to the main body dielectric, to aid controlling shrinkage characteristics during the firing of MLC devices. Competing surfactant reactions can occur between metal powders and dielectric powders during dispersion into the vehicle base. Low adsorption energies of surfactants on metal powder, for example, may favor a stronger adsorption with the dielectric material added to the paste. Surfactants for the dielectric and the metal may compete and result in dispersion failure with settling, agglomeration, and creaming in the paste. Control of the organic reactions requires knowledge of the surface chemistries of the electrode powder, dielectric material, and the relative solubilities of each organic component with each other.

The solvent has a profound effect on the adsorption of surfactant molecules or polymers on surfaces [3-5]. The solvent quality influences the surfactant adsorption in two ways. The first is by changes in conformation of the surfactant. An organic surfactant molecule or polymer expands in good solvents and contracts in poor ones. A surfactant molecule or polymer situated at a particulate surface in suspension can occupy a larger surface area in good solvent and a smaller surface area in a poor solvent. As a consequence, a larger adsorption is found from poor solvents. The second influence a solvent has on adsorption of a surfactant is the stability of the 'solution'. A very soluble surfactant molecule or polymer has a tendency to remain in the bulk solvent phase, whereas a less soluble species will seek any opportunity to 'escape' the solvent such as by adsorbing on a surface.

The choice of solvent can also have a profound effect on wetting the electrode powder and dielectric material of the paste. Turbidity assessments of electrode powders in solvents and measurements in paste systems give information about electrode materials dispersion performance. Figure 3 shows the results of a suspension stability test using nickel electrode powder with various solvents and in a commercial base metal vehicle system. Large changes in the transmittance or backscatter are indications of sedimentation and flocculation phenomenon in the case of the solvent tests. It can be seen that the choice of Solvent 3 or the combination of Solvent 2 + 3 offers good dispersion characteristics for this nickel powder in terms of suspension stability. The dispersion characteristics show good behavior after some relaxation during the first hour of storage.

Reversibility of surfactant molecules or polymers from the surface of suspended solids depends on the surface chemistry of the particles, the functional groups of the dispersant, the temperature, and the solvent system [6,7]. Further, the degree of shear applied to the paste during milling or agitation impacts how well dispersants are adhered to particulate surfaces. The surface chemistry of a particle in suspension generally has two components, chemical and physical, and these are typically inter-related. Chemical surface properties include contaminants from manufacturing (transition elements, carbon, salts etc.), oxidation, atmospheric moisture, and designed surface engineering (such as organic or inorganic coatings). Organic functional groups of surface active agents can interact with metal particles by charge association, dipole association, or chemical reactivity.

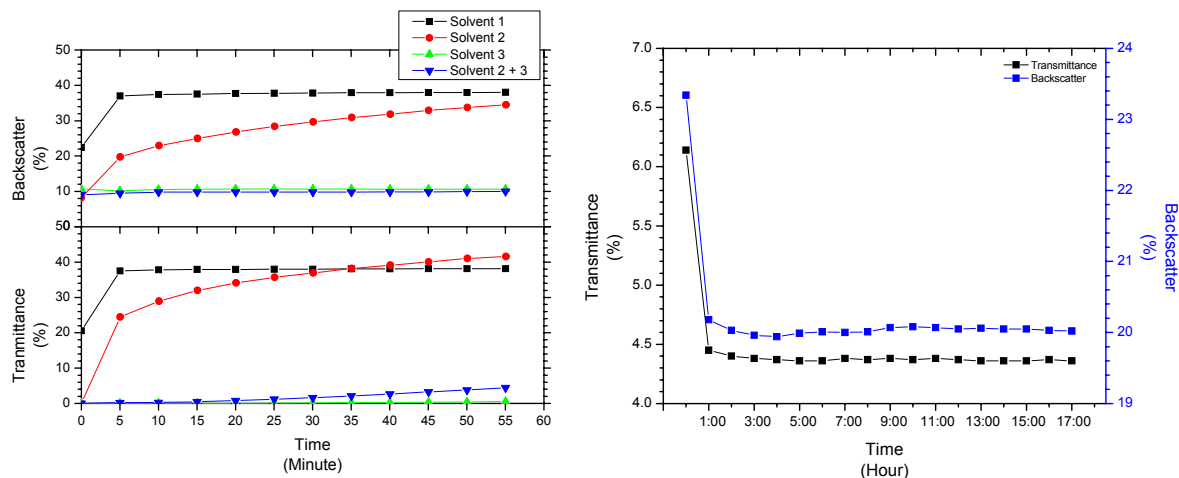


Figure 3. Suspension characterization by turbidity monitoring of nickel electrode powder in various solvents (left) and in a paste formulation (right).

In paste manufacturing the choice of surfactant is typically a non-ionic variety in order to avoid introducing counter-ion contaminants (impact on electrical properties).

Organic reactions also have an impact on printed electrode roughness. Electrostatically balanced paste systems containing high quality electrode and dielectric powders typically will produce smooth and continuous printed films. Paste systems containing low-compatible organic components and molecules that do not interface well with other organic and inorganic components frequently produce film discontinuities and inhomogeneous electrode powder distribution in the printed film resulting in rough textures.

Experimental Section

Electrode pastes were made with either AgPd alloy powders or Ni powders and ethylcellulose vehicle (36% aliphatic solvent, 35% terpineol, 20% hexanol, 4.5% Herculyn D, and 4.5% EC N200). The electrode powder comprised 50 wt.% of the total paste basis. The electrode powder was wetted with 5 wt.% hexanol and thoroughly mixed prior to adding the vehicle base. The final paste composition was 50 wt.% electrode powder, ~45 wt.% solvents, ~2 wt.% tacifier, and ~3 wt.% resin. For these tests, to more clearly show the results, a simple system was used that did not contain ceramic or glass modifiers.

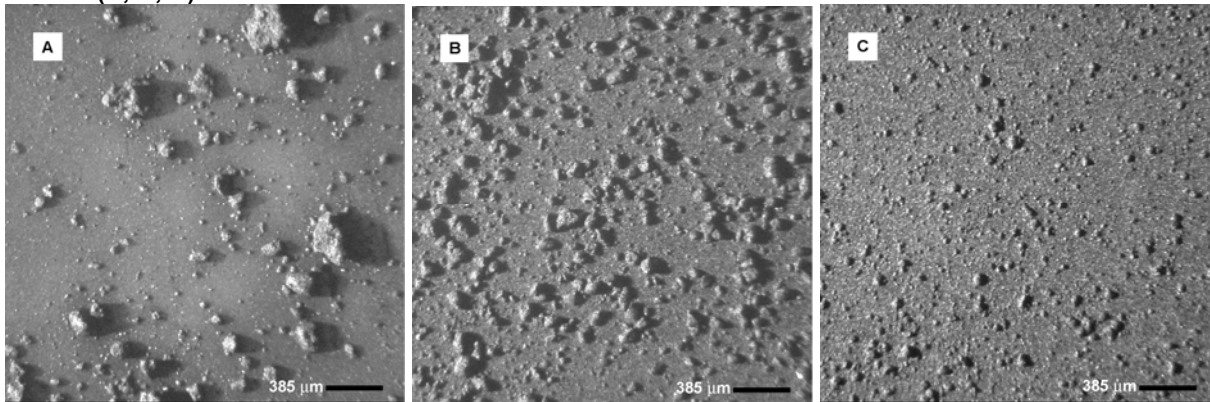
Three roll milling was performed by setting an initial gap space of 38 μm . The mixture is vigorously agitated briefly before immediate application to three roll milling. A sample is collected after the first pass low-angle light (LAL), finess of grind (FOG), and viscosity measurements. The paste is continually milled for five passes decreasing the mill gap with each pass by ~5 to 10 μm . Another sample is collected at the end of the fifth pass and again examined for LAL, FOG, and viscosity. The fifth pass paste is aged 24 hours and for 7 days. The paste is vigorously mixed for 15 minutes and re-tested for viscosity, LAL, and FOG.

Optical polarized images of the drying and dried film of the FOG gauge were taken at the 7 μm and 2 μm marks for the AgPd systems and at 7 μm , 2 μm , and 1 μm for the Ni electrode pastes using a light reflection microscope equipped with polarizing filters.

Results and Discussion

Current industrial manufacturing of MLC devices largely employs either nickel (majority of ceramic capacitor manufacturing) or silver-palladium powders as the electrode material in passive components and LTCC's. Figure 4 compares the LAL images of AgPd electrode pastes from two different AgPd powder vendors in the same vehicle system. Of these results, Vendor 2 (D→F) shows better performance and acceptable characteristics based on the LAL images. However, additional optical microscopy investigation shows the pastes of Vendor 2 to possess some underlying problems. Figure 5 shows the optical microscope images of the paste of Vendor 2 in bright field and polarized dark field. In these results is seen the non-uniform distribution of electrode paste after the paste has been printed. Clearly seen are regions of organic-rich phases and electrode powder rich regions. At higher magnification,

Vendor 1 (A, B, C)



Vendor 2 (D, E, F)

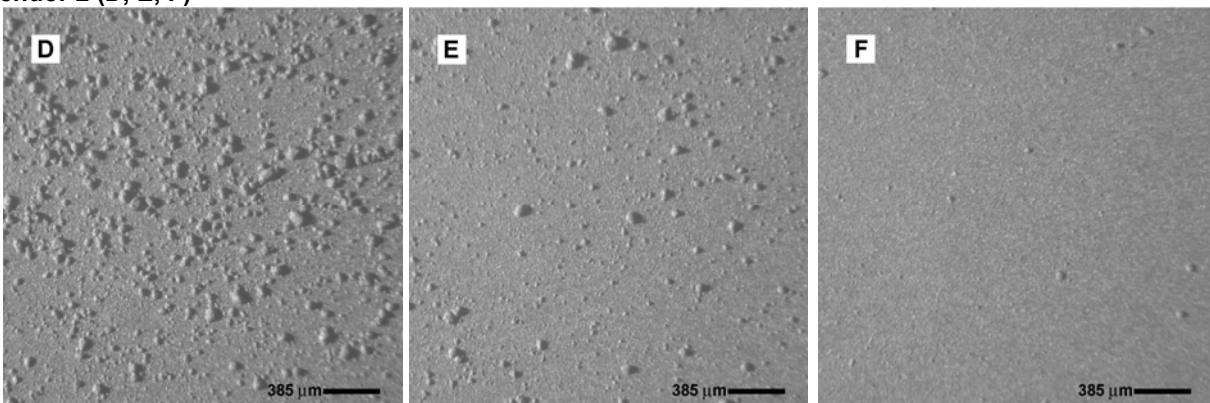


Figure 4. Low angle light (LAL) images of two varieties (A→C and D→F) of 90%Ag / 10%Pd electrode paste before three roll milling (A,D), after pass 1 (B,E), and after pass 5 (C,F).

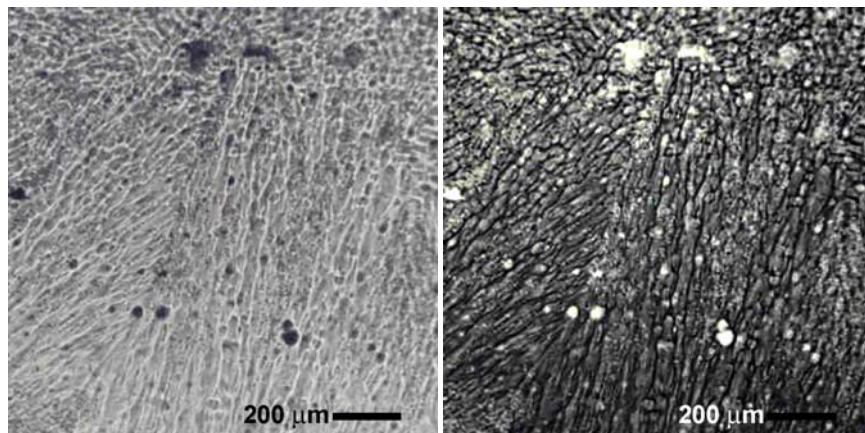


Figure 5. Optical microscopy images of dried AgPd (90%Ag/10%Pd) electrode paste in bright field (left) and polarized dark field (right).

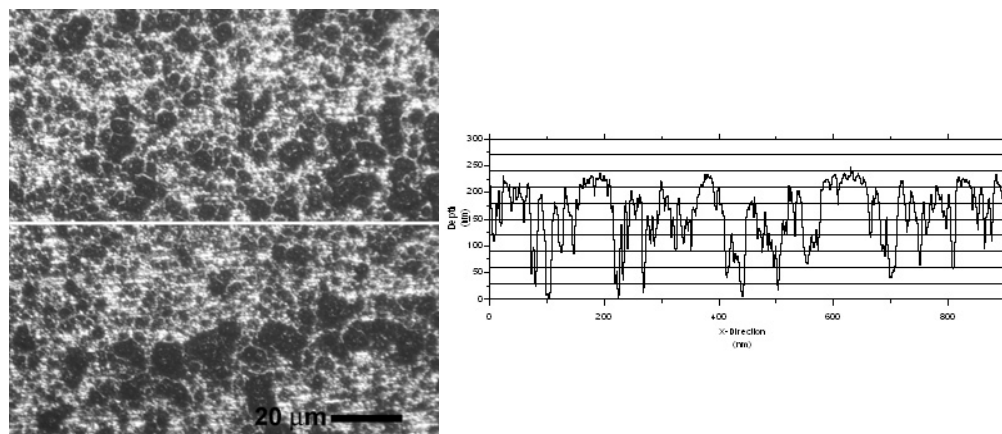


Figure 6. High magnification optical microscope image of AgPd (90%Ag10%Pd) electrode paste in polarized bright field illumination along with theoretical depth profile of the dried film along the line in the x-direction for a printed film thickness of 2 micron.

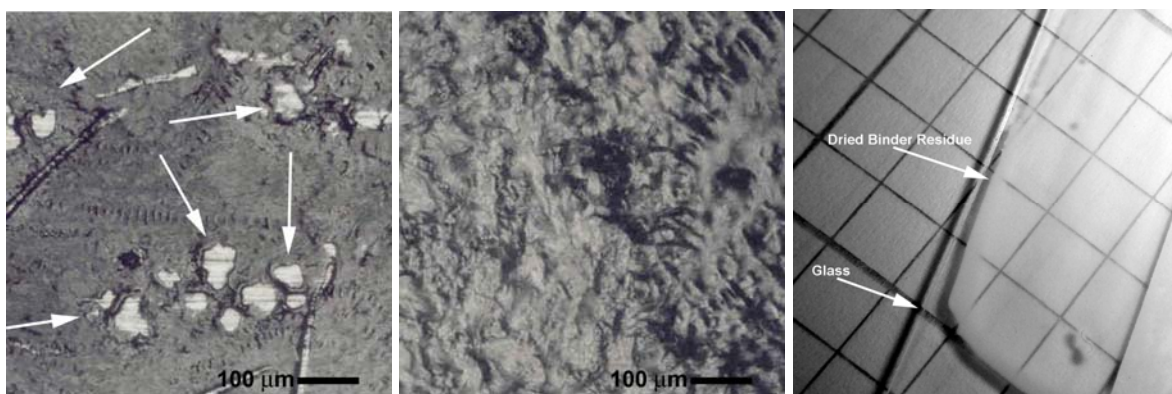


Figure 7. Polarized light microscopy images of printed Ni electrode paste showing poor adhesion (left), rough surface morphology (center), and residue from dried vehicle on glass.

additional morphological relief is observed as shown in Figure 6. This printed micro-morphology can result in high surface roughness and electrode discontinuity when fired. Poor dispersibility in this AgPd electrode paste system gives rise to unevenly dispersed AgPd powder and unacceptable surface roughness of the printed film.

Further defect structures of printed electrode films arise from competing phenomena, namely polymer domain formation and particle agglomeration, as shown in Figure 7. Paste systems containing poorly soluble resins can quickly react when drying is initiated after being printed. Loss of low-boiling point solvents, in which many resins have appreciable solubility, can force the polymer chains out of the continuous organic phase to form resin-rich regions in the printed film. During film drying, the polymer domain region forms an isolated 'island' that is carbon rich and creates large, localized voids during burn-out. This phenomenon may result in 'lacy' electrodes, delaminations, and induce crack stresses.

Conclusion

Several aspects of electrode powder dispersion can be determined before manufacturing an MLC device. Standard characterization techniques, such as rheology, LAL, and FOG may not adequately reveal the dispersion performance characteristics of electrode materials and pastes. Polarized light microscopy has been shown to provide much greater detail of printed and dried films than is available in the standard optical inspection techniques used to classify and compare electrode pastes. Polarized light microscopy has been used to identify and show precipitation of resin polymers, metal powder agglomeration, and formation of two-phase regions of organic components of electrode pastes. These phenomena can be addressed prior to testing electrode paste in device applications. Organic phases that form as the electrode paste is printed or during drying tend to produce rough films and discontinuous electrodes. Organic phases can arise as a consequence of resin polymer solubility, competing or incompatible surfactants, and solvent drying.

Revealing some of the various adverse reactions that can occur during paste development and testing by polarized light microscopy can yield significant information for very little effort. It is a low cost, simple inspection technique in resolving paste formulations, paste processing difficulties, and electrode paste materials dispersion characterization. It is our observation that some of the difficulties in forming smooth, thin, continuous electrodes start as problems that arise in the paste system itself causing the dispersion to destabilize or fail during processing, and can result in gaps in the electrode.

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