Evaluation of the Performance and Compatibility of INCOTRONICS™ Ni Paste in Different Vehicles

Richard Stephenson[1], Ann Pogue[1], and Faranak Shojai[2]

[1]Ann Pogue & Associates, Inc., 258 Barbara Avenue, Solana Beach, CA 92075, Tel: (858) 755-7182 ann@annpogue.com
[2]INCO Technical Services Limited, 2060 Flavelle Boulevard, Sheridan Park, Mississauga, Ontario, Canada L5K 1Z9, Tel: (905) 403-2400, fshojai@inco.com

Abstract

INCOTRONICS™ powders for MLCC applications are produced by the chemical vapor decomposition (CVD) method based on the decomposition of Ni carbonyl gas. Several pastes were prepared from vehicles to evaluate the behavior of powder in different vehicle systems. The performance of the pastes was evaluated by viscosity measurement, Low Angle Light images (LAL) and FOG, during and after paste processing. The compatibility of powder with these vehicles was also assessed.

Performance of the pastes was evaluated after various surface treatments. The stability of the pastes was assessed after accelerated aging test.

Introduction

Nickel base metal electrode (BME) technology plays an expanding role in the multilayer ceramic capacitor market. Nearly 80% of MLCC units consumed in 2003 were Ni BME [**1**] and is expected to reach 90 – 95% by 2005.

Advanced MLC devices, such as capacitors, target thin, continuous , and high layer-count dielectric and electrode layers. Advances in dielectric powder technology [**2**,**3**] permit dielectric layers of less than 2 microns. New technology allowing fabrication of very thin layers of dielectrics and electrodes are also being developed [**4,5**]. BME-MLCC state of the art combines less than 2 micron dielectric thickness with over 300 active layers in an 0805 design [**6**]. Critical to these developments are the control of particle size, agglomeration, and dispersion characteristics of the Ni electrode powders.

Several manufacturing methods are used to make electrode grade Ni powders suitable for MLCC construction. These include chemical vapor deposition (CVD), wet chemical precipitation (WCP), spray pyrolysis (SP), and others [**7,8,9**]. Although standard testing procedures [**10**] yield similar physical data of Ni powders from different manufacturing methods, the performance of these Ni powders are not the same in paste applications and ultimately as electrodes in MLCC's. Crystallinity, crystallite size, particle shape, surface chemistry, and carbon and oxygen content also play important roles in Ni powder performance. These properties are related to engineering and method of manufacture.

Surface chemistry of Ni powder particles can be controlled in the manufacturing process by careful selection of additives, either organic, inorganic, or both. Additives can be used to alter oxidation characteristics, sintering behavior, and dispersion properties.

Key in the organic design of conductive Ni BME paste is the rheological behavior, the burn-out characteristics, and dispersion properties of the Ni powder. A variety of resin systems are used to make Ni electrode layers for MLCC's [**11**]. Currently, many resin systems are designed to allow the burn-out phase of the Ni pastes to occur in air, usually up to 400ºC. One of the necessary features of the Ni electrode powder is to resist oxidation at the burn-out temperature and as such, the Ni electrode powders are evaluated based on the oxidation onset temperature and 5% mass increase temperature as determined by TGA [**12**]. As mentioned above, the manufacturing process and choice of additives can improve the surface chemistry of Ni electrode powders. Oxidation resistant Ni powders typically have large crystallite size, and few grain boundaries. CVD type Ni electrode powders, such as the Incotronics™ powders, exhibit these characteristics and generally perform better in electrode applications than do chemically precipitated (wet process, WCP) or spray pyrolyzed powders (SP).

Figure 1 shows Field Emission Scanning Electron Micrographs (FESEM) of three Ni powders made by different manufacturers. Powder A (Incotronics™) and B (competitor) are both manufactured by a CVD process, however, powder B shows a high number of very fine particulates present. Very fine Ni particles result in lower oxidation onset temperature and lower temperature sintering (Figure 2). Powder C also shows fine material present but also poor particle morphology (shape) control, which can lower the tap density of the powder due to poor packing efficiency. A more common problem is the impact on the oxidation reaction between the Ni electrode and dielectric layers [**13**].

Fine particles and broad particle distributions also impact paste behavior. Very fine particles can be reactive in paste formulations by strongly interacting with resin polymers, dispersants, and other very fine particles. Broad particle distributions tend to destabilize the paste, thereby reducing its shelf-life. The ideal Ni electrode powder will be fairly single-sized, spheroidal in shape, and easily dispersed into a variety of organic systems. The ideal Ni electrode paste will be easily fabricated, stable, and inert to the dielectric, producing a smooth film with good conductivity.

In this work, we examined the performance of Incotronics™ INP-400 powder in various paste formulations. Table 1 summarizes the base vehicle compositions utilized in this study.

Table 1. Test Paste Descriptions

Paste Type	Vehicle Base	Resin Type
A	Commercial	Cellulose
B	Dipentene	Cellulose
C	Terpinol	Cellulose

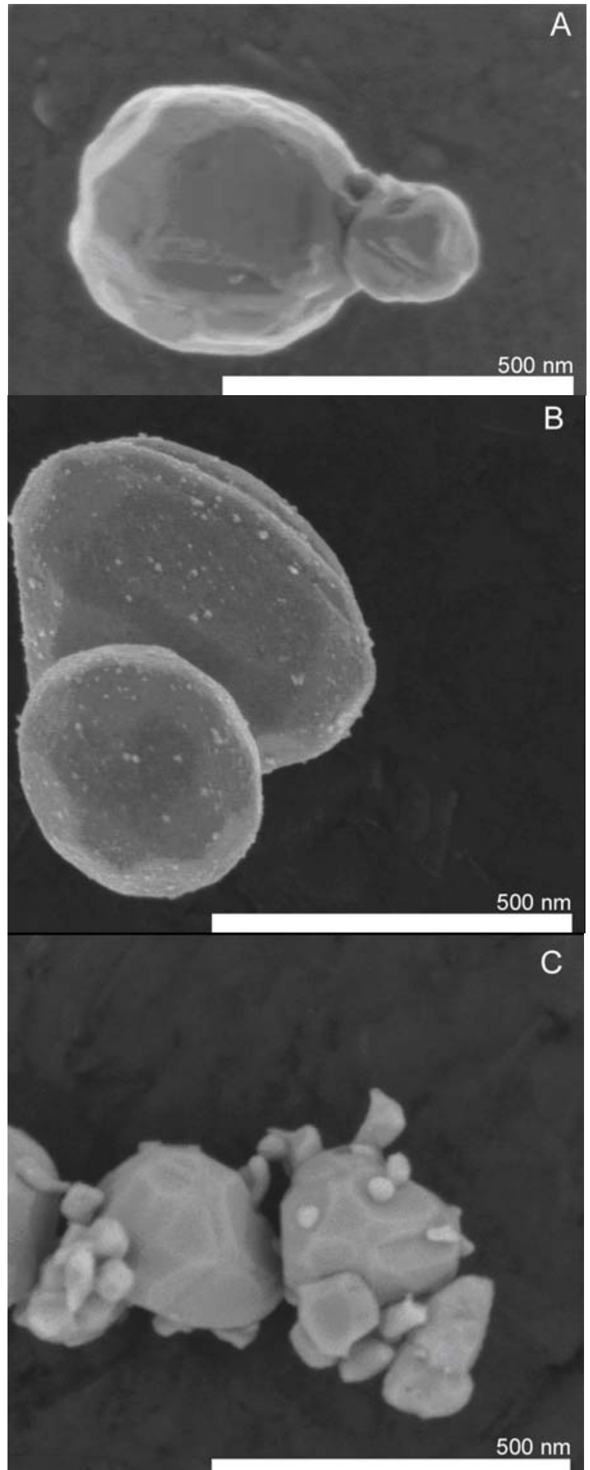

Figure 1. FESEM image of A) Incotronics™ Ni powder, B) CVD competitor powder, and C) wet process competitor powder. Magnification: 110,000X.

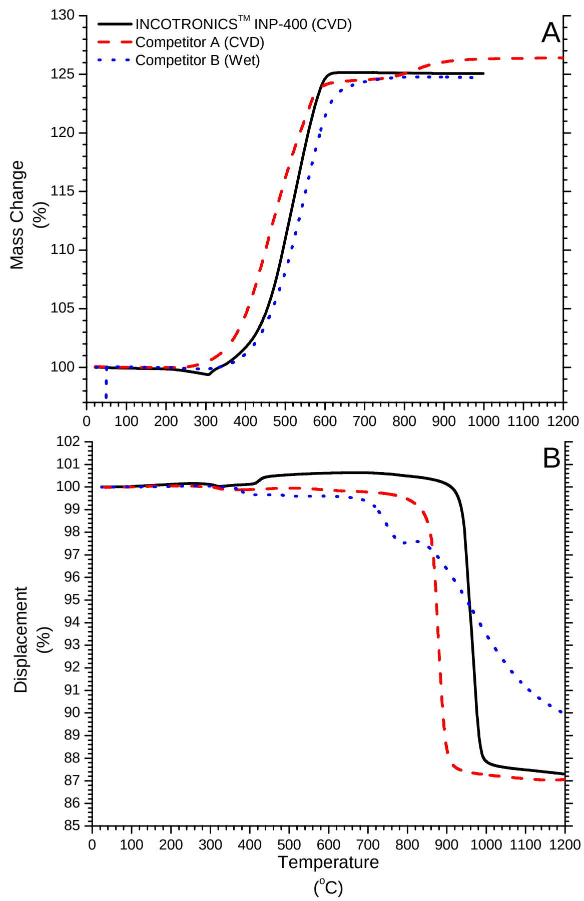

Figure 2. Comparison of thermal results of three different Ni electrode powders. A) TGA with scan rate of 10ºC·min^{-1} in air and B) TMA in 1%H_2-N_2 at scan rate of 10ºC·min^{-1}.

Experimental

Several aspects of the test pastes were examined in the course of this study. Viscosity, fineness of grind (FOG), and low angle light (LAL) images are three of the primary tests.

Ni Electrode Paste

The Ni electrode pastes were prepared by adding one of the solvent components of a vehicle to a mass of Ni powder. The Ni powder and solvent are then mixed to ensure good wetting. The vehicle system is then added to the wetted Ni powder and again mixed. The mixed paste is then three roll milled (stainless steel rolls) for five passes with an initial roll gap of 0.0015 inch (38 μm) and final roll gap of 10 – 15 μm.

The Ni electrode pastes are then tested (viscosity, FOG, LAL, aging). The Ni pastes are also tested after aging by placing the paste in a sealed container at 40ºC for 100 hours.

Results and Discussion

Inco has evaluated several varieties of Ni powders from our own processes and other materials that are commercially available to BME paste and MLCC makers. It is clear that Ni powder characteristics, such as tap density, particle size distribution, specific surface area, and thermal properties are not the sole indicators of high performance Ni powder. We have found for equivalent reported physical properties that different Ni powders do not perform equivalently in paste applications. We have also seen results of varying performance of Ni powders in different Ni electrode paste formulations.

Figure 3 shows the LAL images of a Ni electrode paste made with an Incotronics™ powder in three different paste vehicle systems. In each case, the LAL image shows smooth and continuous printed paste. Some defects were observed in the case of Paste C, but only minor and with low size and number density. In addition, we have shown in Figure 4 the viscosity responses of each of these pastes after three roll milling and see reproducible and stable behavior even after accelerated aging.

The results shown in Figure 3 and Figure 4 show a Ni electrode powder that has been designed to be compatible with different paste systems. We have found that the Incotronics™ powder is readily dispersed during the pre-milling phase, easily three roll mills, and is stable in the finished paste phase. Table 2 shows the viscosity at 5 RPM of three Ni pastes, each made with different Ni powder surface chemistry.

Table 2. Viscosity of Ni Powders in Three Pastes With Various Surface Chemistries

Surface Type	Paste A (mPa·s)	Paste B (mPa·s)	Paste C (mPa·s)
Inorganic	76000	2400	12000
Organic-Anionic	1700	1900	3800
Organic-Nonionic	14000	1000	7500

Figure 5 shows the LAL images of a Ni electrode powder in each of the same paste

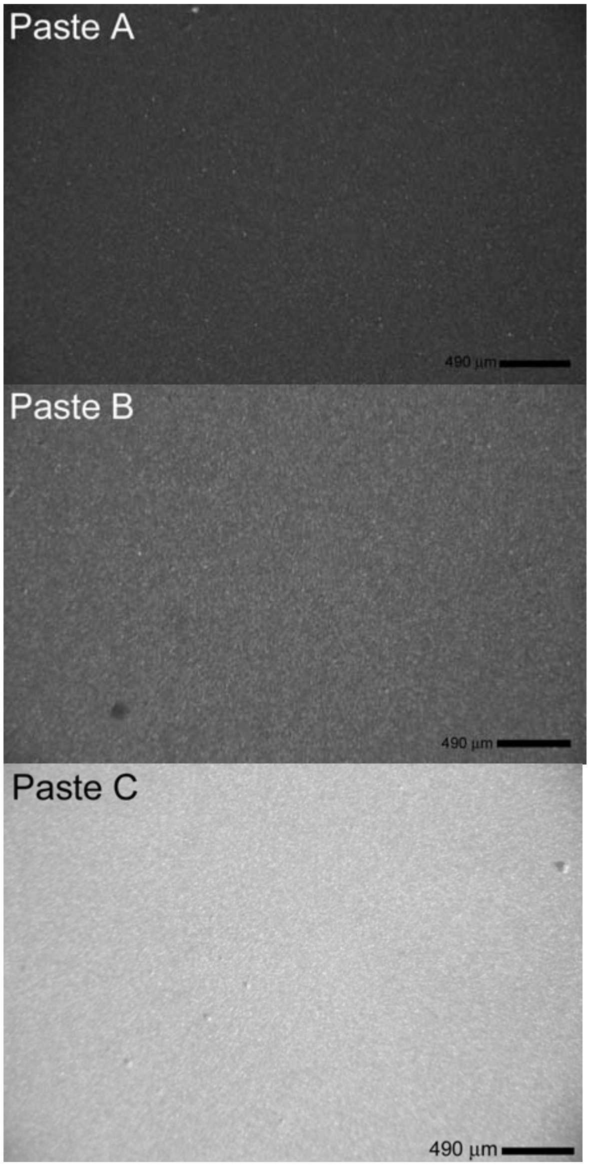

Figure 3. Low angle light (LAL) images of Ni electrode paste (from same Ni powder) in three different vehicle systems.

systems tested in Figure 3. In this case, we see moderately good behavior in Paste A, with small defects present in the printed film. Paste B, however, shows very poor behavior with large and numerous defects along with an 'orange peel' texture on the film surface. Paste C shows good behavior with very few defects. This is an example of an incompatibility between the electrode powder and the vehicle. This is largely due to stronger Ni particle-to-particle reaction/interaction and organic phase 'exclusion'. In the case of Paste B of Figure 5 there is also a serious problem with the aging of the paste as seen in Figure 6. The viscosity

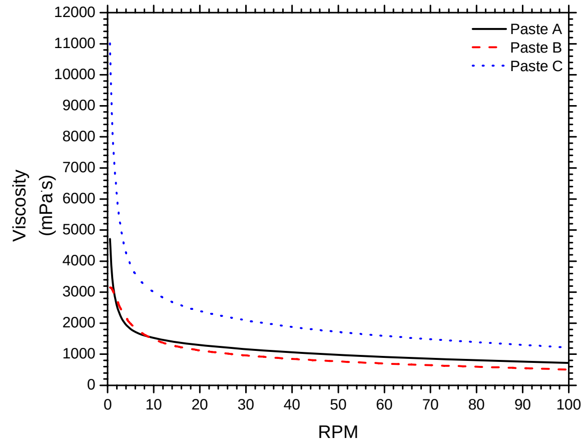

Figure 4. Viscosity responses of Ni electrode pastes after three roll milling (from Figure 3).

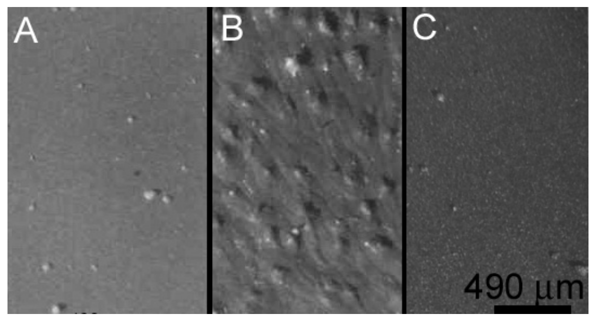

Figure 5. Low angle light (LAL) image of a Ni powder in three different vehicle systems. Paste A shows moderate behavior, Paste B shows very poor behavior, and Paste C shows good behavior.

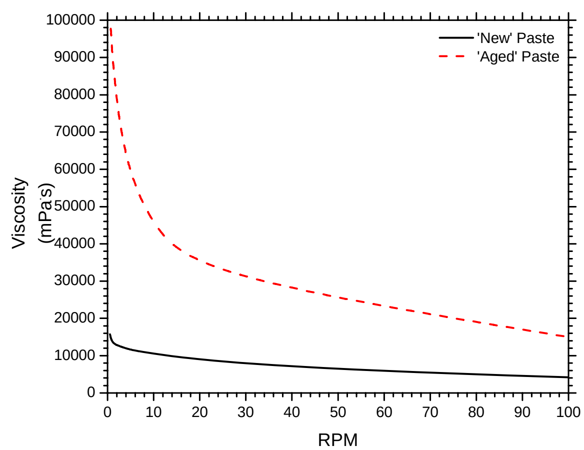

Figure 6. Viscosity responses of Ni electrode Paste B (Figure 5) showing dramatic aging effect.

response of the aged paste is an indication of slow post-three roll milling reactions occurring in the paste phase. In this example, we were able to observe the formation of the defects seen in the LAL image for Paste B in Figure 5 as the film was slowly dried. We also noted the formation of gel particles in the aged paste.

In some cases, the mixing of Ni powders into the vehicle systems was easy, but we found that in other cases, the Ni powder does not readily disperse, even in a three roll mill. For example, Figure 7 shows the LAL image of a Ni paste after one and five passes on a three roll mill. Although the pre-milling mixing was in no way difficult, the LAL image after the first pass shows a dramatic incompatibility. Some systems that exhibit this behavior after one pass on a three roll mill can still be dispersed with additional processing, however, in this case we observed no significant improvement.

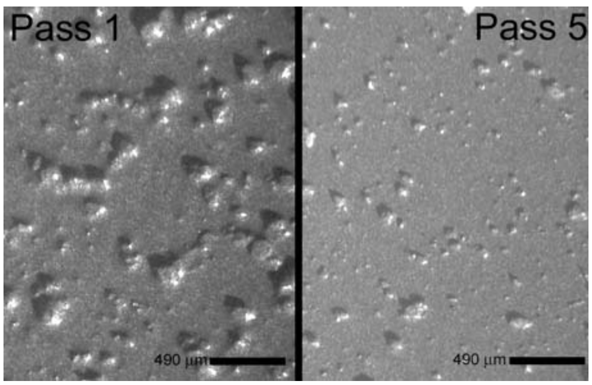

Figure 7. Low angle light (LAL) image of poorly dispersed Ni powder after 1st and 5th pass on a three roll mill.

Additional study of controlled thickness printed films on stainless steel allowed us to observe conditions where Ni particles agglomerate in the paste system. Figure 8 shows a polarized light image of two printed Ni films, 2 μm thick. Figure 8A shows large, irregular agglomerates (indicated by arrows). In this example, the Ni powder used to make this paste exhibited poor dispersion into the vehicle system. Figure 8B (Incotronics™ powder) shows a continuous film indicating good dispersion of the Ni powder into the vehicle system.

Conclusion

We have shown for different paste systems that proper control of the surface chemistry of Ni powder will produce good compatibility with a variety of paste systems, resulting in smooth and continuous Ni electrode ink prints. It has also been shown that there are several ways surface incompatibility can develop. If the electrical balance is not right with the total

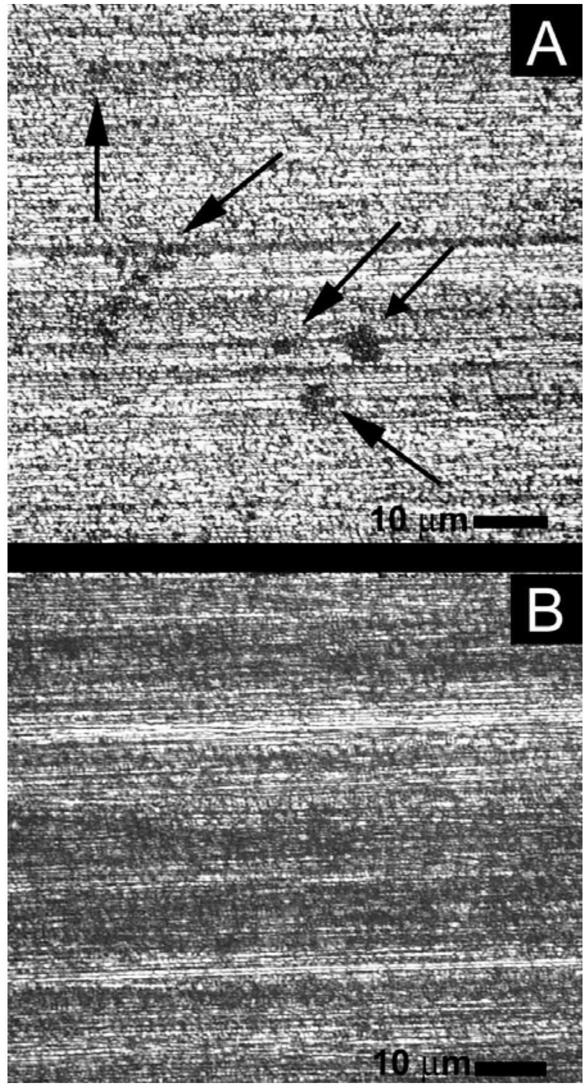

Figure 8. Polarized light image of 2 μm thick Ni pastes at the same magnification. A) Poor dispersion showing Ni agglomerates (arrows). B) Good dispersion showing no agglomeration. (Terpinol-cellulose type paste.)

system, then the powder will not wet easily and will have a very high viscosity, similar to a caulking compound. When the incompatibility is found with the resin or plasticizer, then a paste that initially looks good when mixed and milled will develop 'bumps' when drying – such as those seen in low angle light images when good FOG have been made of the paste.

Incompatibility can also be seen with one of the solvents. This can be shown with the agglomerations seen with polarized light of Figure 8A.

Changes in viscosity with age can represent several different challenges. Increased viscosity can suggest that the powder is continuing to disperse and the fines are raising the viscosity. It can also indicate, particularly if observed in one type of system and not another (such as Figure 5) an agglomeration with time relating to the resin system. It is very important, therefore, to look at compatibility at several different stages of the paste life cycle to determine the consistency of the paste performance in the component.

Inco has done extensive work with Ni powders and understanding interactions with organic systems for conductive pastes in MLCC applications. We have developed dispersible powders through engineering the surface of our Ni powders suitable for a wide range of electronic pastes. We work intimately with our customers to develop and supply superior Ni powders for MLCC processes. Inco's INCOTRONICS™ powders have been used successfully in MLCC parts of over 150 layers in several different process environments. We look forward to working with your engineers for your Ni paste applications.

References

[1] Stephenson R., Trends & New Technology, CARTS EUROPE 2003.
[2] Kishi H., Mizuno Y., Chazono H., Jap. J. Appl. Phys., Vol. 42 (2003).
[3] Mann, L., Beeson J., Proceedings of CARTS USA 2000, 109.
[4] Yamashita K., Matsuda M., Inda Y., Umegaki T., Ito M., Okura T., J. Am. Ceram. Soc., 80 (1997) 1907.
[5] Zhang J., Lee B., J. Am. Ceram. Soc., 83 (2000) 2407.
[6] Randall, M., Gurav A., Skamser, D., Beeson, J., Proceedings of CARTS USA 2003, 134.
[7] Stephenson R., Pogue A., Shojai, F., Proceedings of CARTS EUROPE 2003, 245.
[8] Goia, D., Kang H., Proceedings of CARTS EUROPE 2003, 239.
[9] Ruscoe M., Abed N., Oehlers M., Yuan D., Proceedings of CARTS EUROPE 2003, 228.
[10] Huenert, R., Proceedings of CARTS EUROPE 2003, p 235 references.
[11] McVicker, K., Gunter, G., Fu B., Sabo, G., Randall, M., Proceedings of CARTS USA 2000, 116.
[12] Gurav, A., Randall, M., Mann, L., Proceedings of CARTS USA 2002, 81.
[13] Opitz, M., Albertsen, K., Beeson, J., Detleve, H., Routbort, J., Randall, C., J. Am. Ceram. Soc., **86** [11] 1879 (2003).