INFLUENCE OF RHEOLOGY ON DEPOSITION BEHAVIOR OF CERAMIC PASTES IN DIRECT FABRICATION SYSTEMS

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ABSTRACT

Rheology and deposition behavior of four commercially available thick-film inks and an aqueous alumina slurry were investigated using two different slurry-based deposition systems. The first of these deposition systems, a Micropen, is a commercially available system designed for the deposition of electronic thick film circuits. The second system, referred to as a Robocaster, is a developmental system designed to build thick or structural parts. Slurry rheology was seen to have a minor effect on deposition behavior and the bead shape when deposited using the Micropen. The deposition behavior was instead dominated by drying rate; too rapid of a drying rate led to excessive clogging of the tip. Slurry rheology had a greater impact on the shape of beads deposited using the Robocaster. Highly viscous slurries yielded initially well-defined beads, whereas beads deposited using fluid slurries spread quickly. In both cases, significant spreading occurred with time. These observations only held for slurries with slow drying rates. It was observed that very fluid slurries produced well-defined beads when the drying rate was suitably high.

INTRODUCTION

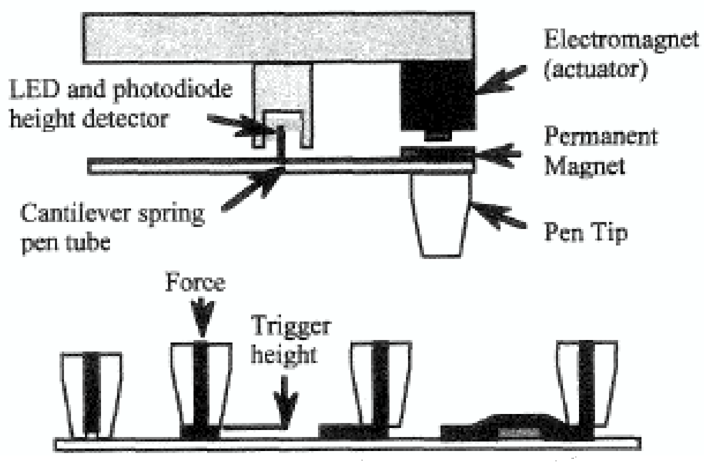
Slurry-based direct fabrication systems offer a number of advantages over conventional fabrication techniques and have capabilities not found on other direct fabrication systems. The material systems are relatively simple and a wide range of materials can be used, including pastes of metals, polymers or ceramics. Additionally, there are a number of commercially available pastes available from the screen-printing industry. Unique capabilities include multi-materials/graded parts, incorporation of tailored porosity via fugitive materials and rapid turnaround of finished pieces. It is also possible to fabricate multilayer thick film circuits directly on a substrate, a difficult task using conventional screen printing techniques.

We are working with two slurry-based deposition systems at Sandia. The first is a commercially available system called Micropen.* The second is a system under development at Sandia called Robocasting. The Micropen is designed for use in the electronics industry for the deposition of thick film circuits and typically uses commercially available thick film inks.[1] The design focus of the Robocaster is for thick or structural parts and typically uses aqueous slurries.[2]

A schematic of the Micropen system is shown in Figure 1, along with a circuit printed onto a curved surface. The system consists of a cantilevered tube to the end of which a pen tip and permanent magnet are attached. An electromagnetic actuator positioned above the permanent magnet controls the height of the pen tip by varying the strength of the magnetic field. A height detector consisting of a flag attached to the tube, an LED and photodiode provides

* Ohmcraft, Inc. Honeoye Falls, NY 14472

height feedback to the processor controlling the electromagnetic actuator. This system employs a stationary Z-axis; a pattern is written by pumping the slurry through the tube and moving an X-Y table beneath the tip. A circuit is deposited as follows; the pen tip is brought into contact with the substrate and ink is pumped through the pen tube into the pen tip. As ink begins to build up under the pen tip, the pen tip rises until it reaches a predetermined trigger height. At this point, the X-Y table begins to move and the pattern is deposited. A small downward force is applied during writing via the electromagnetic actuator. This helps to ensure that a uniform line of material is deposited. An advantage of this type of system is that in addition to the feedback provided by the height sensor, there is a force feedback provided by the electromagnetic actuator. Thus, the system can vary the pen height based on the force feedback to account for topography on the substrate. This enables a uniformly thick circuit to be deposited onto a curved surface or over existing features on a flat substrate. The Micropen typically uses pen tips in the size range of 25-250 μm. A typical slurry composition is 25-30vol% solids, 40-50vol% resin and 25-30vol% solvent.



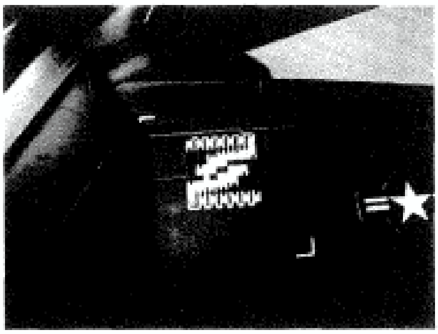


Figure 1: Schematic of the Micropen system and a circuit printed on a curved surface.

In contrast, the Robocaster, shown in Figure 2, is a more straightforward design. The slurry is extruded from a syringe mounted on a Z-axis above a moving X-Y table. Once a layer is completed, the Z-axis is incremented by a predetermined layer height and the next layer is deposited. Currently, this system provides no feedback about the actual distance between the build surface and the pen tip. However, a laser height system is under development at Sandia that will provide this information. This system should allow for feedback to the pumping system to account for imperfections in the build of previous layers. The Robocaster typically uses pen tips in the size range of 250-1500 μm. A typical slurry composition is very highly loaded with 58-61vol% solids, 40vol% water and a very small amount of processing aids such as Darvan and citric acid. Typical parts are also shown in Figure 2.

Both systems rely on good bead definition to build accurate parts. The electrical properties of electronic components deposited with the Micropen often depend on the accuracy of the line width which is in turn influenced by the degree of bead spreading after the line has been printed. Minimum feature sizes and the minimum spacing between components are also influenced by bead spreading. These aspects are important for both systems. Electronic components that are too close together may be subject to shorting or electromigration. The dimensional accuracy of 3-D parts fabricated with the Robocaster is highly dependent on bead spreading. Additionally, significant bead spreading of one layer leads to problems during the deposition of subsequent layers, resulting in gross defects within the finished piece. The rheology of the slurries used in these systems was investigated to gain an understanding of its influence on bead shape. This information will drive both system development and materials processing as new slurries are developed for each system.

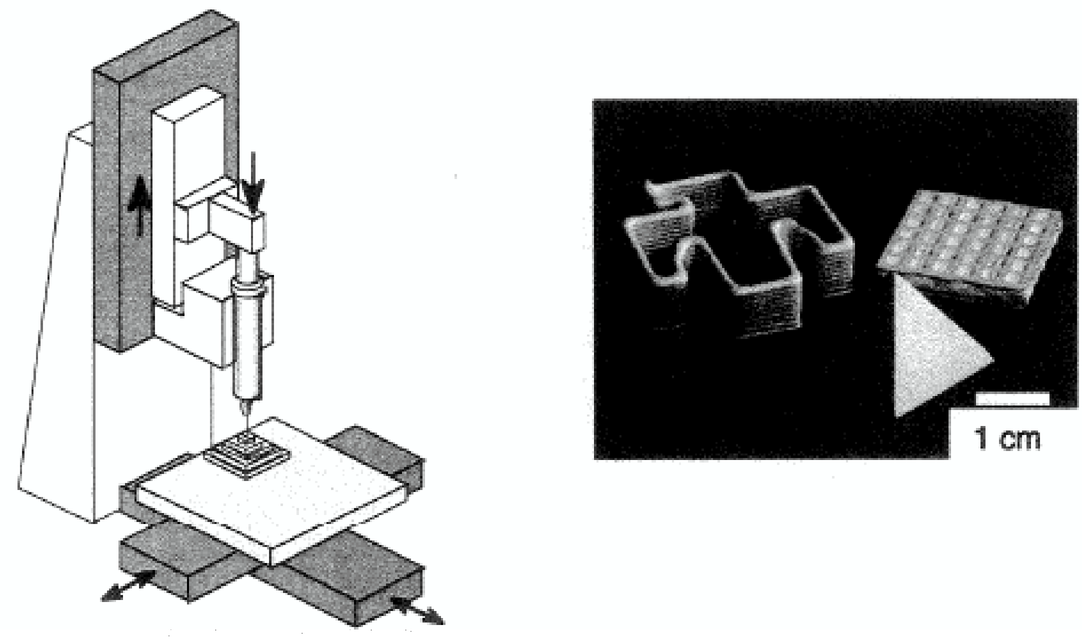


Figure 2: Schematic of the Robocaster and examples of complex shapes fabricated with it.

EXPERIMENTAL

A number of slurries were investigated, four commercial thick film pastes and an aqueous alumina slurry prepared at Sandia. Two of the commercial inks were DuPont[*] post-fire inks; 5715, a gold conductor paste, and 1731, a ruthenium oxide-based resistor paste. Both of these pastes are designed to be printed on dense alumina substrates and fired at high temperatures (> 1200°C). The other two commercial pastes were polymer thick film (PTF) pastes, Minico[†] M-4100 silver conductor paste and Asahi[‡] TU-1k carbon resistor paste. Both of these pastes consist of solids (either silver or carbon) loaded in an epoxy carrier and are designed to be printed on FR4 epoxy board. The epoxy carrier is cured at low temperature (≈ 200°C). The aqueous alumina slurry was prepared at Sandia by ball milling 60vol% Alcoa A-15 alumina for 2 weeks in deionized water with Darvan 821A dispersant and citric acid.

[*] DuPont Electronic Materials, Research Triangle Park, NC 27709
[†] Emerson and Cuming, Lexington, MA 02173
[‡] Multicore Solders, Inc., Richardson, TX 75081

The rheology of the five pastes was characterized using a controlled stress rheometer*. The commercial pastes were characterized with a 1° cone and plate geometry, while the aqueous alumina slurry was characterized using a cup and bob geometry. All rheology data was plotted as viscosity (cP) vs. shear rate (1/s) on a semi-log plot.

In addition to rheology, the slumping behavior of beads printed from each paste was investigated when deposited from each of the two systems. In all cases, a single bead of material was deposited onto the substrate and the shape of the bead was characterized via laser profilometry.† The post-fire inks were deposited onto alumina substrates, while the PTF inks were deposited onto FR-4 epoxy board. The aqueous alumina slurry was deposited onto dense alumina substrates. Pastes deposited with the Micropen were deposited using a 250 μm (10 mil) tip and bead profiles were obtained at times ranging from 1 minute to 1 hour after printing. Pastes deposited with the Robocaster were deposited with an 890 μm (35 mil) tip. In this case, the profilometer was mounted on the equipment and profiles were obtained within ≈ 10 seconds of printing. Profiling of each bead was performed for up to 30 minutes after printing. To investigate the effect that the substrate has on the profile, these experiments were repeated for the silver PTF paste deposited on a dense alumina substrate. From these profiles, the bead width and area as a function of time after printing were obtained.

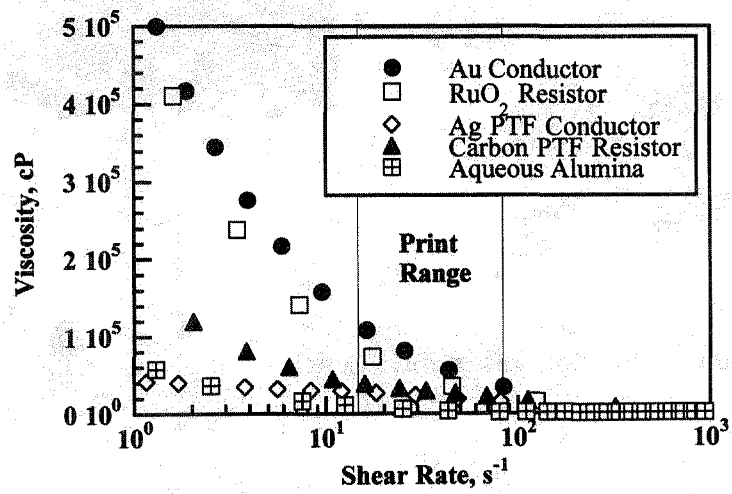


Figure 3: Viscosity as a function of shear rate for commercial screen printing inks and aqueous alumina slurry.

RESULTS

Viscosity as a function of shear rate for each of the pastes is shown in Figure 3. Included on the plot is the calculated range of shear rates experienced during printing.[3] Of the slurries investigated, the post-firing inks were by far the most viscous. At low shear rates, the PTF inks were significantly lower. The carbon resistor ink was the more viscous of the two, but they converged in the print range. At low shear rates, the aqueous alumina slurry exhibited a higher

* Bohlin CS-10, Bohlin Instruments, Cranbury, NJ 08572
† CyberScan Cobra, CyberOptics, Minneapolis, MN 55416

viscosity than the silver PTF conductor, but at high shear rates its viscosity was the lowest of the five pastes. All pastes were observed to converge to the same viscosity at very high shear rates, however this is above the print range.

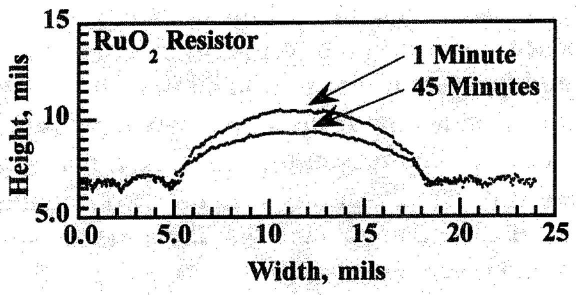


Figure 4: Profile of a resistor paste bead printed with the Micropen at times of 1 minute and 45 minutes after printing.

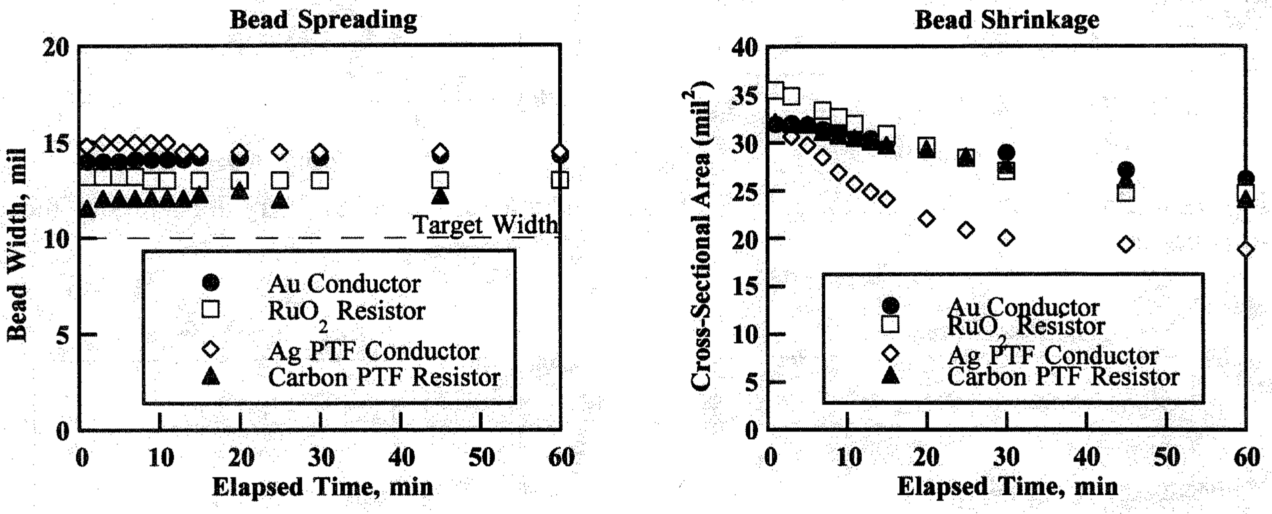


Figure 5: Spreading and Shrinkage as a function of time after printing of thick film inks printed with the Micropen.

Profiles similar to the profile shown for the ruthenium oxide resistor paste in Figure 4 were obtained for all of the pastes printed in the Micropen, with the exception of the alumina slurry. This slurry proved to be impossible to deposit with the Micropen due to excessive drying. Figure 5 plots width and cross-sectional area as a function of time after printing. Of the remaining four slurries, minimal spreading was observed after the first minute after printing. However, a significant change in the cross-sectional area of each bead was noted over the course of an hour. This change in area may be attributed to drying shrinkage.

Figure 6 compares the profiles of pastes printed with the Robocaster. In this case, only three pastes were printed for comparison; the highly viscous ruthenium oxide resistor paste, the relatively fluid silver PTF conductor paste and the aqueous alumina slurry. Initially, the ruthenium oxide resistor paste had a well-defined profile. However, the bead spread quite rapidly and continued to spread for up to 20 minutes. This is shown clearly in Figure 7, which plots bead width as a function of time after printing. The fluid silver PTF paste, on the other hand, spread significantly before the first profile was taken. After this, spreading continued but at a much slower rate. In contrast, the alumina slurry exhibited a well-defined bead initially. Unlike either of the thick film pastes, it exhibited no spreading with time. This is contrary to what would be expected based on the rheology measurements; the viscosity of the aqueous system indicated that it should have an initial profile similar to the silver PTF conductor paste and should probably have spread in a similar manner. However, as is shown in Figure 7, there was no change in width with time. The reason for this behavior is also shown in Figure 7; the alumina slurry was seen to shrink rapidly during the first two minutes after printing. Beyond that, there was no shrinkage. It can be concluded that the aqueous alumina slurry dries rapidly enough to form a hard shell that prevents spreading.

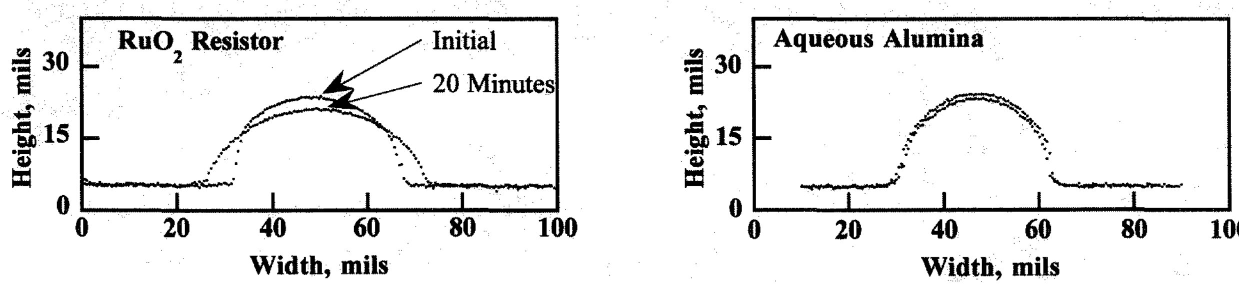


Figure 6: Profiles of ruthenium oxide resistor paste and aqueous alumina slurry deposited by the Robocaster

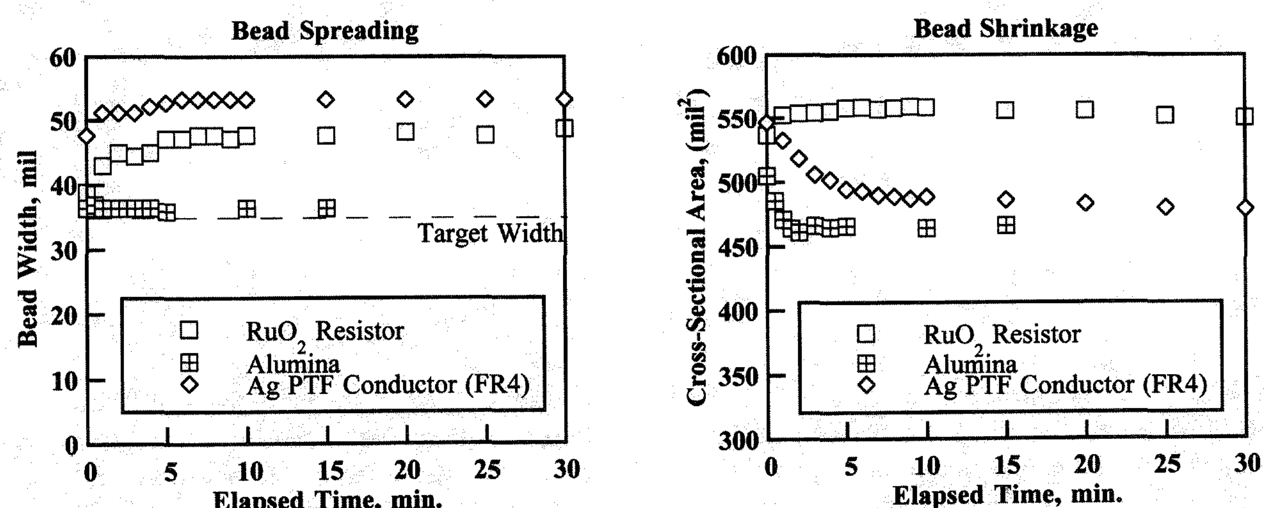


Figure 7: Spreading and Shrinkage as a function of time after printing of thick film inks and aqueous alumina slurry deposited with the Robocaster.

A series of experiments were performed to investigate the effect that the substrate has on spreading. These experiments were performed using silver PTF beads printed on FR4 and on alumina. The results are shown in Figure 8. It was seen that when printed on the alumina substrate, the silver paste spread to a greater extent initially and also continued to spread for a longer period of time than when printed on the FR4. At first, it appeared that this was a matter of wetting. However, when the plot of bead shrinkage vs. time was examined for the two different substrates, it was seen that shrinkage occurred much more rapidly when the bead was printed on FR4 than when printed on alumina. Shrinkage on the FR4 was rapid during the first 5-7 minutes after printing, at which time the shrinkage rate changed to a much slower rate. Since the ink and printing conditions were identical in both cases, this shrinkage can be attributed to solvent loss into the FR4 substrate. There are at least two possible explanations for this behavior. One explanation is that the substrate was porous, extracting the solvent from the ink through capillarity. Another possible explanation is that the solvent dissolved into the epoxy matrix of the substrate. At this time, not enough is known about the substrate/solvent system to distinguish between the two mechanisms for solvent removal. Regardless of the mechanism for solvent removal, it is evident that the extra drying provided by the FR4 substrate slowed the rate of bead spreading and resulted in less spreading overall.

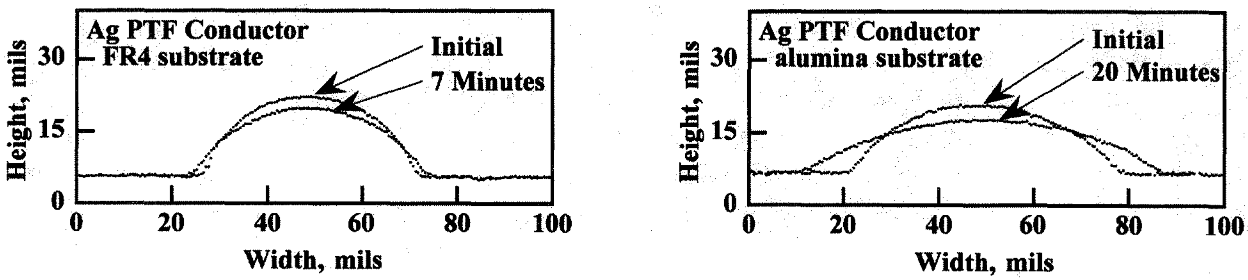


Figure 8: Profiles of silver PTF conductor paste deposited with the Robocaster onto FR4 substrate and alumina substrates.

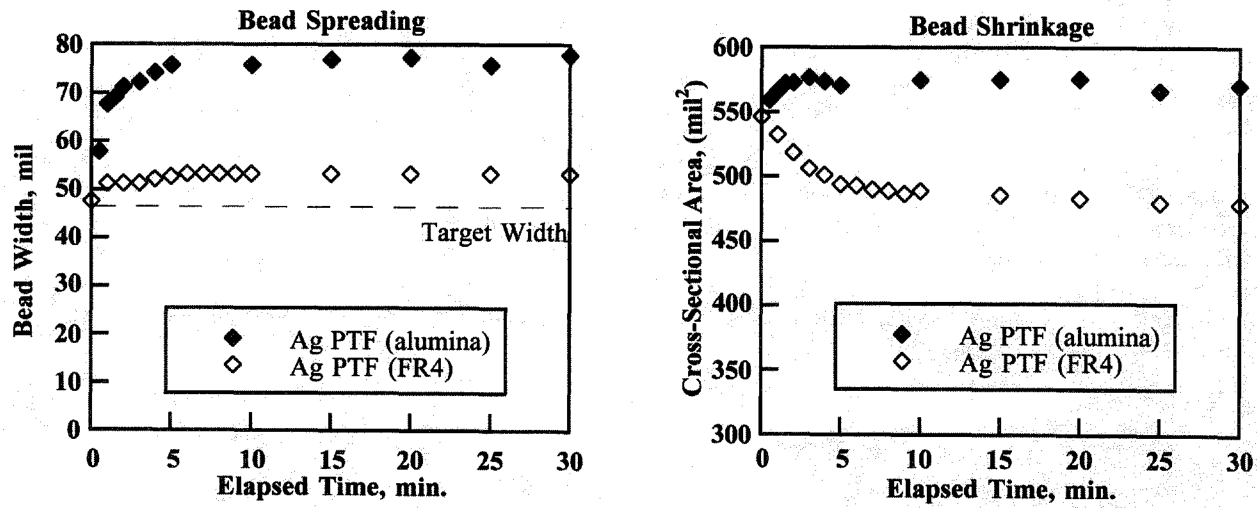


Figure 9: Spreading and Shrinkage as a function of time after printing of silver PTF paste deposited with the Robocaster onto FR4 substrate and alumina substrates.

SUMMARY

Five different pastes were investigated; two commercial post-fire inks, two commercial polymer thick film inks and an aqueous alumina slurry produced at Sandia. The post-fire inks were observed to be the most viscous of the five, while the polymer thick film inks and aqueous slurry were similar to each other and significantly more fluid than the post-fire inks. When printed with the Micropen, an insignificant amount of spreading occurred after the first minute with commercial screen printing inks. The aqueous alumina slurry dried too rapidly to be printed with the Micropen. In contrast, a significant amount of spreading occurred when the commercial screen printing inks were printed with the Robocaster. There was an insignificant amount of spreading when the aqueous alumina was deposited using the Robocaster. This was contrary to expectations based on the rheological examination. Examination of the cross-section of the aqueous alumina bead deposited with the Robocaster indicated that it dried very rapidly, allowing the bead to hold its shape. Drying was also seen to be a significant factor in the case of the silver PTF ink printed on the FR4 substrate. Significantly less bead spreading was noted when compared to a bead of the same ink printed onto a dense alumina substrate. This behavior was attributed to solvent wicking into the FR4 substrate.

Several conclusions can be drawn from the experimental results. In general, the Micropen requires slurries with low vapor pressure solvents to slow drying times and prevent clogging. In contrast, the Robocaster requires slurries with high vapor pressure solvents to speed drying times. This reduces the amount of bead spreading and leads to an ideal bead shape. Finally, it can be concluded that the influence of viscosity on the bead shape is not as important as the effect of solvent removal through drying and wicking.

ACKNOWLEDGEMENTS

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