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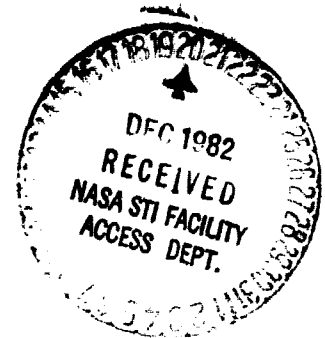
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QUARTERLY TECHNICAL REPORTS NO. 4

for

DEVELOPMENT OF TECHNIQUE FOR  
AR COATING AND NICKEL AND COPPER  
METALLIZATION OF SOLAR CELLS  
FPS PROJECT  
PRODUCT DEVELOPMENT



PERFORMANCE PERIOD

April 1, 1982 to June 30, 1982

JPL CONTRACT NO. 955986

DRL NO. 159

July 15, 1982

Prepared by:  
Dr. William Taylor ✓

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FOR AR COATING NICKEL AND COPPER  
METALLIZATION OF SOLAR CELLS FPS PROJECT  
PRODUCT DEVELOPMENT Quarterly Technical  
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Technical Director  
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"The JPL Low-Cost Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE."

## PREFACE

The objective of this program is to analyze and evaluate a base metal system for metallizing solar cells. The system to be investigated is printed nickel overplated with copper and applied on top of a pre-deposited silicon nitride anti-reflective coating.

## 1.0 SUMMARY

Experimental matrices were conducted to determine a suitable firing schedule for fritless tin printing ink. Considerable difficulties were encountered with oxidation. Best results were obtained with a firing cycle consisting of 400<sup>0</sup>C for 20 minutes in nitrogen followed by 5 minutes in air at 500<sup>0</sup>C. Elimination of oxidizing conditions impaired the adhesion of both tin and copper fritless printing inks, although adhesion of fritless copper inks was obtained when fired in nitrogen with slight oxidation.

## 2.0 TECHNICAL DISCUSSION

During this period attention was turned to the use of fritless pastes in order to avoid the loss of adhesion which had been experienced when contacts formed with fritted pastes are electroplated.

Preliminary experiments were conducted with TFS 5522 Oxyfine fritless nickel. In the first experiment, samples with 0, 2 and 5% silver fluoride were fired in oxygen for 25 minutes at 500°C followed by 10 minutes at 650°C in forming gas. All samples were shorted with no electrical output. The sample with no fluoride added had good adhesion both before and after copper plating. Addition of fluoride resulted in loss of adhesion during plating. When fired at 800° and 850° for short periods, some electrical output was obtained, but adhesion degraded during plating. IV curves obtained with the unmodified TFS 5522 ink are shown in Figure 1, and as modified by 5% silver fluoride in Figure 2.

A fritless paste composed of 19.5% molybdenum, 80% tin and 0.5% titanium hydride was obtained from Thick Film Systems. This paste gave very high series resistance with practically no short circuit. The firing cycle used was 25 minutes at 500°C in air followed by 5, 10 or 25 minutes at 650°C in forming gas. Similar results were obtained when the prefire drying cycle was dropped to one hour at 400°C in an attempt to reduce oxidation effects. No improvement was observed with the addition of 2% silver fluoride. These samples could not be plated, apparently because of the presence of a fine dark colored insulating powder which coated the sintered metal. This was attributed to oxidation of the molybdenum component of the paste. Adhesion of the contact was poor when subjected to tape testing. This ink was replaced with a pure tin-2% titanium hydride formulation in subsequent work.

Several experiments were conducted to identify a suitable firing schedule for the tin-titanium hydride printing ink. Initial procedures of baking at 400°C followed by 5-10 minutes at 675°C in air

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FIGURE 1. Current-voltage curves for TFS 5522 nickle fired at 850°C on Si<sub>3</sub>N<sub>4</sub>

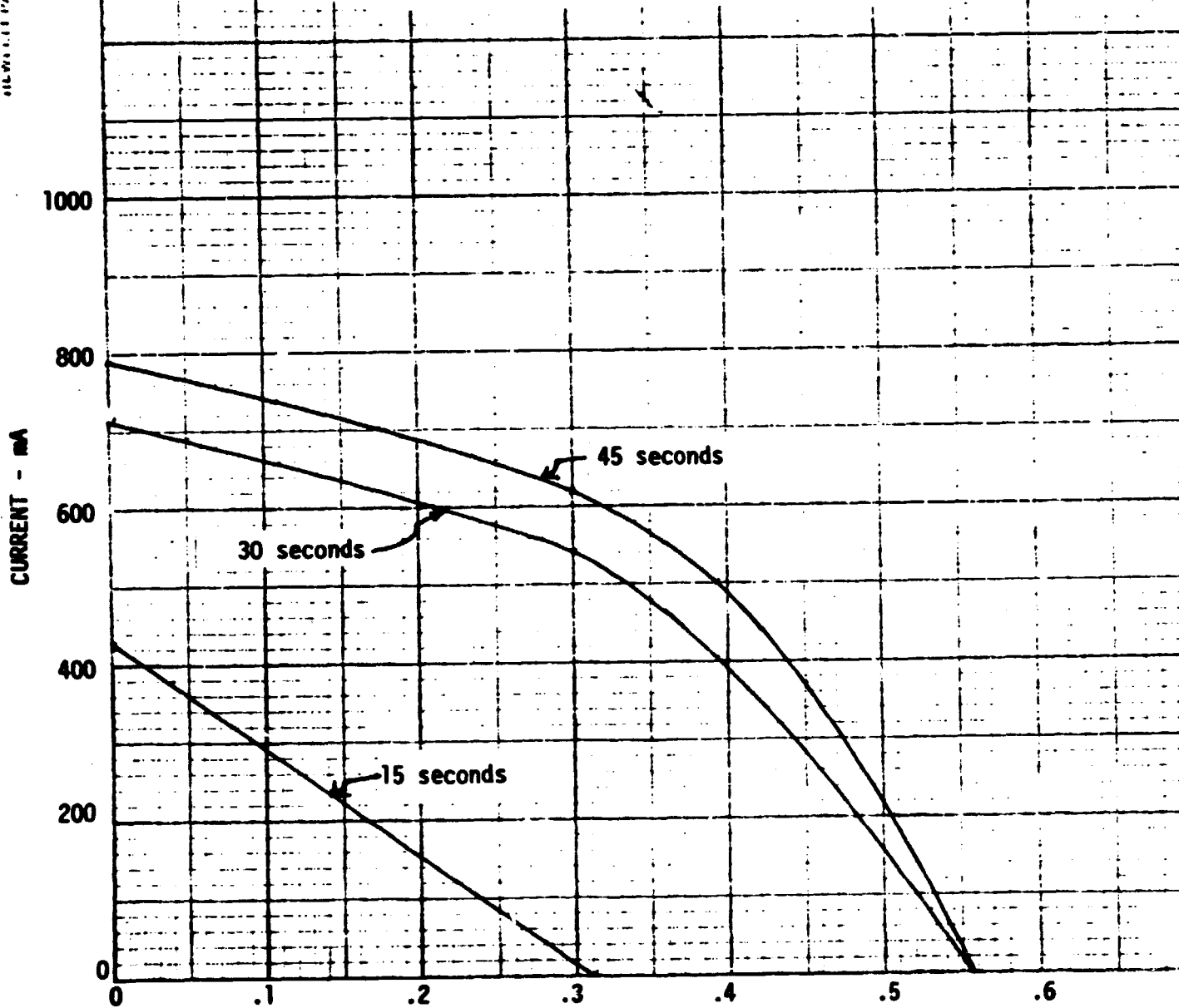
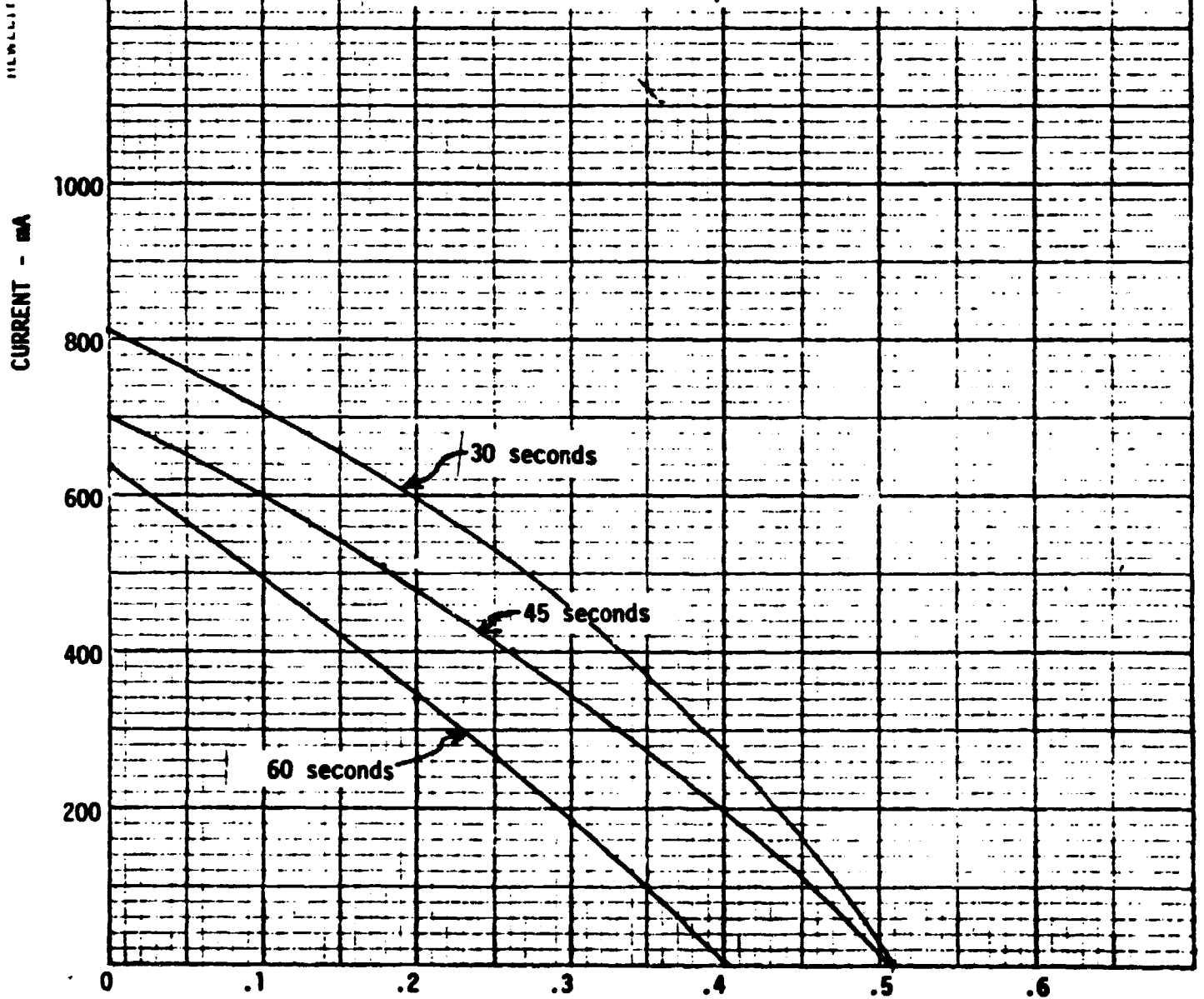




FIGURE 2. Current-voltage curves for TFS 5522 nickel +5% AgF fired at 850° on Si<sub>3</sub>N<sub>4</sub>



resulted in non-sintered, powdery deposits with extensive oxidation. Based on these observations, the following firing strategy was selected:

1. Low temperature prefire in nitrogen to initiate sintering and agglomeration while the metal is still protected from oxidation by the organic vehicle.
2. Fire at moderate temperature in air to burn off organics.
3. Fire at 675<sup>0</sup>C in forming gas to complete sintering and reduce metallic oxides.

The experimental matrix shown in Figure 3 was devised to generate information about the firing cycle conditions. One wafer was set aside from each of the matrix cells for evaluation. Observed characteristics for cells fired in the various regions of the matrix are given in Figure 3 and discussed below.





The tan color observed in the samples after prefire is believed to be due to residual organics which act as a glue to hold the metal powder together without actual sintering. The structure is thus analogous to peanut brittle, accounting for its character of being cohesive but brittle. Under the SEM, the deposit has the appearance of a boulder field with tin particle dimensions in the range of 5 to 30 microns. In the sample fired at the lowest temperature of 400<sup>0</sup>C shown in Figure 4, the tin "boulders" are quite porous and appear to be composed of smaller particles clustered and sintered together. It is likely that these agglomerations are present in the paste before firing. There does not appear to be any bonding of the large tin particles to each other.

After firing in air at 500<sup>0</sup>C for 5 minutes the appearance of the metal powder has changed drastically (Figure 5). The substructure is no longer visible and each particle is surrounded by a shrunken bag, presumably of oxide. Evidence of the oxide is still present after 1 and 10 minutes of further firing at 675<sup>0</sup>C in forming gas (Figure 6 and 7). The best cohesion and adhesion of the sintered tin and least oxide were found in the samples prefired at 400<sup>0</sup>C. Evidence of bonding

FIGURE 3  
 EXPERIMENTAL MATRIX TO TEST  
 INITIAL FIRING STRATEGY

STEP	VARIABLE CONDITIONS					
	400°C		450°C		500°C	
1. Prefire 20 min. in N <sub>2</sub>						
2. Organic Burnoff 500°C in Air	2 min.	5 min.	2 min.	5 min.	2 min.	5 min.
3. Final Sinter 675°C in forming gas	1 min. 10 min.	1 min. 10 min.	1 min. 10 min.	1 min. 10 min.	1 min. 10 min.	1 min. 10 min.

Observations:

-  Tan color, cohesive but brittle
-  Dark powdery deposits
-  Best adhesion and sintering
-  White, fluffy residue

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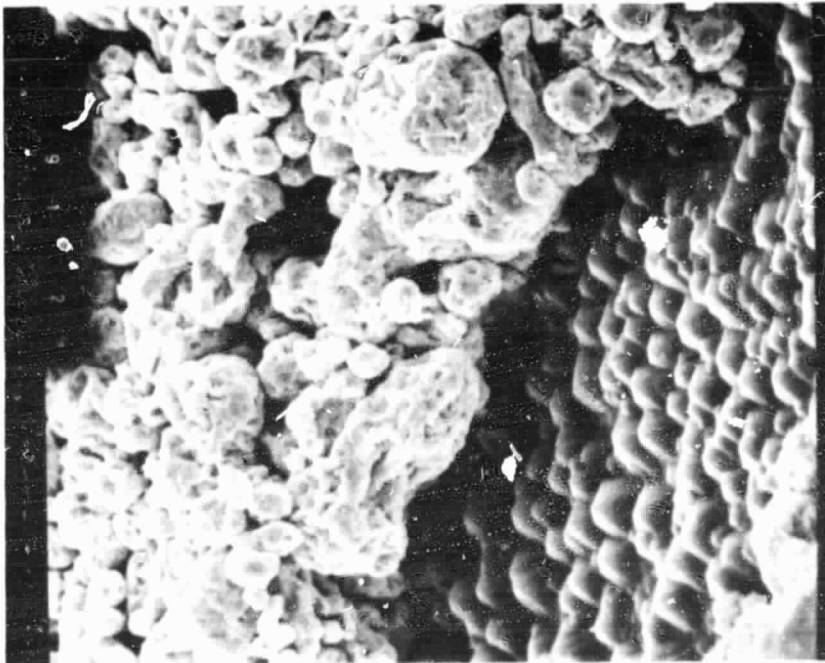


FIGURE 4. Tin-titanium hydride  
400°C for 20 min. in N<sub>2</sub>  
1000X, 45°

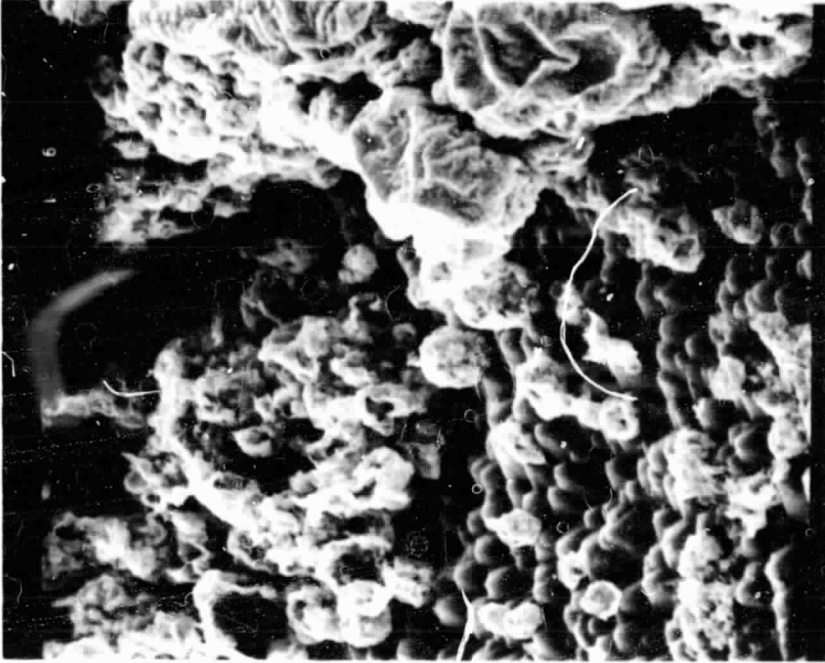


FIGURE 5. Tin-titanium hydride  
400°C for 20 min. in N<sub>2</sub>  
500°C for 5 min. in air  
1000X, 45°

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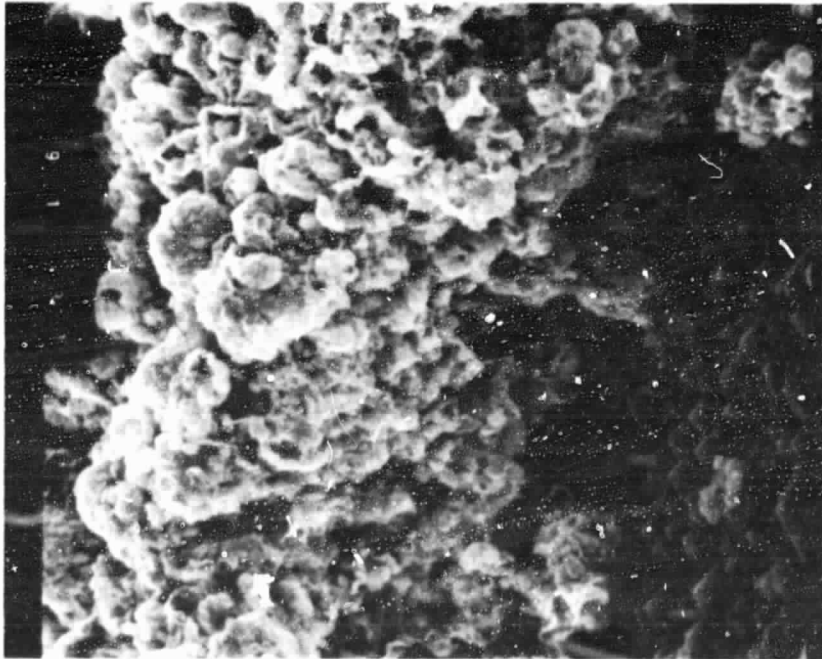


FIGURE 6 . Tin-titanium hydride  
400°C for 20 min. in N<sup>2</sup>  
500°C for 5 min. in air  
675°C for 1 min. in forming gas  
1000X, 45°

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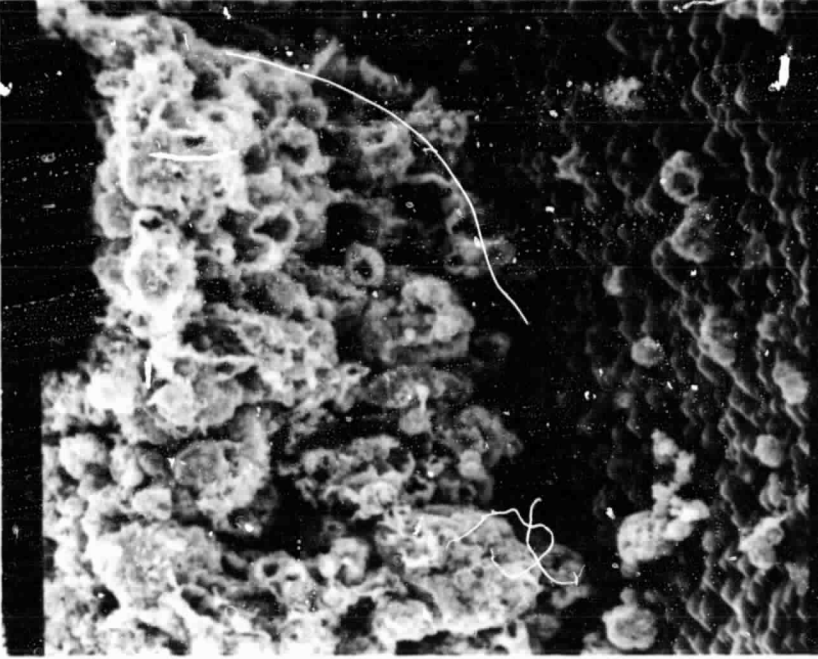


FIGURE 7 . Tin-titanium hydride  
400°C for 20 min. in N<sub>2</sub>  
500°C for 5 min. in air  
675°C for 10 min. in forming gas  
1000X, 45°

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between tin particles is difficult to find in the SEM photographs (Figures 4 through 7).

The samples in this sequence (400°C prefire) had copious quantities of a white ash or residue after firing at 675°C in forming gas. This white substance also showed up after the 675°C reducing step in samples prefired at 450°C and 500°C. The white residue was believed to be a manifestation of oxide. In subsequent experiments it became more prevalent as precautions to exclude oxygen were increased, but eventually was successfully eliminated by oxygen exclusions.

Samples prefired at 450°C and 500°C were powdery and poorly cohesive after the oxidation firing at 500°C and the final sintering at 675°C in forming gas. The deposits were dark colored and believed to be heavily oxidized.

In view of the extensive oxidation observed, even after the forming gas firing, a second matrix experiment was conducted, shown in Figure 8, in which the 500°C air firing step was omitted. A prefiring temperature of 450°C was selected with time of prefire between 5 minutes and 10 minutes. The final firing step at 675°C was tested with both nitrogen and forming gas atmospheres. In this experiment the samples after 450°C prefire resembled closely those after prefire in the previous experiment. After final sintering the deposits were powdery with large amounts of the white residue previously described.

Based on the results of the second matrix experiment, a firing cycle consisting of 20 minutes prefire at 400°C followed by 5 minutes sinter in air at 500°C was tested. This firing cycle gave good sintering, although with some evidence of oxidation. A nickel-tin paste was then blended by mixing 10% of the tin-titanium hydride fritless paste with a pure nickel fritless paste. In order to flux the oxides a small amount of zinc chloride was blended into the paste. This was done by adding 2 per cent of isopropyl alcohol saturated with zinc chloride. Cells printed

FIGURE 8  
 EXPERIMENTAL MATRIX TO TEST  
 MODIFIED FIRING STRATEGY

STEP	TIME VARIABLE					
	5 minutes		10 minutes		20 minutes	
1. Prefire 450°C - N <sub>2</sub>						
2. Sinter 675°C - N <sub>2</sub>	2 min.	5 min.	10 min.	2 min.	5 min.	10 min.
3. Alt. Sinter 675°C - forming gas	2 min.	5 min.				

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with this nickel-tin paste were then fired 20 minutes at 400°C in N<sub>2</sub> followed by 2 minutes at 500°C in air. This deposit was very powdery and poorly sintered.

SEM photographs of the tin-titanium hydride deposit at 400°C and then at 500°C are shown in Figures 9, 10 and 11. Figure 9 shows a general view suggesting less oxidation than previously observed (Figure 5). Sintering of the tin particles shown at larger magnification in Figure 8 is somewhat obscured by the oxide. The photograph shown in Figure 9 was taken in the "halo" region along the edge of a grid line. This region forms from the residues of the clear organic vehicle which segregate out after printing, carrying with it small quantities of the solids. The numerous small particles (about 1 micron) appearing in this photograph are believed to be the original tin particles which agglomerate together to form the larger particles, some of which also appear in the picture. Partially consolidated clusters of the small particles can be seen at several locations.

A SEM photograph of the blended nickel-10% tin paste after firing is shown in Figure 12. The visual impression that the large tin particles are widely separated in the fine (about 1 micron) nickel powder is confirmed by the tin x-ray image of same area shown in Figure 13. The tin particles in Figure 12 do not show the oxide bag structures previously observed (Figures 5, 6, 7 and 10) indicating that the zinc chloride was effective in performing its fluxing function.

The observations of the tin distribution in the nickel-tin paste suggest that the tin will not play significant role in sintering the deposit unless the concentration is very high (about 80% Sn).

In view of the persistent oxidation problems, further attempts were made to improve the firing procedures and equipment. At the end of the period reducing conditions in forming gas were being obtained and fritless tin and copper pastes were fired in nitrogen with only minor oxidation. In



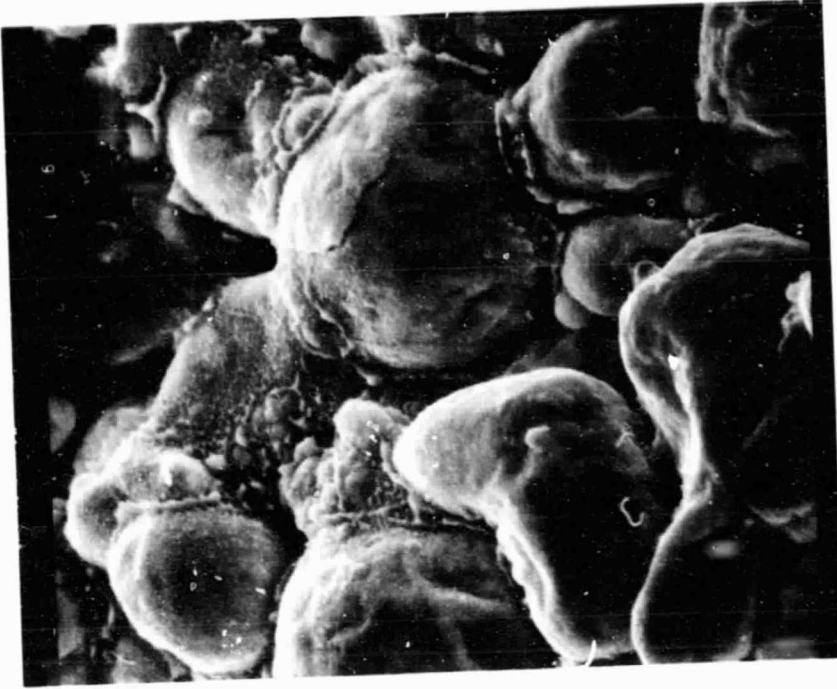


FIGURE 10. Tin-titanium hydride  
400°C for 20 min. in N<sub>2</sub>  
500°C for 5 min. in air  
4000X, 30°

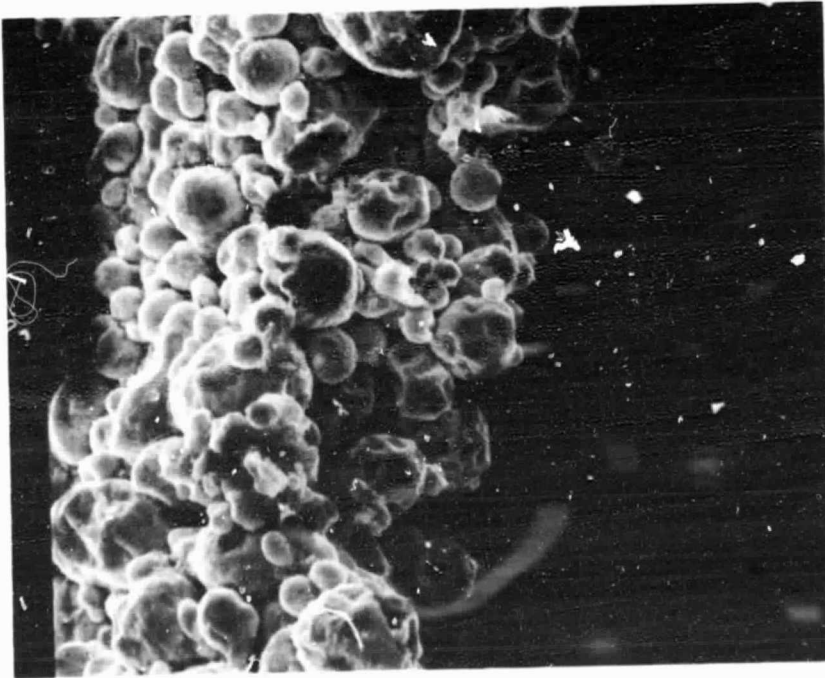


FIGURE 9. Tin-titanium hydride  
400°C for 20 min. in N<sub>2</sub>  
500°C for 5 min. in air  
1300X, 45°

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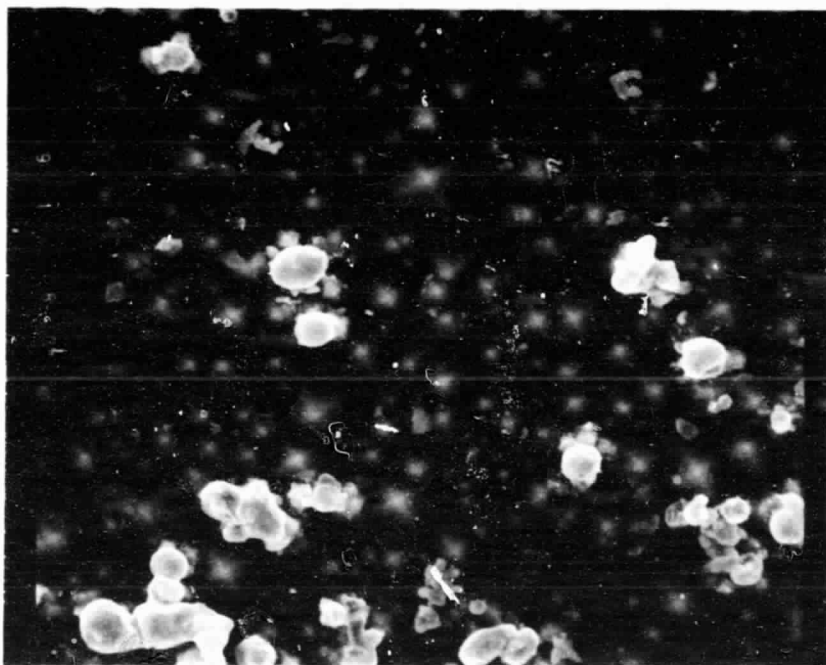


FIGURE II. Tin-titanium hydride "Halo Area"  
400°C for 20 min. in N<sub>2</sub>  
500°C for 5 min. in air  
1300X, 0°

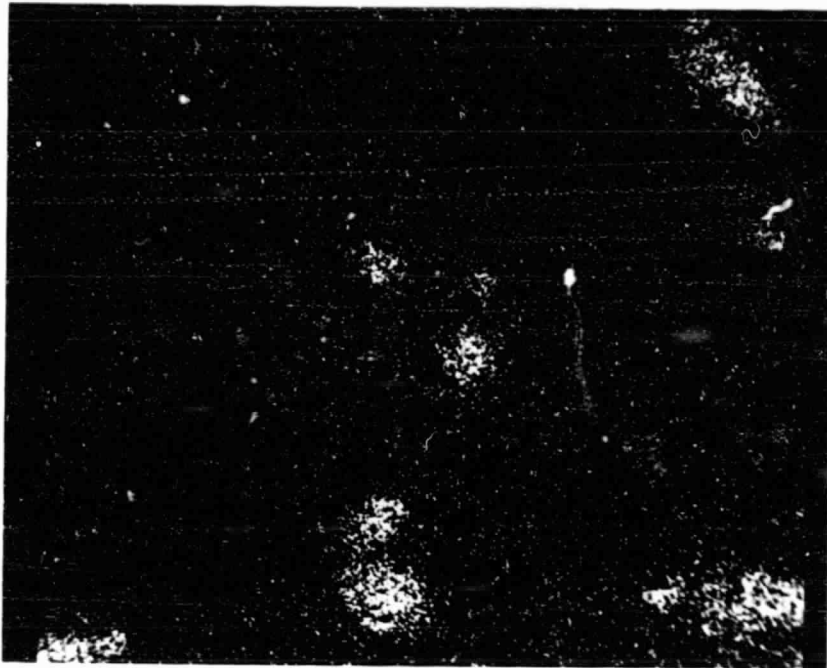


FIGURE 13. Tin X-ray image of the area shown in Figure 10.

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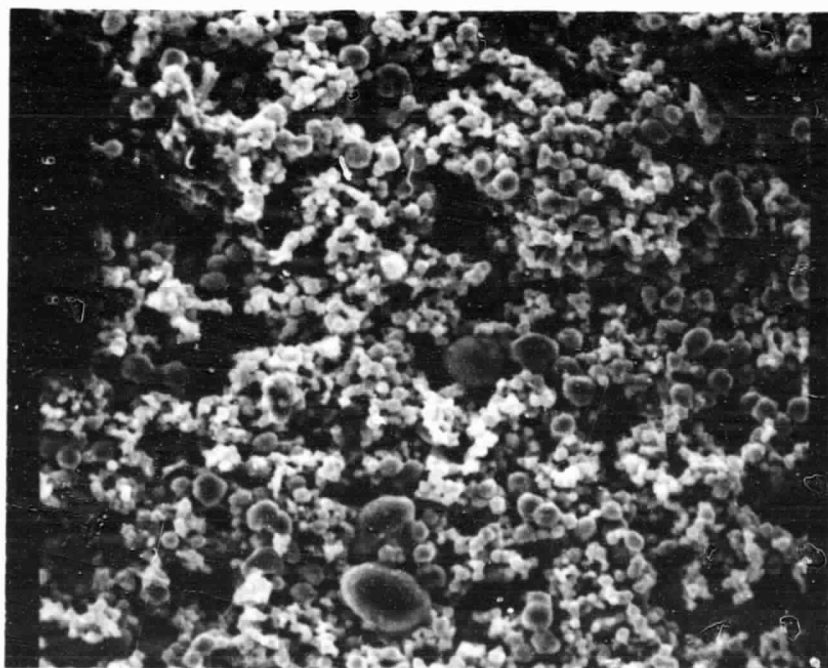


FIGURE 12. Ni + 10% Sn + ZnCl<sub>3</sub>  
400°C for 5 min. in N<sub>2</sub>  
500°C for 2 min. in air  
i200X, 0<sup>2</sup>

preliminary experiments in the improved furnace atmospheres, moderate adhesions were obtained with pure copper and silver fluoride doped copper on silicon nitride surfaces fired in nitrogen, but not when fired in forming gas. Tin-titanium hydride deposits were non-adherent in both atmospheres and on both bare silicon and silicon nitride.

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### 3.0 DISCUSSION

The fritless tin and copper pastes which were fired during this period were found to be extremely sensitive to oxidizing conditions. In the absence of oxidizing conditions the printed deposits tend not to bond to silicon and silicon-nitride surfaces, supporting the tentative hypothesis that frits play a significant role in bonding. Titanium hydride does not appear to improve the situation. The failure of tin to wet and spread through fine nickel powder suggests that tin-nickel mixtures will be limited to those having a small nickel content.

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