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SOLDERING OF THIN FILM-METALLIZED, SODA-LIME GLASS SUBSTRATES*

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ABSTRACT

The ability to produce reliable electrical and structural interconnections between glass and metals by soldering was investigated. Soldering generally requires premetallization of the glass. As a solderable surface finish over soda-lime-silicate glass, two thin films coatings, Cr-Pd-Au and NiCr-Sn, were evaluated. Solder wettability and joint strengths were determined. Test samples were processed with Sn60-Pb40 solder alloy at a reflow temperature of 210°C. Glass-to-cold rolled steel single lap samples yielded an average shear strength of 12 MPa. Solder fill was good. Control of the Au thickness was critical in minimizing the formation of $AuSn_4$ intermetallic in the joint, with a resulting joint shear strength of 15 MPa. Similar glass-to-glass specimens with the Cr-Pd-Au finish failed at 16.5 MPa. The NiCr-Sn thin film gave even higher shear strengths of 20-22.5 MPa, with failures primarily in the glass.

INTRODUCTION

The overall objective of this effort was to develop an improved joining technology for sealing photovoltaic modules. The specific technological goal was to develop a soldering process for glass. The process involved the deposition of a thin metal film on the glass, which promoted wetting by a Sn-Pb solder alloy. Soldering was performed at 200-220°C without flux.

The photovoltaics industry has been developing a thin film technology for fabricating solar arrays (Lerner, 1996). One of the concepts uses CdTe-based grid lines. The primary advantages of the technology are: 1) the simplicity of the processing equipment, 2) the forgiving nature of the active semiconductor materials (CdS and CdTe), and 3) the resulting low processing costs.

The primary obstacle in obtaining the desired field life of 20 years or greater is that the active semiconductor material in an unencapuslated module would degrade in the presence of excessive humidity. Expected field life is, therefore, directly related to the permeability of water into the module through the edge seal. Exposure to an 85°C and 85% relative humidity (RH) environment for extended periods characterizes the total measured permeability of the current design. To increase the life of the module in the field and reduce or eliminate desiccant in the current module design, a significant reduction in permeability is required. The resulting module must also pass "Recommended Practice for Qualification of Photovoltaic Modules," prepared by the IEEE Standards Coordinating Committee 21, Photovoltaics. This includes thermal cycling (dry and humidity-freeze), hail impact, twist, flexion, and various loading tests.

Whatever sealing materials or techniques are used (Humpston and Jacobson, 1993; Schwartz, 1990; Lea, 1988; Tummala and Rymaszewski, 1989), they must be compatible with the soda lime glass front and rear panels, the aluminum frame around the panels, and the various photovoltaic materials (NiCr, carbon, CdTe, CdS). The sealing technology must eliminate the desiccant, be compatible with module assembly, and yield a fifteen-twenty year life span under relatively severe service conditions.

Research (Glass, et all, 1998) was initiated by Sandia National Laboratories to demonstrate that glass could be bonded with conventional solder alloys, using existing soldering technology (Hosking, et al, 1992; Banks, 1995). The main constraint on the sealing technology was that the peak soldering temperature could not exceed 200°C for long times to

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avoid degradation of CdTe-based gridlines. Higher temperatures, up to 250°C, were acceptable if processing times were kept short and the heat input was localized. Two approaches were investigated.

The first involved soldering Sn-Pb and In-Pb-Ag alloys to metallized glass. Because the panel seal would be hermetic and corrosive flux residues in the sealed package would be unacceptable, fluxless soldering was investigated. The second approach used a low melting temperature glass frit in conjunction with localized heating. This paper describes the soldering results.

TEST MATERIALS & CONDITIONS

The base material was a soda-lime glass, nominally 3 mm (0.118 inches) thick. The glass was cleaned prior to metallization. The ultrasonic cleaning procedure used a four step wash process: (a) reagent grade trichloroethylene, (b) mild detergent solution, (c) deionized water rinse, and (d) isopropyl alcohol. A final dry was done with technical grade nitrogen gas. The cleaned glass was then sputter deposited with 0.15 µm Cr, 0.15 µm Pd, and 2.5 µm Au, respectively.

A Sn over NiCr coating was also evaluated. Thickness of the NiCr layer varied from 100 to 10,000 Å. The Sn overlayer was 1.5 µm thick. An evaporative process was used to deposit these coatings. A thin tin oxide film was pre-deposited on the glass prior to depositing the NiCr layer. The oxide is normally deposited on glass to promote adhesion of subsequent "active" layers in the photovoltaic cell.

Sessile drop or area-of-spread experiments were initially performed on the Cr-Pd-Au surface finish to characterize the solderability of several solder alloys that satisfied the peak process temperature threshold. The primary candidates were 63Sn-37Pb (T_{mr} = 183°C), 60Sn-40Pb (T_{mr} = 183-188°C), and 80In-15Pb-5Ag (T_{mr} = 148-149°C), where T_{mr} is the melting range. The wetting tests were conducted in a batch furnace without flux in slightly positive nitrogen or vacuum atmospheres at 205-210°C. Subsequent tests included a helium atmosphere. Helium would permit in-situ leak testing of sealed assemblies.

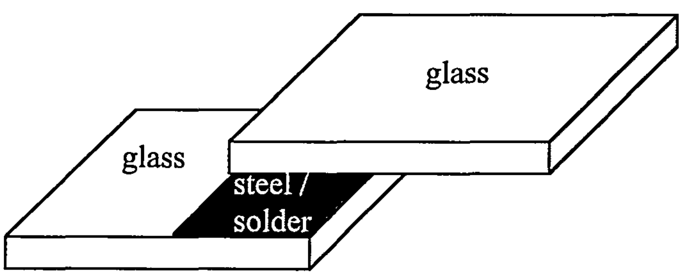

Figure 1. Lap-shear test specimen, glass-(steel)-glass.

Lap-shear mechanical specimens were fabricated. The specimen design is shown in Fig. 1. The glass pieces were 25 x 25 mm square (1 x 1 inches), with either a 6.4 mm (0.25 inches) overlap with a cold rolled steel (SAE 1018) interlayer or 12.7 mm (0.5 inches) overlap without an interlayer. The steel spacer simulated a metal standoff used in the solar panel design. To facilitate fluxless soldering, the steel piece was electroplated with 3.8 µm (150 µin.) of Ni, followed by 1.3 µm (50 µin.) of Au. Solder preforms were sandwiched between the glass and metal pieces. The preforms were 0.127 mm (0.005 inches) thick and degreased with isopropyl alcohol before assembly. The mechanical samples were soldered on a controlled temperature hot plate or in an inerted, conductive reflow machine. The reflow machine had four hot zones, with the zones set at 100°C, 160°C, 246°C, and 120°C. Travel speed was 2 mm/s (5 inches/min). Nitrogen flow rate was set at 30 scfh. This profile gave a topside glass temperature of 210-215°C. Similar topside temperatures, ± 5°C, were obtained with the hot plate. Time above the melting temperature was generally 30 to 45 s.

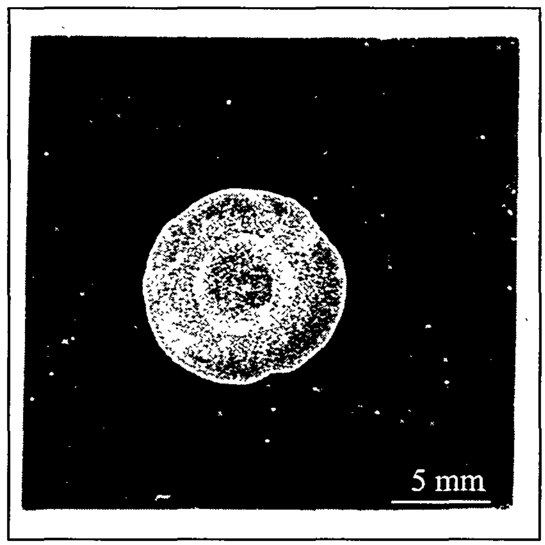

Figure 2. Metallized soda-lime glass wetting specimen (63Sn-37Pb on Cr-Pd-Au soldered in nitrogen at 210°C).

The shear samples were cut into smaller individual test pieces with an abrasive water saw. The cut surfaces were ground parallel and the shear area was measured. Shear tests were conducted with a servo controlled, closed loop hydraulic test frame in stroke control at 0.01 mm/s. The test fixture was centered on a compression platen. The fixture was designed to hold the specimen upright, with Teflon sheet supporting the sliding surfaces. A "push" plate was positioned over the solder joint to be tested. Shear was applied by pushing the plate between a stationary spacer and the outer fixture block. The resulting breaking load was used to calculate the shear stress.

RESULTS AND DISCUSSION

The wetting results on the Cr-Pd-Au surface finish were generally very good, particularly for the Sn-Pb alloys. The eutectic 63Sn-37Pb alloy demonstrated the best solderability, with contact angles less than 10 degrees (see Fig. 2). Similar wetting was observed on samples processed at 210°C in vacuum, nitrogen, or helium.

The In-Pb-Ag contact angles were higher than the Sn-Pb wetting results, 30-45 degrees, but the values still satisfied good wetting conditions. Based on these results, 60Sn-40Pb alloy foil was exclusively used to fabricate the shear test specimens. In addition to soldering in a protective atmosphere without flux, lap shear specimens were also processed with noncorrosive, rosin (R) flux, adjusted to 25 percent solids. Chemical residues from this R-type flux should not cause any long term corrosion problems if entrapped in the panel because of their general ionic inertness.

Initial shear strength results for glass-steel-glass test specimens averaged 11 MPa (1600 psi), with test values ranging from 7.6-14.7 MPa. The stronger joints appeared to have more solder adhering to the glass pieces. Weaker joints tended to have a web-like coverage of the glass by the solder. Most voids in the joint were caused by dissolution of the metallized film and solder dewetting.

Microanalysis of cross-sectioned glass-steel-glass joints exhibited good coverage and adhesion by the solder to the coated glass and steel pieces (Fig. 3). The solder structure was

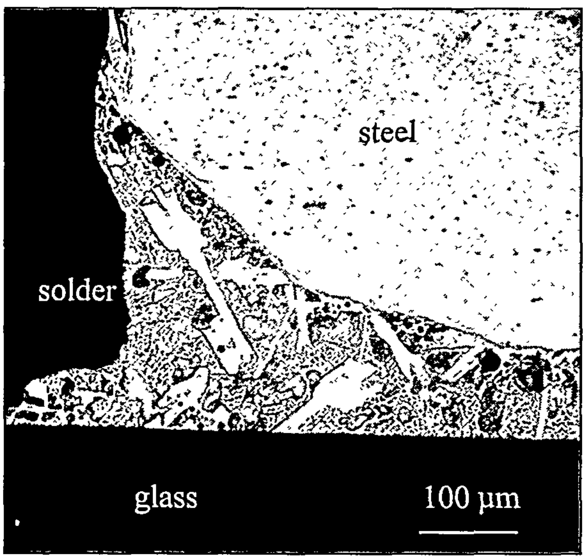

Figure 3. Optical image of glass-steel solder joint processed in nitrogen at 210°C with 60Sn-40Pb.

somewhat inhomogeneous, with three major phases identified by Energy Dispersive Spectroscopy (EDS). There is a Pb-rich dark phase, a plate-like Sn-Au intermetallic phase and the Sn-rich matrix, as shown in Fig. 3. The intermetallic was identified as $AuSn_4$. The relatively low shear strength for these samples was attributed to the high volume of $AuSn_4$ intermetallic in the joint. Subsequent glass pieces were metallized with a thinner overcoat of Au, 1.0 µm, compared to the original thickness of 2.5 µm. The thinner Au coating significantly reduced the amount of intermetallic, with a corresponding increase in shear strength to 15 MPa (2200 psi). Figure 4 shows a sectioned shear specimen that used a 1.0 µm Au overcoat. Without the steel spacer, comparable glass-glass samples yielded 16.5 MPa (2400 psi) strengths. Similar results were obtained for test pieces processed in helium. Shear strength data are summarized in Table 1.

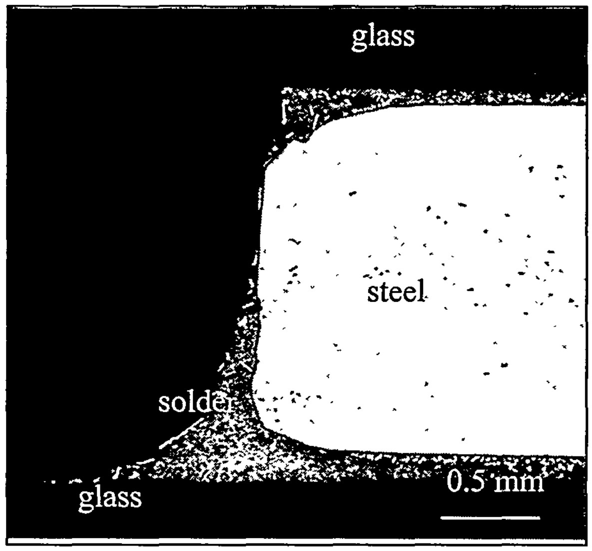

Figure 4. Optical image of glass-steel solder joint processed with 1.0 µm Au glass overcoat.

At this point in the investigation, the focus shifted to a different and more economical metallization scheme. The thin film system was based on a 26Ni-74Cr coating, nominally 75-100Å thick. The coating was deposited by evaporation along the flat surfaces of the smooth and edge-roughened glass substrates. A SnO_2 coating was deposited on the glass before applying the metallic thin film. A final overcoat of Sn, 1.5 µm thick, was deposited over the NiCr layer to minimize loss of solderability due to exposure prior to soldering.

The Sn-Pb solders wetted the NiCr-Sn thin film well, including the edge-roughened glass. The smooth surfaces appeared to have greater solder coverage, 70-80%. However, the rough surfaces exhibited substantially more dewetting, resulting in reduced solder bonding, with as low as 5-30% coverage for samples soldered with the R-type flux. The coverage was 90-100% complete for smooth glass samples soldered without a flux in an inert atmosphere.

To address a potential coating uniformity problem on the rougher glass surface, three different coating thickness of NiCr were evaluated, 100, 1000 and 10,000Å. The 100 Å coating was the baseline thickness. There was less NiCr film dissolution and dewetting by the solder on these surfaces than on the first set of processed samples, probably due to better process control during the latter deposition procedure. Earlier efforts yielded incomplete glass coverage, particularly in the "valleys" of the roughened features. Figure 5 shows an image of a glass-glass joint, using the NiCr-Sn thin film and 60Sn-40Pb solder. The sample was processed at 220°C without a flux. The joint does not contain any intermetallics and exhibits a typical Sn-Pb eutectic microstructure.

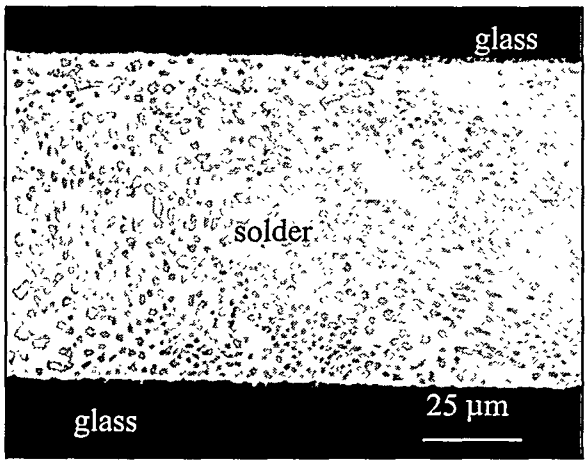

Figure 5.. Optical image of a cross-sectioned glass-glass solder joint, with NiCr-Sn thin film and 60Sn-40Pb solder.

Shear strengths were measured for samples with different glass surface conditions (rough vs. smooth), different NiCr-Sn glass coating thickness, and different soldering conditions (atmosphere and flux)/no flux). The results are summarized in Table 1. The lap shear strength for smooth-to-smooth glass samples was in the range of 20.5-23.0 MPa (3000-3300 psi), with failures primarily in the glass. The smooth-to-rough glass joints failed at lower values, having a larger distribution range, from 9.0-14.5 MPa (1300-2100 psi). The smooth-rough samples generally failed along the glass and solder interface on the "rough" side of the joint.

The lower bond strengths for the soldered rough (edge-roughened) surfaces were attributed to the removal of the intermediate SnO_2 film during the edge-roughening operation and variable NiCr-Sn coating thickness. Its absence appears to have reduced the overall adhesion of the succeeding thin films. It is also likely that the roughening process introduced surface flaws or cracks that lowered joint strengths.

To determine the effectiveness of the protective nitrogen cover during reflow, experiments were performed in air with the R-type flux. The resulting joints exhibited more voids and dewetting than those samples processed in nitrogen or helium. Shear strengths ranged from 5 to 19 MPa, depending on the surface condition and percent bonded. These tests were conducted on the 100Å NiCr – 1.5 µm Sn - SnO_2 thin film surface finish. The protective atmosphere clearly enhanced solder wetting and joint strength.

Finally, the effect of SnO_2 on bond strength was investigated. Individual 25 x 25 mm (1 x 1 inch) NiCr-Sn coated glass coupons without SnO_2 were fabricated. Shear test specimens were soldered using the same processing and test conditions used to evaluate the SnO_2 coated glass substrates. The NiCr thickness was 100 Å. The resulting smooth-smooth glass shear strengths were nominally 20.0 MPa (2860 psi), comparable to the SnO_2 coated samples. Therefore, the lower strengths of the roughened samples appear to be more influenced by induced surface flaws and uneven coating introduced by the roughening process.

Based on the above soldering results, plans were made to fabricate a scaled–down version of the actual solar module, whose full scale measurements are 0.6 x 0.6 m (24 x 24 inches). The dimensions for the prototype assembly were 150 x 150 mm (6 x 6 inches). Four glass plates, without the SnO_2 film, were metallized with 100 Å NiCr and 1.5 µm Sn along the outer 12.5 mm (0.5" inch) plate perimeter. A resistance heater was designed and fabricated to direct heat to a very localized region around the glass perimeter. The thermal energy was supplied to the exposed sides of the stacked glass panels via an aluminum electrical resistance heating element embedded in an insulating block. Before the soldered prototype assemblies could be processed, the project ended.

The results from the development work did demonstrate the feasibility of the thin film and soldering process. They also serve as the baseline for conducting future materials compatibility experiments, including addressing field performance and reliability issues, such as the long-term response to thermal, mechanical, and corrosive environments. A better understanding of how the solder process and service conditions affect stress levels, which are expected to play an important role in joint reliability, can be obtained through finite element stress modeling. Finally, the issue of Pb-containing solders and their impact on the environment need to be considered (NCMS, 1999).

CONCLUSION

A thin film, glass soldering process was developed for hermetically sealing glass panels in solar modules. Wetting and shear test specimens were processed with Sn-Pb and In-Pb-Ag solders. Glass pieces were metallized with Cr-Pd-Au or NiCr-Sn coatings to facilitate solder wetting. Control of the deposited Au thickness was critical in minimizing brittle $AuSn_4$ intermetallic in the joint, with 1 µm or less required. Glass-to-glass test specimens with 1 µm Au had an average shear strength of 16.5 MPa. The NiCr-Sn thin film yielded the highest shear strengths, up to 23.0 MPa. A smooth glass surface with an intermediate film of SnO_2 enhanced the NiCr adhesion to the glass and by the solder. The use of a protective nitrogen atmosphere with the rosin flux also yielded better solderability results than air soldered samples. Materials compatibility and joint performance under service conditions require further investigation.

ACKNOWLEDGMENTS

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Table 1.
Shear Strength of Metallized Glass Soldered Test Specimens (tested in stroke control at 0.01 mm/s)

Metallized Shear Test Specimen	Soldering Conditions	Smooth-to-Smooth Glass, MPa (psi)	Smooth-to-Rough Glass, MPa (psi)
AuNi/Steel-to-CrPd2.5μmAu/Glass	210°C in N_2, no flux	10.9 ± 2.7 (1580 ± 400)	none tested
Glass-AuNi/Steel-Glass (CrPd1.0μmAu on Glass)	210°C in He, no flux	15.2 (2200)	none tested
Glass-to-Glass (with CrPd1.0μmAu)	210°C in He, no flux	16.5 (2400)	none tested
Glass-to-Glass (< 100 Å NiCr-Sn coating)	220°C in N_2, R flux	11.6 ± 1.2 (1675 ± 180) ~ 50% bonded	2.1 (300) ~ 20% bonded
Glass-to-Glass (100 Å NiCr-1.5μm Sn)	220°C in N_2, R flux	23.0 ± 0.6 (3335 ± 85)	14.8 ± 3.9 (2140 ± 560)
Glass-to-Glass (100 Å NiCr-1.5μm Sn)	220°C in air, R flux	18.6 (2690) ~ 90% bonded	4.8 (690) ~ 50% bonded
Glass-to-Glass (without SnO_2 glass film + 100 Å NiCr-1.5μm Sn)	220°C in N_2, R flux	19.8 ± 1.9 (2860 ± 280)	none tested
Glass-to-Glass (1000 Å NiCr-1.5μm Sn)	220°C in N_2, R flux	23.0 ± 2.8 (3340 ± 400)	9.6 ± 1.5 (1830 ± 220)
Glass-to-Glass (10000 Å NiCr-1.5μm Sn)	220°C in N_2, R flux	20.9 ± 3.7 (3030± 530)	9.0 ± 4.0 (1310 ± 580)