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WELD BONDING OF TITANIUM WITH POLYIMIDE ADHESIVES

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16. Abstract

A conductive adhesive primer and a capillary flow adhesive were developed for weld bonding titanium alloy joints. Both formulations contained ingredients considered to be non-carcinogenic. Lap-shear joint test specimens and stringer-stiffened panels were weld bonded using a capillary flow process to apply the adhesive. Static property information was generated for weld bonded joints over the temperature range of 219K (-65°F) to 561K (550°F). The capillary flow process was demonstrated to produce weld bonded joints of equal strength to the weld through weld bonding process developed previously under this contract.

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WELD BONDING OF TITANIUM WITH POLYIMIDE ADHESIVES

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SUMMARY

The objective of this program was to perform a development study to assess the potential of weld bonding titanium with polyimide adhesives. This objective was accomplished by 1) evaluating polyimide adhesives and developing detailed processing procedures for fabricating weld bonded joints, 2) performing static and fatigue tests on weld bonded joints, and 3) demonstrating the applicability of the weld bonding process for fabricating stringer-stiffened skin panels.

During this program, the P4/A5F polyimide adhesive developed under Contract NAS 1-9532 was evaluated for weld bonding. This work was reported in NASA CR-132434, Polyimide Weld Bonding For Titanium Alloy Joints. Because one of the ingredients in the P4/A5F adhesive formulation was identified as potentially carcinogenic, an additional task was added to the program to evaluate alternative adhesive formulations.

During this additional task, polyimide adhesives containing aromatic diamines considered to be non-carcinogenic were evaluated. A conductive adhesive primer was developed which permitted resistance spot welding through primed titanium alloy components. Also, a capillary flow adhesive was developed consisting of a high flow A-type polyimide resin and an amine chain extended *bis*maleimide resin. Detailed evaluation of weld bonded joints established that there was no significant difference in the strengths of joints formed by either weld-through or capillary flow processes.

I. INTRODUCTION

This final report presents the work accomplished by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS 1-11689 during the period 10 February 1974 through 28 March 1975. The objective of this program was to perform a development study to assess the potential of the application of resistance spot welding-polyimide adhesive bonding to structural panel fabrication. TRW Systems demonstrated the feasibility of fabricating weld bond joints under Purchase Order L66.028 for NASA Langley Research Center using the polyimide adhesive developed by TRW Systems under Contract NAS1-9532. During this program under Tasks I, II and III, the adhesive system (P4/A5F) developed under Contract NAS 1-9532 and the weld-through weld bonding process used to fabricate specimens under Purchase Order L66.028, were optimized. Also, a new capillary-flow weld bond process was developed. Detailed static and dynamic mechanical properties of weld bonded lap shear test specimens were determined and the applicability of the process for fabricating structural, stringer-stiffened skins was demonstrated. These stringer-stiffened skin panels then were tested by TRW Systems in various test environments. Lap shear specimens and structural test panels also were supplied to NASA Langley Research Center for independent evaluation. This work was documented in NASA CR-132434 (Reference 1).

An additional Task IV then was added to the program to evaluate alternative adhesive formulations to the P4/A5F adhesive system previously used. This was necessary because one of the key ingredients in the P4/A5F resin formulation has been identified as potentially carcinogenic and consequently has been withdrawn from commercial availability. Task IV repeated most of Tasks I, II and III (Reference 1), using addition-type polyimide adhesives containing aromatic diamines considered to be non-carcinogenic and supplied by NASA Langley Research Center. The work was concentrated on the development and evaluation of a capillary flow weld bonding process. Key technical requirements during this effort were to develop a weld-through adhesive primer and to develop an adhesive which

would flow through spot welded joints and fill the gap in the joint. A weld-through adhesive primer was required in order to obtain good adhesion to the prepared titanium alloy surface prior to oxidation. The capillary flow process necessitates exposure of the welded joint to a 533K (500°F) to 589K (600°F) air environment which increases the oxidation rate.

Development of an adhesive system for the capillary flow process provided requirements not usually associated with adhesive development activities. These requirements included high flow during cure (the opposite to most adhesive applications) as well as providing good gap filling characteristics (usually applicable to casting resins). Consequently, the main thrust during Task IV was to optimize resins and adhesive formulations to meet these requirements, whereas previous efforts had concentrated on optimization of adhesive properties (Reference 1, 2 and 3).

The Task IV activities described in this volume consisted of repetition of the earlier work (Reference 1) except the fatigue tests were omitted. This task was planned to develop a capillary flow weld bonding process using resins considered to be non-carcinogenic and to demonstrate that the subsequent weld bonded joints are equivalent to those reported previously (Reference 1).

This volume is divided into sections covering each of the key activitity areas:

- Resin Development
- Weld Bonding Process Development
- Weld Bonding Process Evaluation
- Structural Panel Fabrication and Evaluation.

The significant conclusions reached and assessments of the results are listed together with recommendations for activities that warrant

further investigations. The information presented in the main body of this volume is supplemented by appendices covering detailed descriptions of procedures used in material preparation and processing.

2. RESIN DEVELOPMENT

During earlier developmental activities on this program (Reference 1) an A-type polyimide resin containing nadic anhydride (NA), thiodianiline (TDA) and *bis*(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA) showed promise as a capillary flow adhesive resin. However, TDA was identified by the manufacturer as a potential carcinogenic material and was withdrawn from commercial availability. Consequently, further developmental studies with TDA-containing resins were discontinued. Recent work at NASA Langley Research Center has identified two new diamines which offer promise as replacements for TDA. These diamines have been used successfully by NASA in adhesive resin formulations and were obvious candidates for capillary flow weld bonding. Resin development and screening studies therefore were performed by TRW Systems under this program in order to identify a candidate capillary flow adhesive resin using the new diamines.

2.1 DEVELOPMENT OF NADIC CAPPED POLYIMIDE RESINS

Two prepolymers of 1300 formulated molecular weight (FMW) were prepared from NA, benzophenone tetracarboxylic acid dianhydride (BTDA), and the two new diamines, *m*,*m*'methylenedianiline (*m*,*m*'MDA) and 3,3'-diaminobenzophenone (*m*,*m*'DABP). Each prepolymer was initially prepared in dimethyl formamide (DMF) and then the solvent was removed at reduced pressure to give the amide-acid prepolymer. The resulting residue was dried *in vacuo* at 443K (338°F) to afford the imidized prepolymer.

The melt-flow cure characteristics of the imidized resins then were determined by heating samples of the prepolymers on a Fisher-Johns melting point apparatus. Both resins displayed the desired low melting point as shown in Table I. The resins then were tested for gel time and cure time at various temperatures (see Table I).

TABLE I.
PRELIMINARY EVALUATION OF NEW PREPOLYMERS

PROPERTY	DIAMINE USED IN PREPOLYMER	
	m,m'-methylenedianiline	3,3'-diaminobenzophenone
Temp. of Complete Melt, K/°F	478/401	508/455
Gel Time at Temp., Min.		
533K/500°F	12	12
547K/525°F	6	6
561K/550°F	6	6
575K/575°F	5	5
Cure Time at Temp., Min.		
561K/550°F	>60	>60
575K/575°F	45	45

The two resins displayed the same gel and cure times at the same temperatures (see Table I) which was expected because these properties are dependent on the nadic end-cap chemistry. The one observed difference in these resins was the melting point value, *i.e.*, the *m,m'*MDA resin melts 30K below the *m,m'*DABP analogue. Preliminary weld bonding studies also indicated that the *m,m'*MDA provided promising resin flow, whereas the *m,m'*DABP containing prepolymer was unsatisfactory (see Section 3).

Based on the results of the preliminary adhesive screening studies, new prepolymer formulations were prepared from *m,m'*MDA and characterized. Two prepolymer formulations were prepared in which a part of the *m,m'*MDA was replaced with *p,p'*MDA. (It was expected that the flow properties for these resins would be decreased). The characterization studies showed that the 50:50 *m,m'*:*p,p'* formulation did not possess the necessary melt flow properties for use as a capillary flow adhesive. However, the 70:30 *m,m'*:*p,p'* formulation did show promise and was selected for use in the adhesive screening studies. The results of the characterization studies are given in Table II.

TABLE II.

PRELIMINARY EVALUATION OF PREPOLYMER FORMULATIONS

Formulation	Temperature of Complete Melt, K/°F	Gel Time at Temp., Min.	
		561K/550°F	575K/575°F
1300 FMW NA/50 *m,m'* MDA:50*p,p'* MDA/BTDA	533/500	10	5
1300 FMW NA/70 *m,m'* MDA:30*p,p'* MDA/BTDA	528/491	12	5
NA/*m,m'* MDA/BSDA	461/370	10	5

2.2 DEVELOPMENT OF ADDITION CURE POLYIMIDE RESINS

The results obtained during the initial adhesive screening studies (see Section 3) showed that the NA/*m*,*m*'MDA/BTDA (1300 FMW) resin was the most promising formulation investigated at that time for use as a capillary flow adhesive. However, inspection of the weld bonded specimens showed void areas present (*i.e.*, the resin did not gap-fill). It was concluded that the voids were caused by evolution of cyclopentadiene formed in the reverse Diels-Alder reaction of the nadic end-caps. Consequently, several approaches were investigated to decrease or eliminate the volatile formation.

The first resin investigated as a possible candidate to reduce the amount of cyclopentadiene evolved during cure was an n = 4 formulation (FMW 2427) of NA/*m*,*m*'MDA/BTDA. This resin, however, displayed only limited melt-flow properties at temperatures up to 575K (575°F). The other approach utilized maleic anhydride (MA) capped prepolymers prepared from *m*,*m*'MDA and BTDA. The first MA capped formulation studied also was prepared with n = 4. Again the resin displayed very little flow at 561K (550°F) or at 575K (575°F). In view of these results, another nadic capped resin was prepared with n = 3, which was found to possess improved flow characteristics over the n = 4 formulation.

Evaluation of these resins during the capillary flow development studies were unsuccessful (see Section 3). However, these studies also indicated that the Kerimid 601, an amine chain extended *bis*maleimide resin, possessed high potential of providing satisfactory gap-fill. As a result, other amine chain extended *bis*maleimide resins were prepared and evaluated

in the adhesive screening studies. The first resin was prepared from the B-type diamine, *bis*(4-aminophenoxyphenyl)sulfone (BDAS), and *bis*(4-maleimidophenyl) methane (BMPM). This combination of ingredients was selected because it results in a higher molecular weight species as compared to Kerimid 601 and more flexible bonds also are present. As a result, the resin was expected to be less brittle than Kerimid 601. The BDAS/BMPM resin displayed outstanding flow and film forming characteristics and was evaluated in the adhesive screening studies (see Section 3).

The final resin prepared for evaluation was the reverse case of the resin described above. Using the same formulation (*i.e.*, ratio of diamine to maleimide), a resin was prepared from *m,m'*MDA and the *bis*maleimide of BDAS. This resin also was evaluated in the adhesive screening studies (see Section 3).

3. WELD BONDING PROCESS DEVELOPMENT

The key steps involved in the development of a capillary flow weld bonding process consisted of primer development, capillary flow adhesive formulation and cure cycle screening. The primer development activities were concerned with formulation of an adhesive primer which possessed low electrical resistance to permit current to flow through during welding. This adhesive primer also had to provide protection to the titanium alloy during cure of the capillary flow adhesive. Another concern addressed during this work was whether the adhesive primer degraded the weld nugget due to contamination during welding. Capillary flow adhesive development activities addressed the unusual combination of requirements for high flow during cure, complete surface wetting and provision of a solid, void-free resin casting in the weld joint. The gap to be filled with the capillary flow adhesive varied from <0.03 mm (0.001-inch) to >0.3 mm (0.010-inch). These requirements were met during the developmental activities described in this section and a satisfactory capillary flow weld bonding process was identified for preparation of subsequent test specimens and panels (see Sections 4 and 5).

3.1 WELD-THROUGH PRIMER DEVELOPMENT

In order to define a specific primer formulation for subsequent detailed capillary flow weld bonding evaluations, it was necessary to identify a procedure for screening candidate primers. A Surface Resistance Analyzer (see Figure 1), which measures the resistance of surface coatings, was utilized to fulfill this requirement. The resistance measurements provided a good indication as to the ability of the substrate to be welded. During the primer development effort two metal fillers were evaluated and promising primers were developed utilizing both of these fillers, *i.e.*, aluminum powder and silver flake. However, due to handleability problems with the aluminum powder, the primer formulations selected for further evaluation used silver flakes as the conductive metallic filler. The resin used in the primer screening studies consisted of NA/*m*,*m*'MDA/BTDA (an A-type polyimide similar to P13N); with the two metal fillers being powdered aluminum (Alcoa 101) and silver flake (Silflake). These formulations are shown in Table III with the results tabulated in Table IV. Formulation VII was similar to P4 primer which was previously used on the program, except that *m*,*m*'MDA was used instead of TDA and MPD. The second phase of the primer development was to ascertain the primer bonding qualities. This was accomplished by bonding lap-shear panels primed with the candidate adhesive primer formulation.

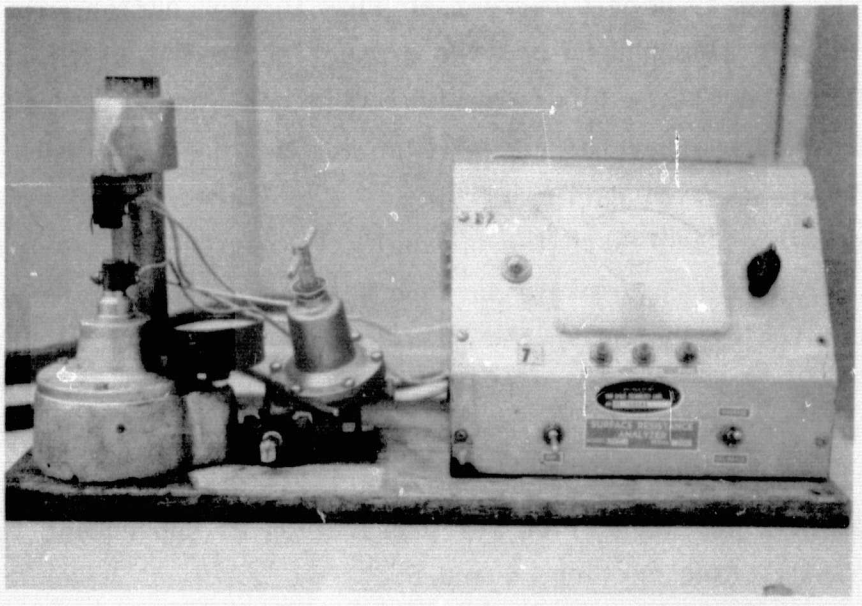

Figure 1. Surface Resistance Analyzer

TABLE III.

FORMULATIONS USED IN PRIMER SCREENING STUDY[1]

Constituent	Formulation (pbw)						
	I	II	III	IV	V	VI	VII
NA/*m,m'*MDA/BTDA	4.5	2.3	2.3	2.3	2.3	2.3	1.1
Amoco AI 1137	-	-	-	-	-	-	1.1
Dimethyl formamide (DMF)	11.5	5.2	5.2	5.2	5.2	5.2	8.5
Aluminum Powder (Alcoa 101)	10.0	6.0	7.0	-	-	-	-
Silver Flake (Silflake)	-	-	-	5.0	6.0	7.0	7.0

[1] Substrate used was 6Al4V titanium alloy, prepared using the Pasa-Jell pretreatment.

TABLE IV.

RESULTS PRIMER SCREENING STUDY[1]

Property/Observation	Formulation						
	I	II	III	IV	V	VI	VII
Thickness coating mm/inch x 10^{-3}	.025/1.0	.025/1.0	.025/1.0	.025/1.0	.005/0.2	.005/0.2	.013/0.5
Surface Resistance x 10^{-8} ohms	(2)	(2)	(2)	(2)	8.5	5.0	6.0
Spot Weld, 6Al4V Titanium	-	W[3]	W[3]	-	W[3]	W[3]	W[3]

[1] Substrate used was 6Al4V titanium alloy, prepared using the Pasa-Jell pretreatment.

[2] Surface Resistance exceeded machine capability to measure.

[3] W - Lap-shear was successfully welded through primer coating.

The values obtained (Table V) were higher than bonded-only values previously obtained on the program. In addition to studying the adhesive quality of the primer, processing conditions were evaluated. Based on the results shown in Table V, the following primer processing conditions were selected for subsequent capillary flow weld bonding experiments:

Substrate:	6Al4V Titanium Alloy
Cleaning Procedure:	Pasa-Jell
Primer Thickness:	0.025mm (0.001-inch) minimum
Drying Conditions:	60 minutes at 298K (72°F) 60 minutes at 334K (150°F)
Staging Conditions:	45 minutes at 408K (275°F) 5 minutes at 450K (350°F)

TABLE V.

SUMMARY OF PRIMER ADHESION STUDY(1)

(3) Staging Cycle K/Min.	Lap Shear Strength		Failure Mode Percent cohesive/ adhesive
	Load N x 10^3 (lbs)	Ultimate Stress Pascals (psi)	
298/60	20.9 (4700)	16.2 (2350)	70/30(2)
334/60	19.3 (4350)	15.0 (2170)	80/20(2)
	22.0 (4935)	17.0 (2470)	90/10
298/60	19.8 (4460)	15.4 (2230)	90/10
334/60	21.2 (4770)	19.5 (2835)	95/5
488/45			
450/5	18.0 (4040)	13.9 (2020)	90/10
298/60	18.8 (4220)	14.5 (2110)	50/50(2)
334/60	17.9 (4020)	13.9 (2010)	60/40(2)
488/45	14.1 (3170)	10.9 (1585)	60/40(2)
450/5			
562/60			

(1)Substrate used was 6Al4V titanium alloy, prepared using the Pasa-Jell pretreatment.

(2)Primary failure mode was primer failure.

(3)Cure cycle: Apply 0.69 Pascals (100 psig) pressure at room temperature, then heat at 10K/min to 562K (550°F), hold for 60 minutes, cool under pressure to below 450K (350°F). Place panel in 562K (550°F) air circulating oven for 16 hours, then cool to ambient conditions.

Work then proceeded in the formulation of a capillary flow adhesive and development of a cure cycle for capillary flow weld bonding. However, during preliminary activities (see Section 3.2), lower breaking loads of welded joints (<23 x 10^3N) were observed than obtained previously (~30 x 10^3N). Consequently, a failure analysis of the titanium alloy spot welds was performed in order to determine whether the conductive primer was degrading the weld nuggets or if the lower values were a result of a non-optimized welding schedule. (A new welding machine had been installed and was being used for welding these test specimens.)

Two lap shear panels were prepared using the same lot of titanium alloy and the same cleaning procedure as reported previously. One panel was primed with the weld-through conductive primer and the other unprimed panel was used as the control. The panels were welded and treated as follows:

Panel 1 - Welded-only with no primer
- 50-1-1 Analyses on untested specimens
- 50-1-2 Analyses on tested specimens
- 50-1-3 Analyses on tested specimen after specimen underwent heat cycle of weld bond process

Panel 2 - Welded-through primer coat
- 50-2-1 Analyses on untested specimen
- 50-2-2 Analyses on tested specimen
- 50-2-3 Analyses on weld bonded specimen

The breaking load values for specimens 50-1-2 and 50-1-3 were 28.2 x 10^3 (6350 lbs) and 30.2 x 10^3 (6785 lbs), respectively, and for specimens 50-2-1 and 50-2-2 the values were 27.2 x 10^3 (6120 lbs) and 27.8 x 10^3 (6250 lbs), respectively.

Metallographic and electron microprobe analyses were performed in order to assess the effectiveness of the spot welding process. Emphasis of these analyses was directed toward:

- The degree of homogenization and penetration at the weld interface.
- The presence or absence of weld defects such as voids, porosity, cracks, *etc*. and the mechanism of formation of such defects.
- Chemical and metallurgical characterization of any second phase which may be detrimental to the weld quality.

Samples studied in this investigation (see Figures 2 through 6) were cut with a slow speed diamond saw and mounted so that the weld area could be examined in cross-section (see Figure 7). The most prominent features

Figure 2. Unprimed Lap Shear Test Specimen
(Broken specimen showing pulled nugget type of failure.)

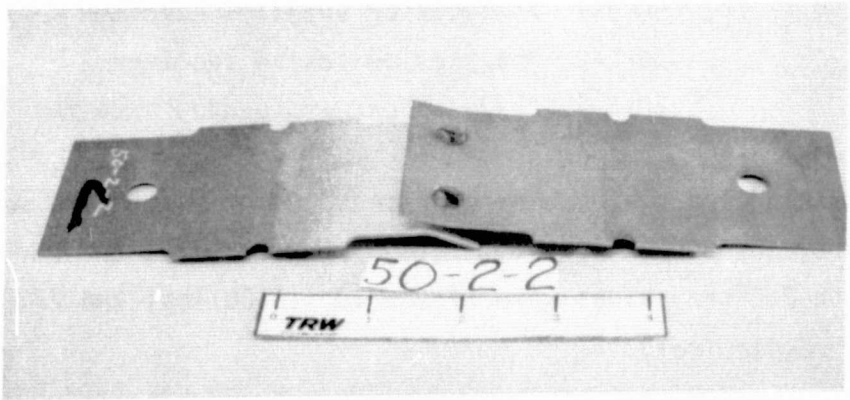

Figure 3. Primed Lap Shear Test Specimen
(Faying surfaces coated with conductive silver-filled adhesive primer, welded and then broken.)

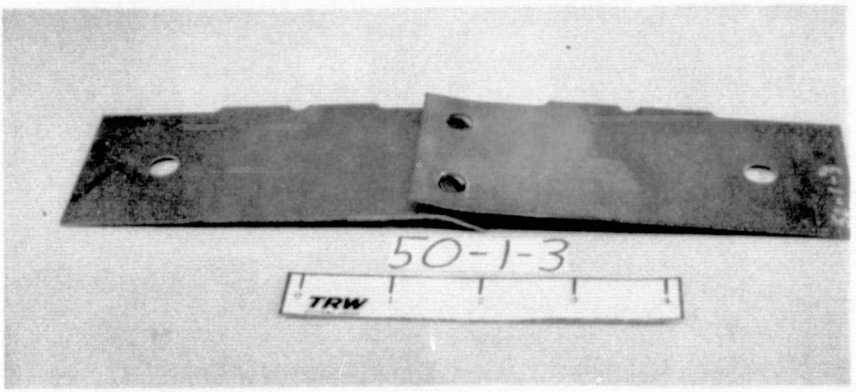

Figure 4. Control Test Specimen

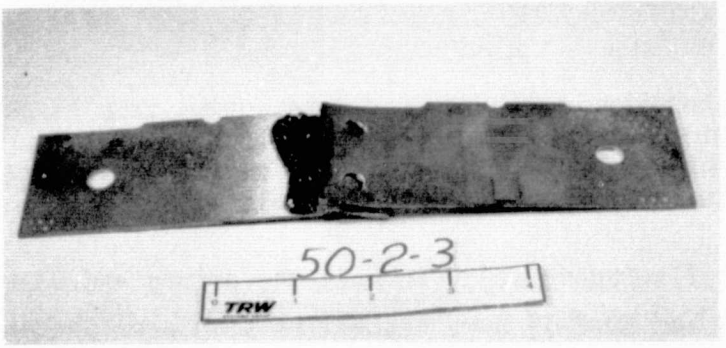

Figure 5. Capillary Flow Weld Bonded Specimen

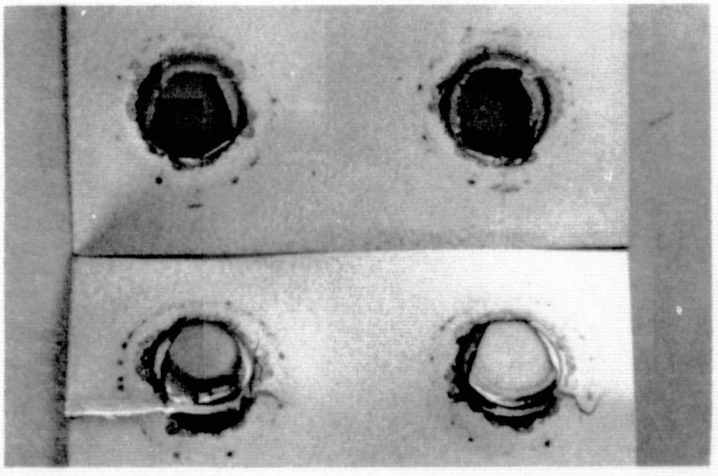

Figure 6. Faying Surfaces of Primed Specimen (Close-up view of primed specimen after testing showing partially carbonized, brown resin spots in the heat affected zone around the weld.)

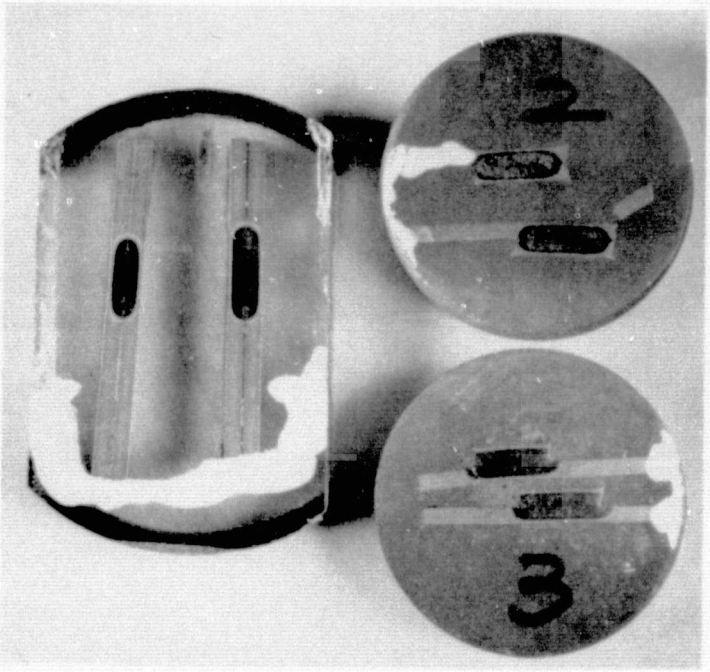

Figure 7. Mounted Samples (Dissected weld nugget samples mounted ready for examination. White areas are silver paint. Mount 1 contains unbroken samples, Mount 2 contains broken samples, and Mount 3 contains broken weld bonded samples.)

observed by metallographic study in both the primed and unprimed control samples (50-1-1 and 50-2-1) were crack-like void areas extending inward from the weld periphery and confined to the vicinity of the bonding interface (see Figures 8 through 14). Void areas were formed near the weld interface due to pulling out in the shear test (see Figures 17 and 18).

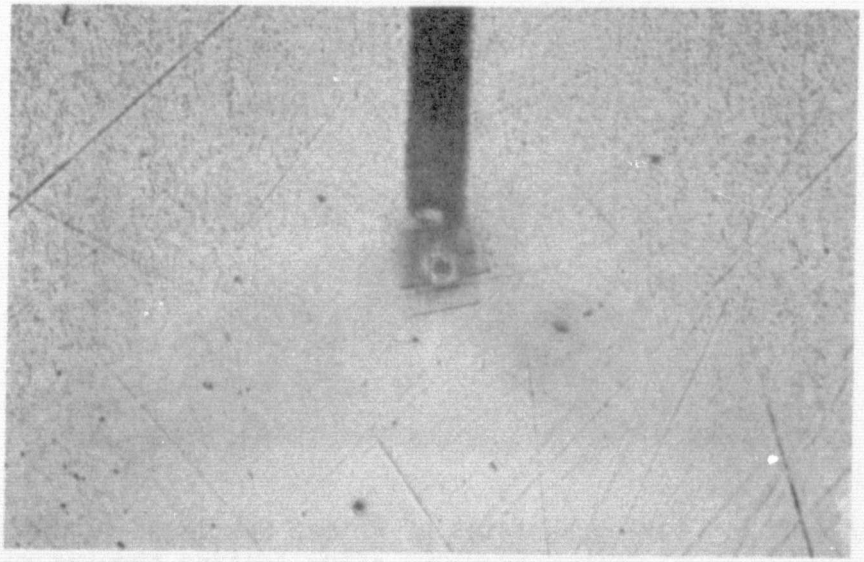

Figure 8. Control Weld Nugget at 50X. (Low magnification picture of sample. The darkened area, horizontal lines and round "hole" near the weld edge are due to microprobe beam damage.)

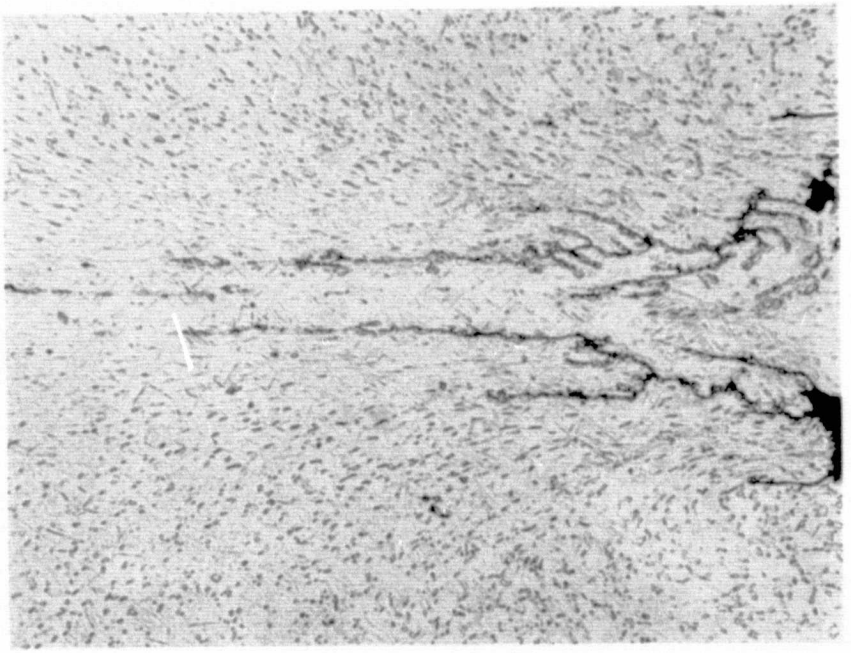

Figure 9. Control Weld Nugget at 400X. (Unbroken section of control weld nugget after etching. Crack-like extensions from the weld periphery into the weld area are shown.)

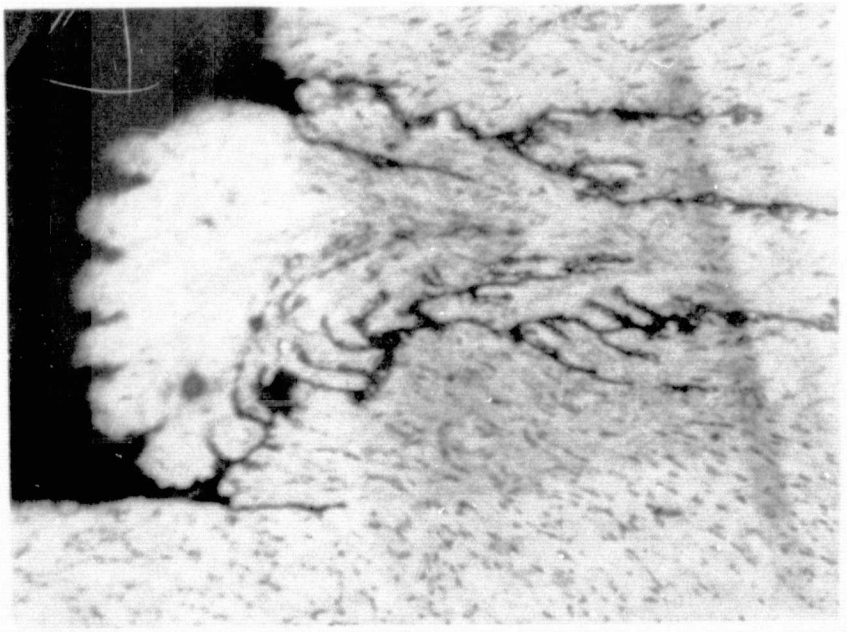

Figure 10. Control Weld Nugget at 600X. (Showing squeezed out flow-type structure adjacent to the weld area.)

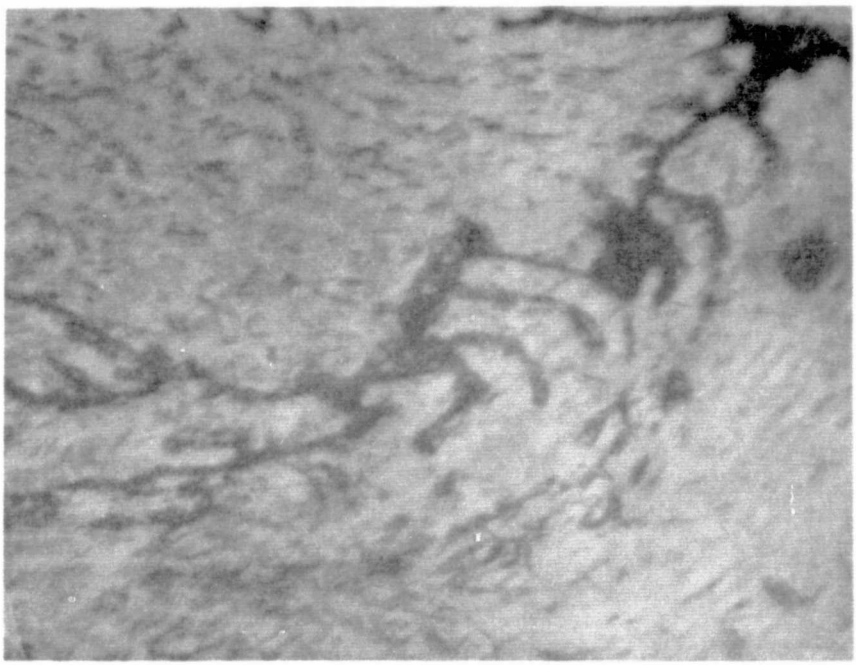

Figure 11. Control Weld Nugget at 1200X

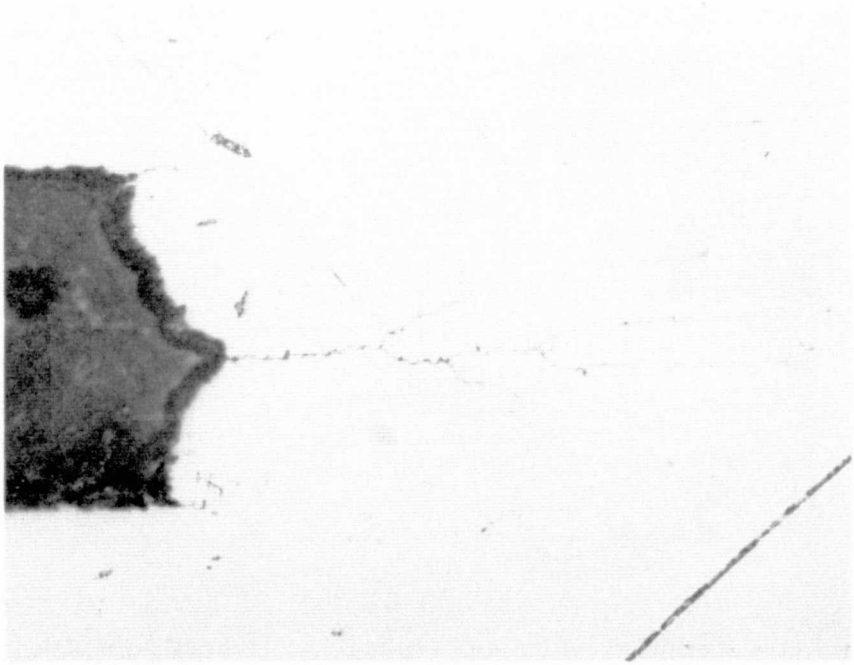

Figure 12. Opposite View of Control Weld Nugget at 400X. (Shows opposite view of weld nugget with crack-like extensions.)

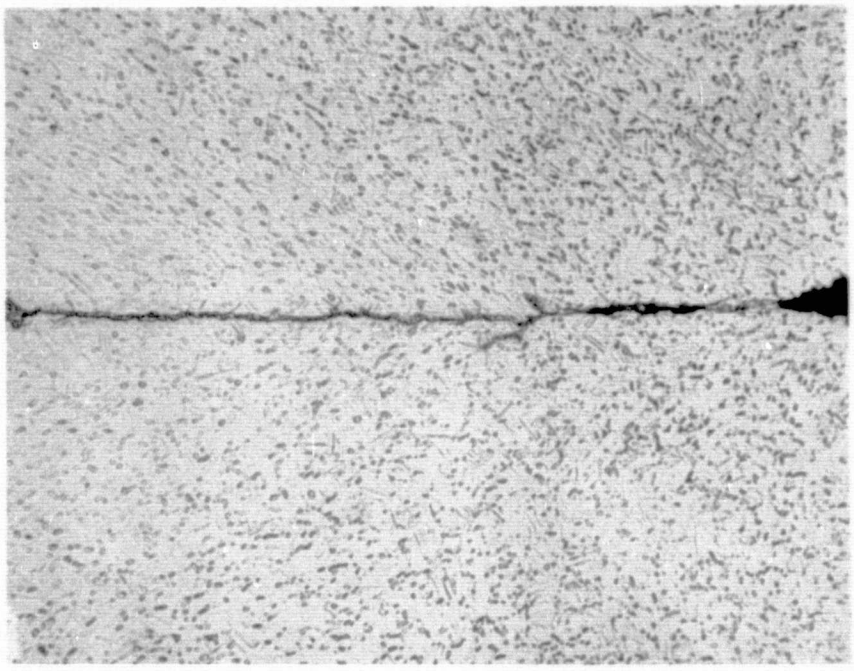

Figure 13. Weld Nugget of Primed Specimen at 400X. (Primed sample showing crack-like extension from the weld edge to the interior.)

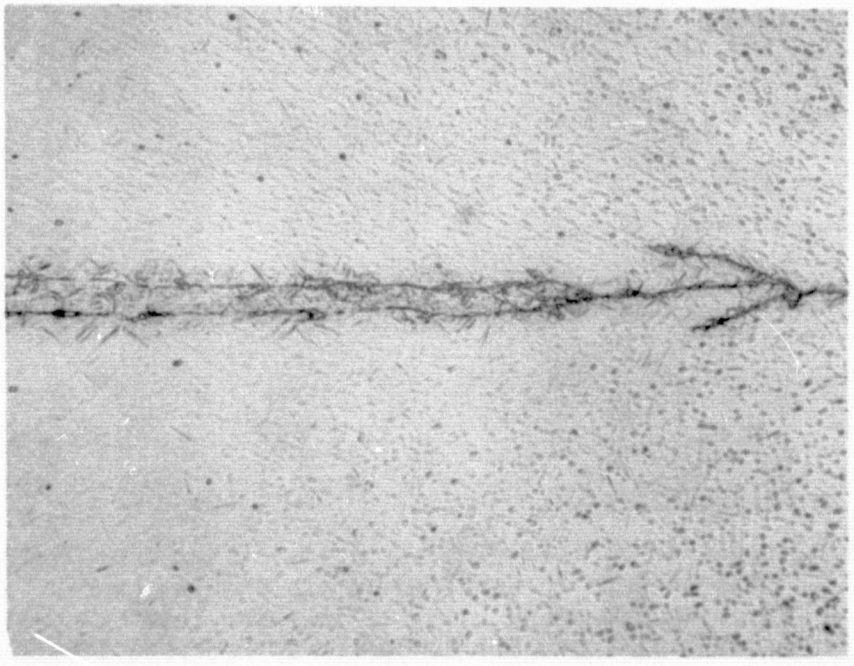

Figure 14. Interior of Weld Nugget at 400X. (Continuation of the crack-like extension shown in Figure 13 further into the interior.)

Photomicrographs of the weld cross-sections of the primed and unprimed samples showed crack-like voids near the edge of the weld extending to about 0.25mm in the unprimed and 1.0mm in the primed sample (see Figures 15 and 16).

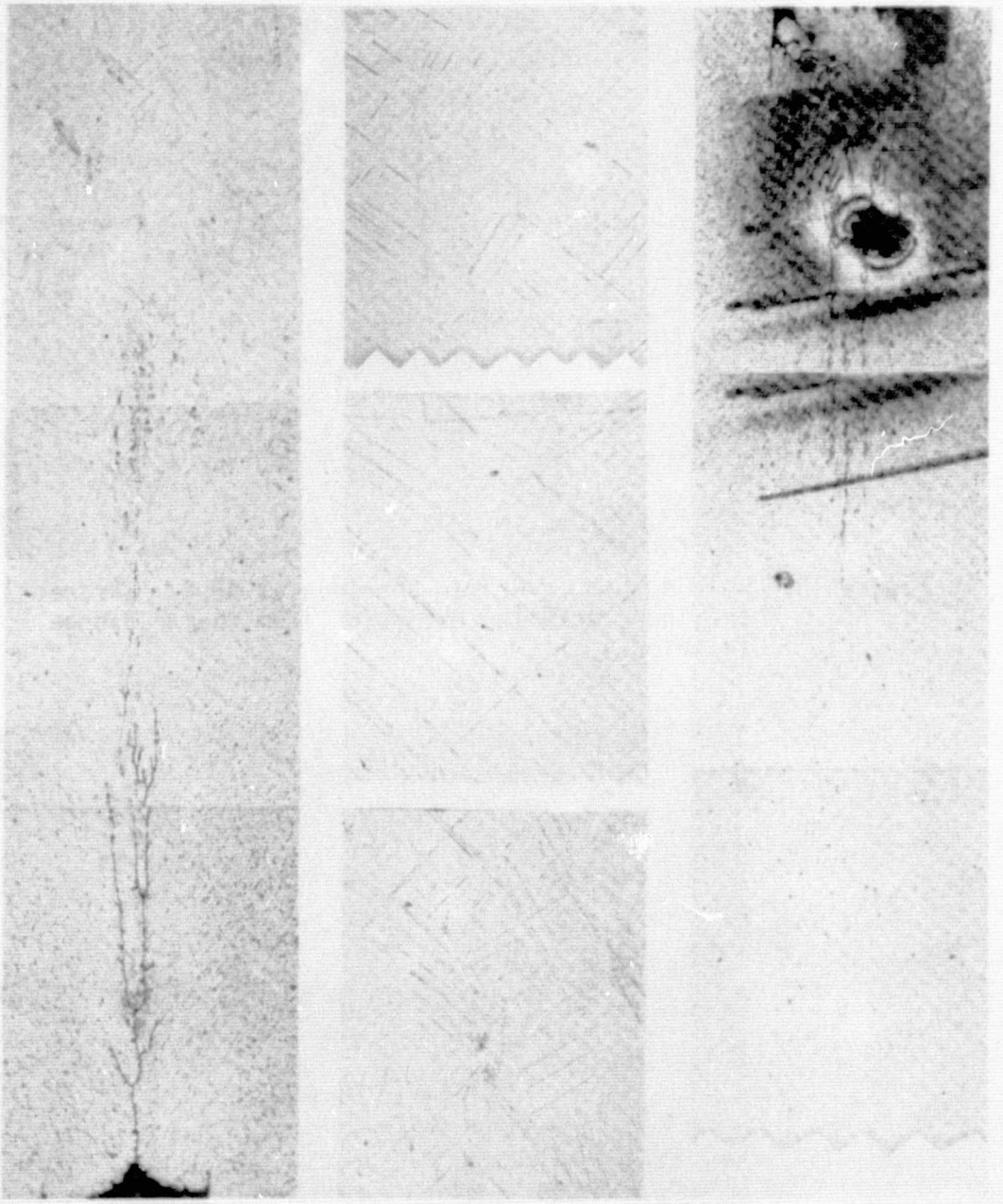

Figure 15. Composite Picture of Control at 15X. (Composite picture of mid-plane of weld in unprimed sample showing crack-like voids and porosity extending into the interior from the periphery. Only a small part of well homogenized, recrystallized, void-free center section of the weld is shown. Broad black lines and hole, and darkened area on the right are microprobe burn marks.)

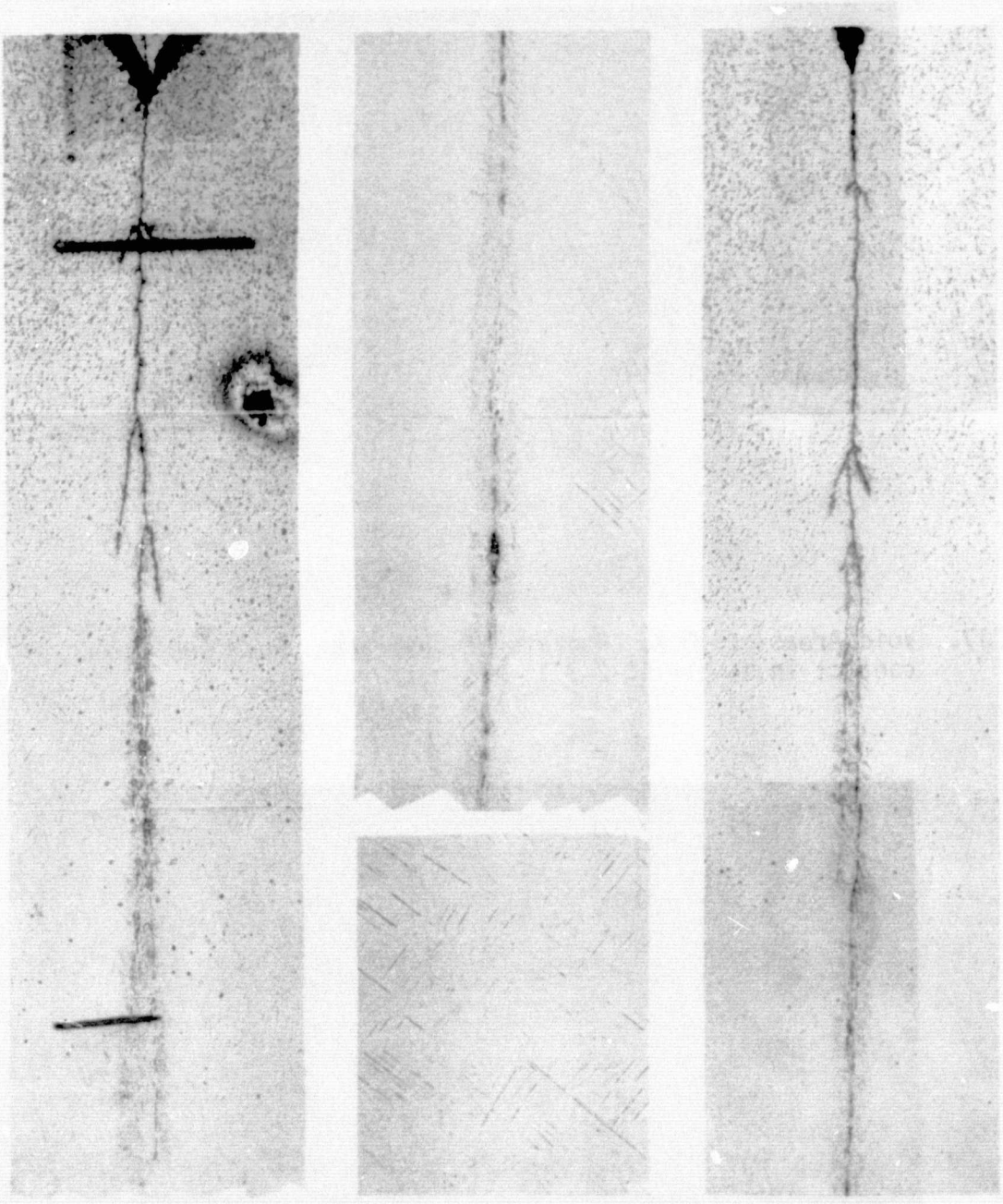

Figure 16. Composite Picture of Primed Specimen at 15X. (Composite picture similar to Figure 15 in the primed sample. The voids extend further into the weld in this sample.)

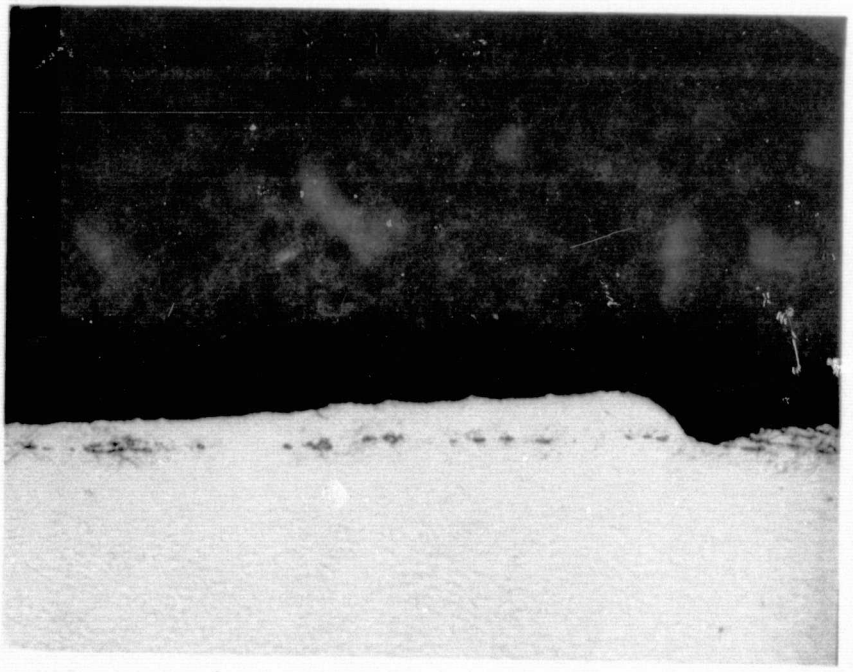

Figure 17. Void Areas at 400X. (Pockets of void areas near the weld contact in sample 50-2-3.)

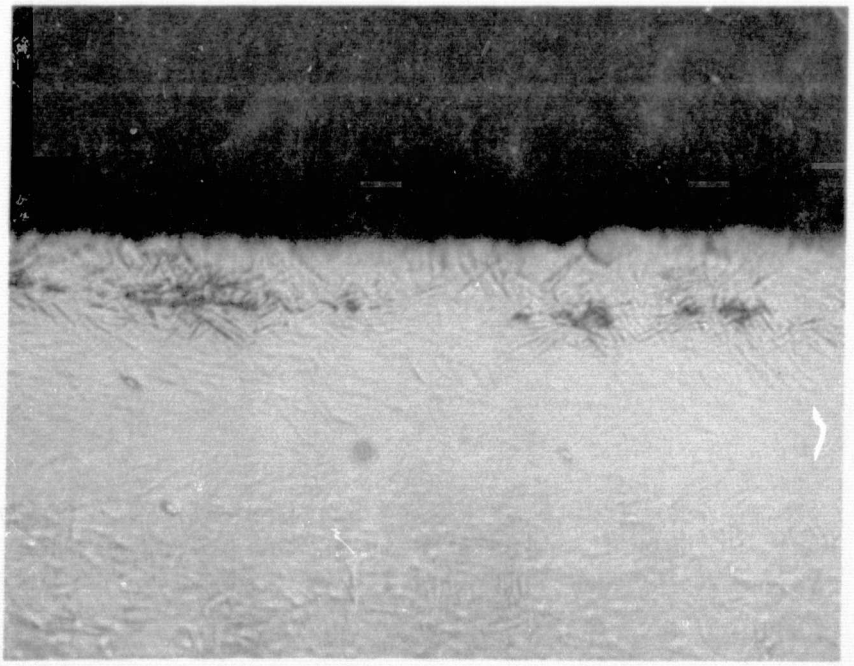

Figure 18. Void Areas at 800X. (Same as Figure 17, but at higher magnification.)

The recrystallized structure in a sheared sample (see Figure 19) showed that good homogenization had occurred in the central region of the weld. A chilled structure was formed near the water-cooled electrode contacts (see Figure 20). Examination of the region near a weld nugget after shear testing showed an absence of adhesive primer near the weld (see Figure 21).

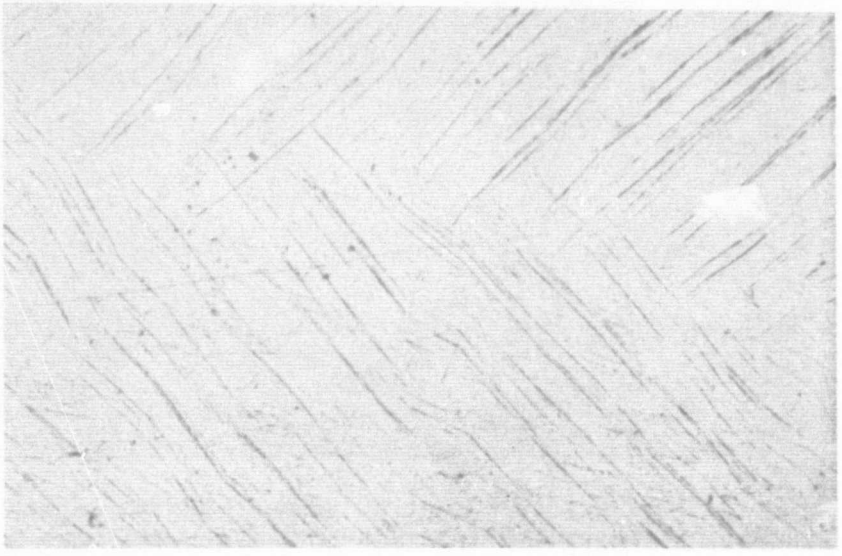

Figure 19. Sheared Weld Structure at 400X. (Sheared and recrystallized basket-weave structure near weld center.)

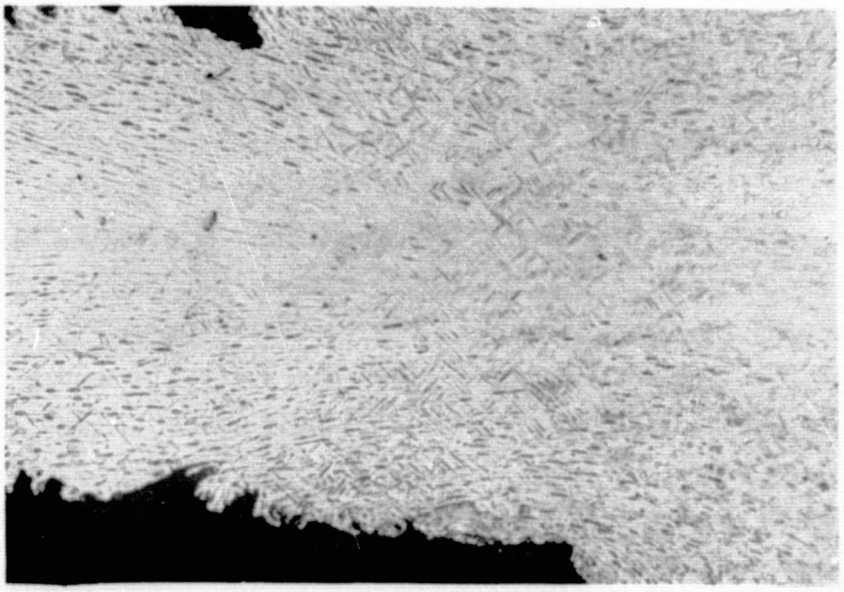

Figure 20. Chilled Weld Structure at 400X. (Chilled structure near weld contact area.)

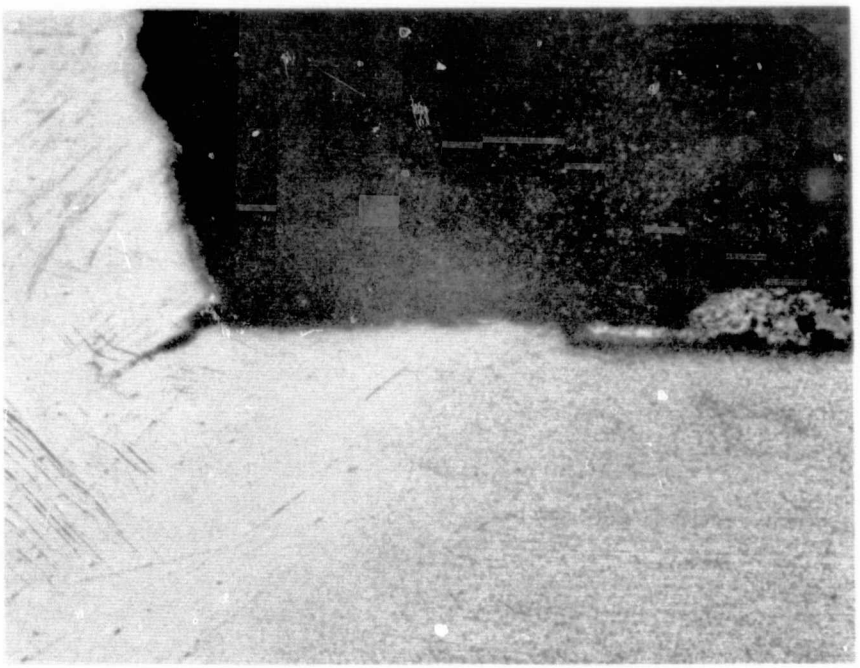

Figure 21. Surface Adjacent to Nugget at 400X. (Region adjacent to weld nugget on the primed specimen 50-2-3 showing bare surface and resin bead resulting from primer flow during the welding operation.)

The chemical distribution of elements along the weld structure was identified in order to determine possible brittle phase regions along which cracks may propogate. A forked area in the crack-like extension was observed in the prime control sample (see Figure 22). The thick burn line occurred when the microprobe scan was made. A titanium and silver profile across the crack (see Figure 23) showed that while titanium content decreased across the crack-like area, silver decreased slightly in the actual crack, but showed a sharp increase and a steep gradient in the matrix. A decrease in carbon along the void region also was observed (see Figure 24). It is concluded from these observations that the lines are actual voids with a higher silver concentration along the edges. These are ascribed to imperfect weld closure along the edges and lack of complete homogenization along the outer periphery of the weld. A back-scatter electron image of the crack-like void extending into the weld (see Figure 25) provided a very faint silver halo (white) along the weld indicating low silver content.

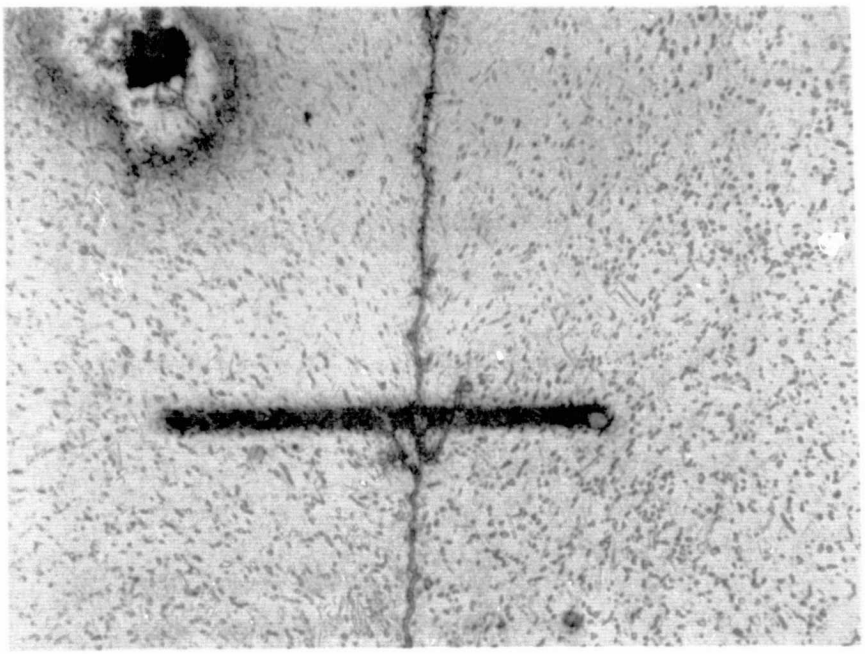

Figure 22. Crack-like Void at 400X. (Crack-like extension in sample 50-2-1. Thick line is due to microprobe scan and dark "hole" also is beam damage that occurred while analyzing a second phase region.)

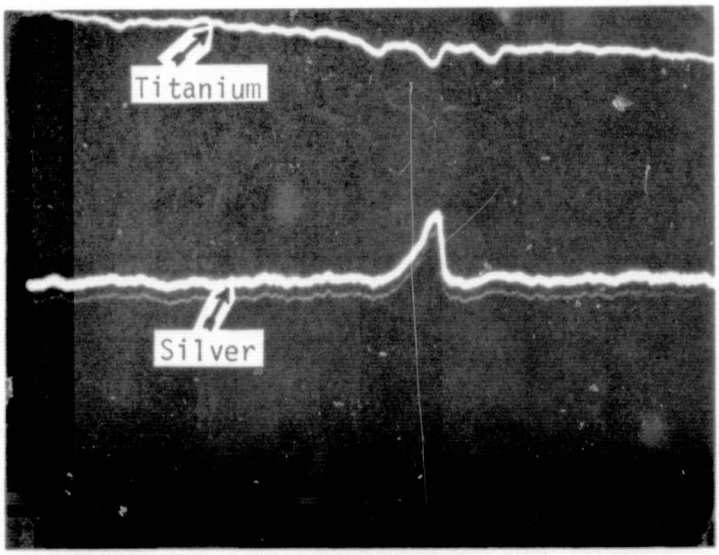

Figure 23. Line Profile of Primed Specimen at 400X. (Line profile across the forked extensions as shown in Figure 22. Top trace shows titanium decreasing and bottom trace shows silver increasing.)

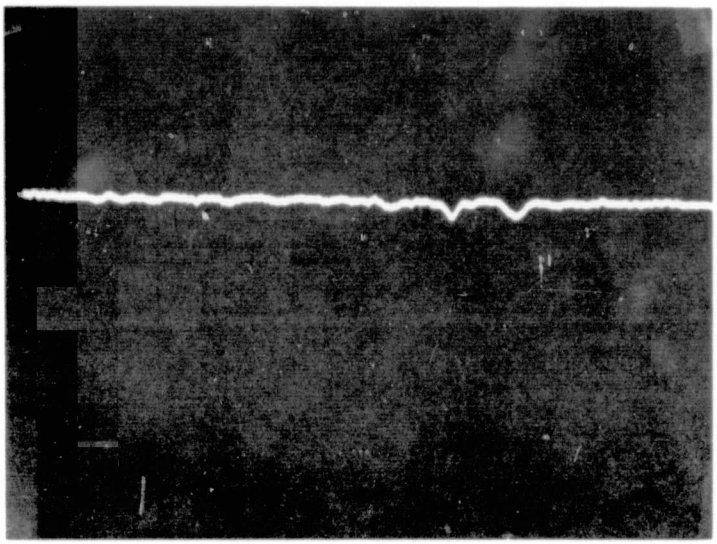

Figure 24. Carbon Profile of Primed Specimen. (Carbon profile showing decrease in carbon.)

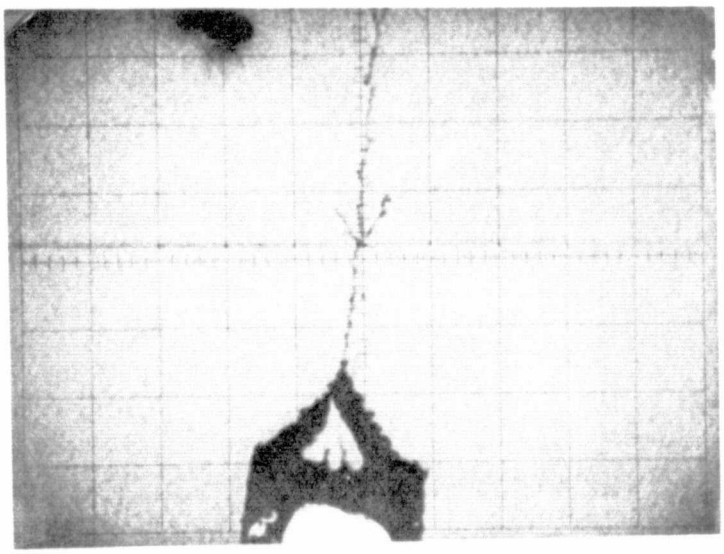

Figure 25. Back-Scatter Electron Image of Crack-Like Void at 400X. (Back-scatter electron image of same region as Figure 22.)

Small islands of a second phase occurred near the weld periphery and were confined to the vicinity of the long voids (Figures 26 to 30 show X-ray and back-scatter electron images of these islands). It was concluded that these were carbon and silver rich areas that were due to incomplete homogenization of the silver/resin primer near the weld edges.

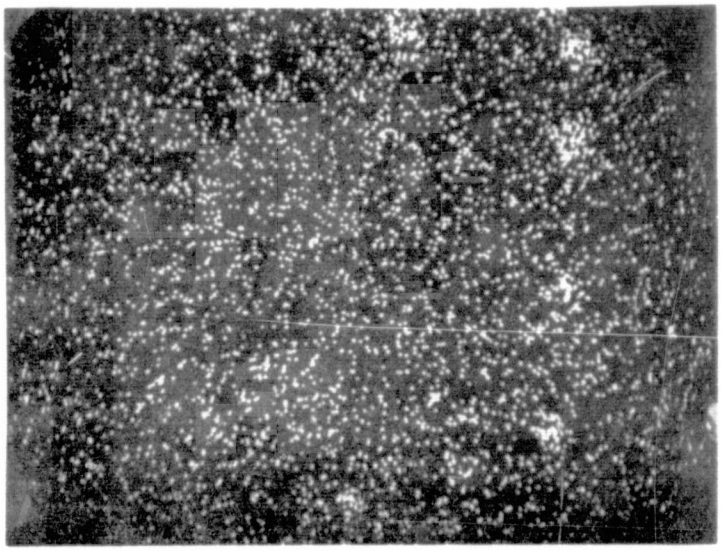

Figure 26. Carbon X-Ray Image at 200X. (Second phase found near the "crack" in sample 50-2-1.)

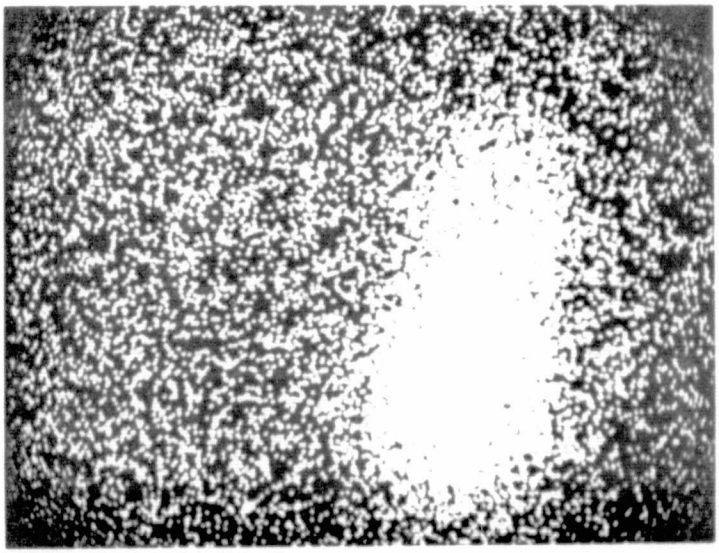

Figure 27. X-Ray Image at 2000X. (Same as Figure 26, but at higher magnification.)

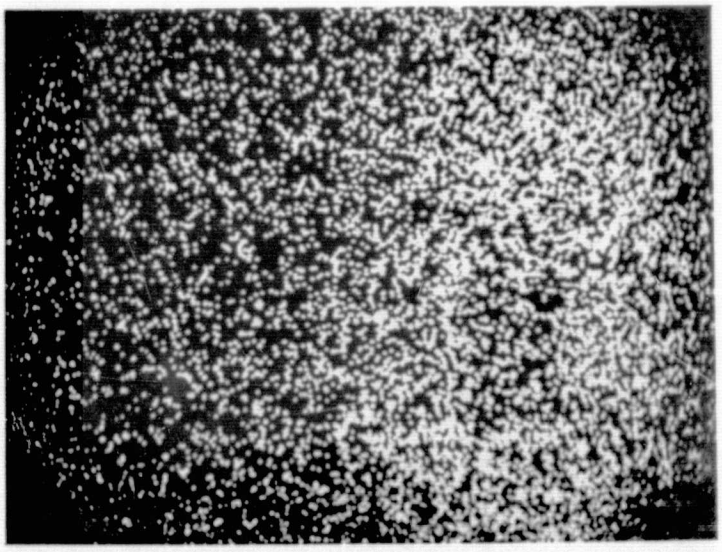

Figure 28. Silver Image at 200X. (Silver image of same area, as in Figure 27, showing a silver rich halo around the carbon-rich phase.)

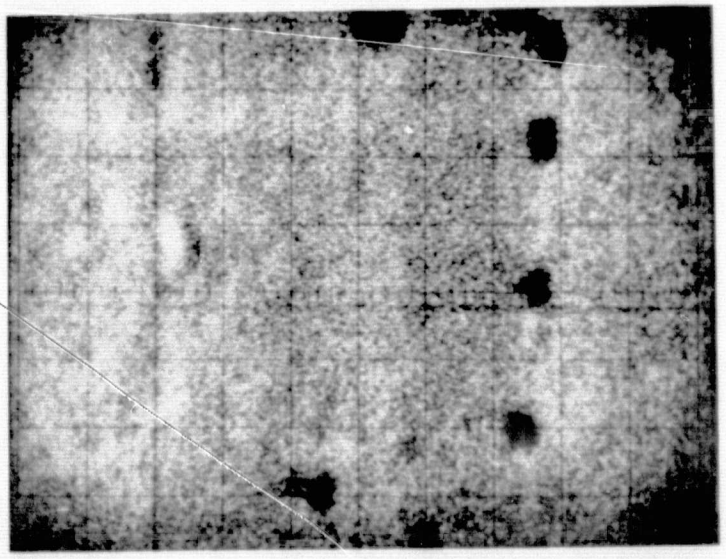

Figure 29. Back-Scatter Electron Image at 400X. (Back-scatter electron image of same areas as in Figure 26 showing dark carbon areas and surrounding white silver areas. The general background is titanium alloy matrix.)

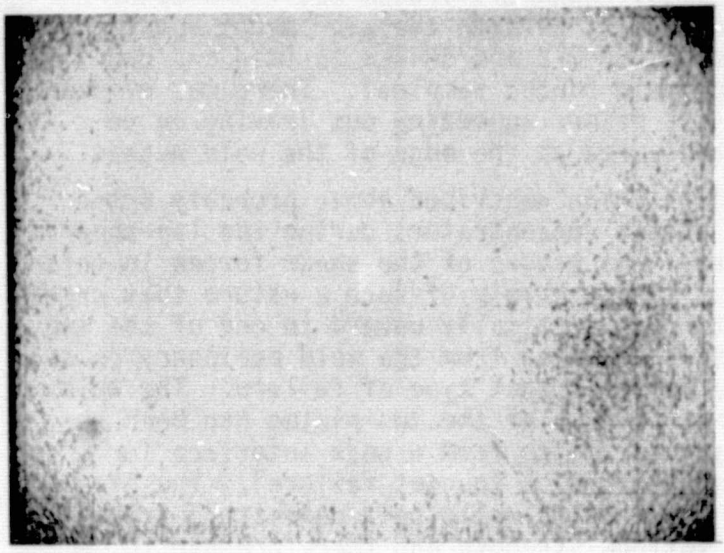

Figure 30. Titanium Image at 200X. (Titanium X-ray image of above area.)

The following conclusions then were drawn based on the results of these failure analyses:

- Voids were left near the outer periphery of the weld edges along the weld mid-plane in both the primed and unprimed samples. These were attributed to imperfect weld closure at the edges due to decreased pressure, low temperature, and presence of undisplaced resin materials.
- The weld edge (periphery of the spot weld) showed signs of having been molten and flowed in the gap outside the weld, but conditions had not been optimal for complete weld closure.
- Silver and carbon rich islands also were present near the elongated voids. These were taken as further evidence for lack of optimal time, pressure and temperature conditions for complete resin displacement to produce a metallurgical bond.
- More nearly equilibrium conditions had prevailed near the weld center where resin displacement and metallurgical bonding had taken place and no bond line interface could be seen.
- The silver rich second phase regions were potential paths along which cracks could propogate. However, when complete solid solution of the silver in titanium occurs, a homogeneous metallurgical structure is achieved.

- No significant difference was found metallographically or with the microprobe between samples 50-2-2 and 50-2-3 (primed and capillary flow weld bonded samples). There was evidence of the primer squeezing out leaving an uncoated area at the edge of the weld nugget.
- Radial voids described above probably acted as stress concentrators during the lap-shear test. The nature of the shear forces in this test were probably of such a nature that cracks extending vertically upward in one of the two plates starting from the weld periphery caused the pulled nugget type of failure. The weld areas in each of the two plates had been recrystallized to form a weak interface for crack extension (nugget failure). The presence of these voids would be a definite detriment to fatigue strength and therefore had to be minimized.

Based on the above findings, it was decided to adjust the welding parameters in order to improve the spot welding quality. The lower breaking loads of the spot welds discussed above were attributed to the need for these adjustments because a new welding machine had been installed and was used for these studies. The failure analyses indicated that the conductive primer is not a concern in obtaining high quality spot weld nuggets.

Consequently, the preliminary weld-through conductive adhesive primer (see Table III, formulation VII) was used in the initial adhesive development studies (see Section 3.2). At the conclusion of these initial adhesive screening studies, two polyimide resin systems were selected as the most promising candidates for use in the capillary flow adhesive formulation. Since it was considered desirable to use the same resins in the weld-through primer, studies were conducted to obtain the following information:

- The resin systems to be used in the primer.
- The specific quantities of each resin in the primer system.

- The condition of the A-type resin to be used in the primer (*i.e.*, amide acid or imide).

Results of these studies (see Table VI) indicated that the resin combination of the primer should be 25 percent NA/BTDA/*m*,*m*'MDA, 25 percent amine chain extended *bis*maleimide, and 50 percent Amoco AI 1137 amide-imide (panel 78-1 and 78-3). In addition, these results also indicated that NA/BTDA/*m*,*m*'MDA and BDAS-*bis*maleimide /*m*,*m*'MDA yielded higher overall lap shear properties when used with aluminum filler, both at room temperature and 561K (550°F) (panels 79-1, 79-2, 82-1 and 82-2) than the other systems.

TABLE VI.

PRIMER AND BONDED ONLY ADHESIVE STUDY

Panel #	Primer Resin[1]	Adhesive resin[1]	Test Temp. K (°F)	Load $Nx10^3$(lbs)	Lap-Shear Strength Pascals (psi)
78-1	NA/BSDA/*m*,*m*'MDA (amide): BDAS maleimide /*m*,*m*'MDA; AI 1137 (amide-imide) (33 : 33 : 33)	NA/BSDA/*m*,*m*'MDA imide: BDAS maleimide /*m*,*m*'MDA (50 : 50)	292(R.T.) 292(R.T.) 561(550)	6.9 (1560) 5.3 (1200) 8.4 (1880)	5.4 (780) 4.1 (600) 3.0 (440)
78-3	NA/BSDA/*m*,*m*'MDA (amide): BDAS / maleimide, *m*,*m*'MDA; AI 1137 (amide-imide) (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide: BDAS maleimide /*m*,*m*'MDA (50 : 50)	292(R.T.) 292(R.T.) 561(550)	7.5 (1680) 6.7 (1500) 6.7 (1500)	5.8 (840) 5.2 (750) 5.2 (750)
79-2	NA/BTDA/*m*,*m*'MDA amide acid: BDAS maleimide/ *m*,*m*'MDA; AI 1137 (amide-imide) (25 : 25 : 50)	NA/BTDA/*m*,*m*'MDA imide; BDAS maleimide/*m*,*m*'MDA (50:50)	292(R.T.) 292(R.T.) 561(550)	10.7 (2400) 8.5 (1900) 11.7 (2600)	8.3 (1200) 6.5 (950) 9.0 (1300)
79-1	NA/BTDA/*m*,*m*'MDA amide acid: BDAS maleimide/ *m*,*m*'MDA : AI 1137 (amide-imide) (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide; BDAS maleimide/*m*,*m*'MDA (50 : 50)	292(R.T.) 292(R.T.) 561(550)	8.7 (1950) 6.7 (1500) 5.5 (1240)	6.7 (975) 5.2 (750) 4.3 (620)
82-1	NA/BTDA/*m*,*m*'MDA amide acid:BDAS maleimide/ *m*,*m*'MDA : AI 1137 (amide-imide) (25 : 25 : 50)	NA/BTDA/*m*,*m*'MDA imide; BDAS maleimide/*m*,*m*'MDA (50 : 50)	292(R.T.) 292(R.T.) 561(550)	11.7 (2640) 11.8 (2660) 8.7 (1950)	9.1 (1320) 9.1 (1330) 6.7 (975)
82-2	NA/BSDA/*m*,*m*'MDA amide acid:BDAS maleimide/ *m*,*m*'MDA: AI 1137 (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide with BDAS maleimide (50 : 50)	292(R.T.) 292(R.T.) 561(550)	3.9 (880) 6.0 (1350) 3.1 (700)	3.0 (440) 4.7 (675) 2.4 (350)
11-1	NA/BSDA/*m*,*m*'MDA amide acid : BDAS maleimide/ *m*,*m*'MDA: AI 1137 (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide with BDAS maleimide (50 : 50)	292(R.T.)	13.1 (2950)	10.2 (1475)
13-2	NA/BSDA/*m*,*m*'MDA amide acid: BDAS maleimide/ *m*,*m*'MDA: AI 1137 (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide with BDAS maleimide (50 : 50)	292(R.T.)	10.5 (2350)	8.1 (1175)
14-3	NA/BSDA/*m*,*m*'MDA amide acid:BDAS maleimide/ *m*,*m*'MDA : AI 1137 (25 : 25 : 50)	NA/BSDA/*m*,*m*'MDA imide with BDAS maleimide and aluminum powder (50 : 50)	561(550)	13.3 (2990)	10.3 (1495)

[1]Unless otherwise noted, all the A-type polyimide resins are formulated at n = 1.

3.2 CAPILLARY FLOW ADHESIVE FORMULATION AND PROCESS DEVELOPMENT

The first step in the capillary flow, weld bonding adhesive formulation and process development studies was the evaluation of resin formulations similar to P11BA (see Reference 1). These resins were considered prime candidates because earlier work during Task I had identified P11BA as a promising capillary flow resin and work at NASA Langley Research Center had shown the new resin formulations to be promising in adhesive formulations. Therefore, the following variables were selected for screening during this first approach to capillary flow adhesive development.

- Resin type - Four different polyimide formulations were evaluated during the initial phase of the adhesive screening study. These four formulations consisted of the direct substitution of *m*,*m*'DABP, or *m*,*m*'MDA for MPD in the standard P11B resin formulation; a 70/30 blend of *m*,*m*'MDA and MDA in a similar formulation and the substitution of *m*,*m*'MDA for TDA in the previously used capillary flow formulation containing BSDA (see Section 2 for details).

- Copolymeric Blends - Use of an amide imide resin (Amoco AI-1137) in combination with A-type polyimide resin provided improved adhesive characteristics over neat A-type polyimide resins (see previous work under Contract NAS 1-9532, References 2 and 3, and Contract NAS 3-16780, Reference 4).

- Thixotropic Agents - Use of thixotropic agents (Cab-O-Sil) during previous studies provided increased gap-filling (see Reference 1).

- Curing Temperature - Due to the fact that the melt viscosity of the polymers are affected by temperature, this variable was evaluated.

An experimental screening matrix was designed that compared the variables depicted above at two levels for each of the resin formulations, the copolymer blends, thixotropic agent level and curing temperature. The adhesive systems were prepared in accordance with Table VII matrix and applied to spot welded specimens as described in Appendix B. These specimens were dried at room temperature for 60 minutes, 334K (150°F) for 60 minutes, and finally 60 minutes at 394K (250°F) before curing. The final cure temperature was 561K (550°F) for sixteen hours.

TABLE VII.
TEST MATRIX ADHESIVE SCREENING STUDY

		Cure Cycle	
		Slow heat-up[a]	Rapid heat-up[b]
A-Type Polyimide and AI 1137 Resin Blend	Cab-O-Sil	X	
	No Additives		X
A-Type Polyimide Resin	Cab-O-Sil	X	
	No Additives		X

[a]Specimens loaded into oven at room temperature and then heated to 561K (550°F).

[b]Specimens loaded into preheated oven at 561K (550°F).

The results of these studies (see Table VIII) indicated high promise of success using the resin formulations containing *m,m'*MDA. However, the breaking loads of the weld bonded specimens [*i.e.*, approximately 24.6 x 10^3 (5500 lbs)] were significantly lower than those previously obtained [30.2 x 10^3 (6800 lbs)]. Therefore, in order to determine if the lower breaking loads resulted from defective welds caused by contamination from the conductive primer, a failure analysis of welded specimens was performed (see Section 2.1). It was concluded from the failure analysis that the lower breaking loads were a direct result of unsatisfactory welding. Therefore, the capillary flow adhesive studies were continued and corrective steps were taken to improve the weld quality. It was identified that the welding problems were related to set-up of a new welding machine used throughout Task IV studies.

TABLE VIII.

PROPERTY DATA ADHESIVE SCREENING STUDY

Resin System	Cab-O-Sil Content % w/w	Oven Loading[1] Temperature K (°F)	Coverage[2] sq.cm (sq.in.)	% [3]	Breaking Load N x 10^3 (lbsf)
NA/*m,m*'MDA/BTDA	10	R.T.	4.03 (0.625)	31.3	23.2 (5210)
NA/*m,m*'MDA/BTDA	0	561 (550)	12.58 (1.950)	97.5	23.5 (5280)
NA/*m,m*'MDA/BTDA and AI 1137	0	561 (550)	5.48 (0.844)	42.2	25.4 (5720)
NA/*m,m*'MDA/BTDA and AI 1137	10	R.T.	0.81 (0.125)	6.3	26.2 (5880)
NA/*m,m*'DABP/BTDA	10	R.T.	0.20 (0.031)	1.6	27.6 (6210)
NA/*m,m*'DABP/BTDA	0	561 (550)	1.61 (0.250)	12.5	26.9 (6050)
NA/*m,m*'DABP/BTDA and AI 1137	0	561 (550)	4.23 (0.656)	32.8	24.2 (5440)
NA/*m,m*'DABP/BTDA and AI 1137	10	R.T.	0.81 (0.125)	6.3	25.6 (5750)
NA/70*m,m*'MDA:30MDA/BTDA	0	561 (550)	0.41 (0.063)	3.1	25.1 (5640)
NA/*m,m*'MDA/BSDA	0	561 (550)	6.45 (1.00)	50.0	21.8 (4900)

(1) Indicates whether panel was placed in a cure oven at R.T. and then heated to 562K (550°F) cure temperature or placed in oven preheated to cure temperature.

(2) Observed coverage of lap area of weld bonded specimen.

(3) Calculated from the following formula: $\frac{\text{Coverage area} \times 100}{\text{Total lap area}}$

Based on the results of the above adhesive screening studies, the NA/*m,m*'MDA/BTDA prepolymer was used for additional processing studies. Due to the criticality of the resin viscosity during processing a series of lap shear specimens were prepared varying only the cure cycle.

It was believed that the resin viscosity could be controlled by the cure process. However, results of this study (see Table IX) indicated that this resin possessed adequate flow but would not provide the gap-filling property that is desired for this application.

TABLE IX.
ADHESIVE PROCESSING STUDY[1]

Panel #	Cure[2] Temperature K (°F)/Min	Coverage[3] sq.cm (sq.in.)	Coverage[4] %	Breaking Load N x 10^3 (lbs)
43-4-2	477 (400)/10	8.07 (1.25)	62.5	23.2 (5210)
46-1-1	477 (400)/20	7.87 (1.22)	60.9	22.2 (5000)
46-1-2	491 (425)/10	8.07 (1.25)	62.5	22.2 (5000)
46-1-3	491 (425)/20	7.87 (1.22)	60.9	20.3 (4560)
46-1-4	505 (450)/10	7.03 (1.09)	54.7	21.9 (4920)
46-1-5	519 (475)/10	8.07 (1.25)	62.5	21.7 (4880)
46-1-6	533 (500)/10	8.26 (1.28)	64.1	21.3 (4800)
46-1-7	561 (550)/960	7.29 (1.13)	56.3	21.8 (4910)

[1] Resin formulation NA/m,m'MDA/BTDA, n = 1.

[2] Cure temperature shown indicates the initial oven temperature. After initial time oven temperature was held for 10 minutes at each subsequent temperature until 561K (550°F) was obtained and specimens then were cured 16 hours.

[3] Observed coverage of lap area of weld bonded specimen.

[4] Calculated from the following formula:

$$\frac{\text{(Coverage area) x 100}}{\text{Lap Area of Weld Bonded Specimen}}$$

Because the nadic capped resins had provided unsatisfactory gap-filling properties, it was decided to evaluate polyimide resins other than those utilizing a reverse Diels-Alder reaction. This approach was selected because the cyclopentadiene released during the cure of nadic capped polyimide resins will foam the resin unless restrained under pressure. Two resins selected for evaluation as the first step in these investigations were Kerimid 601 and a TRW PDA resin consisting of *bis*(furfuryl)benzophenone tetracarboxylic imide (BFBI) and *bis*(4-maleimidophenyl) methane (BMPM).

Initial test results (see Table X, Specimen numbers 43-5-1 and 43-5-2) indicated high promise for these resins. Additional panels then were fabricated to screen cure temperatures. Results of these studies (see Table X) indicated that either system provided capillary flow but the Kerimid system demonstrated the highest potential of providing satisfactory gap-fill, *i.e.*, >90% gap-fill with Kerimid and <80% with PDA.

TABLE X.
RESIN SCREENING STUDY

Panel #	Resin	Cure[1] Temperature K (°F)/Min	Coverage[2] sq.cm (sq.in)	Coverage[3] %	Load[4] N x 10^3 (lbs)	Cohesive Failure %
43-5-1	Kerimid 601	477(400)/20	11.45 (1.75)	87.5	23.8 (5340)	50-70
43-5-2	BMPM/BFBI (PDA)	477(400)/20	11.78 (1.80)	90.0	25.0 (5610)	50-60
43-5-3	NA/m,m'MDA/ BTDA	519(475)/20	7.87 (1.22)	60.9	24.1 (5425)	>10
50-3-1	Kerimid 601	477(400)/20	12.26 (1.90)	95.0	24.4 (5485)	60-70
50-3-2	Kerimid 601	477(400)/20	12.26 (1.90)	95.0	20.5 (4615)	50-60
50-3-3	Kerimid 601	450(350)/20	12.52 (1.94)	97.0	21.5 (4835)	80-90
50-4-1	BMPM/BFBI (PDA)	477(400)/20	12.26 (1.90)	95.0	26.1 (5875)	50-60
50-4-2	BMPM/BFBI (PDA)	477(400)/20	12.52 (1.94)	97.0	29.1 (6540)	70-80
50-4-3	BMPM/BFBI (PDA)	450(350)/20	12.26 (1.90)	95.0	23.8 (5345)	40-50

[1] Cure temperature shown indicates the initial oven temperature. After initial time temperature was raised to 533K (500°F) for 10 minutes, 547K (525°F) 10 minutes, and then 16 hours at 561K (550°F).

[2] Observed coverage of lap area of weld bonded specimens.

[3] Calculated from the following formula:

$$\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$$

Concurrent with the evaluation of PDA and *bis*maleimide resins, maleic (MA) and methyl nadic (MN) end-capped, as well as BSDA containing A-type polyimide resins, were evaluated (see Tables XI and XII). These A-type polyimide formulations were prepared by NASA Langley Research Center and TRW Systems as designated in the tables. Results of these studies indicated that a slight improvement was obtained with BSDA containing formulations (see Table XII), but again the gap-filling property was not satisfactory. The resins studied also included the substitution of methyl nadic anhydride (MN) for NA.

TABLE XI.

A-TYPE POLYIMIDE RESIN SCREENING

PANEL #	RESIN	CURE (1) TEMPERATURE K(°F)/HRS	COVERAGE (2) Sq. Cm (Sq. In.)	COVERAGE (3) %	BREAKING LOAD N X 10^3 (Lbs)	COHESIVE FAILURE %
59-1-1	MN/BTDA/*m,m'*MDA (NASA VI-43)	561(550)/16	12.90 (2.0)	100	34.7 (7800)	>5
59-1-2	MA/BTDA/*m,m'*MDA (NASA III-43)	561(550)/6	1.10 (0.17)	8.5	33.4 (7520)	0
59-1-3	NA/ODPA/*m,m'*MDA (NASA V-64)	561(550)/16	(4)	(4)	29.8 (6700)	0
59-2-1	NA/BTDA/*m,m'*MDA (TRW n=2)	561(550)/16	1.23 (0.19)	9.4	29.2 (6575)	0
59-2-2	NA/BTDA/*m,m'*MDA (TRW n=4)	561(550)/16	(4)	(4)	29.4 (6610)	0
59-2-3	MA/BTDA/*m,m'*MDA (TRW n=2)	561(550)/16	(4)	(4)	28.6 (6425)	0
59-3-1	MA/BTDA/*m,m'*MDA (TRW n=1)	505(450)/20 533(500)/10 561(550)/16	1.10 (0.17)	8.5	30.0 (6740)	0
59-3-2	MA/BTDA/*m,m'*MDA (TRW n=1)	505(450)/20 533(500)/10 561(550)/16	1.23 (0.19)	9.4	29.2 (6555)	0
59-3-3	MA/BTDA/*m,m'*MDA (TRW n=1)	533(500)/10 561(550)/16	(4)	(4)	30.1 (6775)	0
60-1-1	MA/BTDA/*m,m'*MDA (TRW n=1)	561(550)/16	1.35 (0.21)	10.3	30.6 (6880)	0

(1) Cure temperature shown indicates the initial oven temperature unless otherwise noted.

(2) Observed coverage of lap area of weld bonded specimens.

(3) Calculated from the following formula: $\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$

(4) Coverage was too small to be measured accurately.

TABLE XII.

COMPARISON OF BTDA AND BSDA CONTAINING RESINS

Panel	Resin	Cure Temperature[1] K (°F) Hrs.	Coverage[2] sq.cm. (sq.in.)	Coverage[3] %	Breaking Load N x 10^3(lbs)	Cohesive Failure %
17-1-1	MA/BTDA/*m,m'*MDA TRW n = 1	533(500)/16	1.55 (0.24)	12	26.8 (6020)	0
17-1-2	MA/BTDA/*m,m'*MDA TRW n = 1	533(500)/16	10.32 (1.60)	80	24.3 (5470)	<5
17-1-3	MA/BTDA/*m,m'*MDA TRW n = 1	533(500)/16	12.26 (1.90)	95	23.4 (5265)	<5
17-2-1	MA/BSDA/*m,m'*MDA TRW n = 1	533(500)/16	7.74 (1.20)	60	21.6 (4850)	0
17-2-2	MA/BSDA/*m,m'*MDA TRW n = 1	533(500)/16	10.97 (1.70)	85	24.7 (5550)	<5
17-2-3	MA/BSDA/*m,m'*MDA TRW n = 1	533(500)/16	11.61 (1.80)	90	24.6 (5525)	<5

(1) Cure Temperature shown indicates the initial oven temperature unless otherwise noted.

(2) Observed coverage of lap area of weld bonded specimens.

(3) Calculated from the following formula: $\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$

Further evaluation of *bis*maleimide resins again demonstrated their suitability for this application (see Table XIII). Consequently, it was decided at this point in time that amine chain extended *bis*maleimide resins similar to Kerimid 601 offered the highest potential for providing acceptable gap-filling. However, it is generally recognized that these resins have poor thermal stability which was a major concern in using them on this program.

TABLE XIII.

*BIS*MALEIMIDE RESIN SCREENING

Panel #	Resin	Cure Temperature[1] K (°F)/Mins.	Coverage[2] sq.cm. (sq.in.)	Coverage[3] %	Breaking Load N x 10^3(lbs)	Cohesive Failure %
61-1-1	Kerimid 601	Cold 477(400)/20 505(450)/10 533(500)/10 561(550)/960	11.61 (1.8)	90	32.2 (7240)	60-80
61-1-2	Kerimid 601	Cold 450(350)/20 477(400)/20 505(450)/20 533(500)/20 561(550)/960	12.26 (1.9)	95	28.0 (6300)	60-70
17-3-1	BDAS-*Bis*male-imide *m,m'*MDA	Cold 477(400)/20 505(450)/20 533(500)/960	12.90 (2.0)	100	25.4 (5710)	40-50
17-3-2	BDAS-*Bis*male-imide *m,m'*MDA	Hot 477(400)/20 505(450)/20 533(500)/960	12.90 (2.0)	100	24.7 (5560)	35-45
17-3-3		Hot 505(450)/20 533(500)/960	12.90 (2.0)	100	22.7 (5100)	20-30
17-4-1	BMPM, BDAS	Cold 477/400)/20 505(450)/20 533(500)/960	12.90 (2.0)	100	22.5 (5050)	40-50
17-4-2	BMPM, BDAS	Hot 477(400)/20 505(450)/20 533(500)/960	12.90 (2.0)	100	23.4 (5260)	45-55
17-4-3	BMPM, BDAS	505(450)/20	12.90 (2.0)	100	23.4 (5260)	55-65

(1) Cure Temperature shown indicates the initial oven temperature unless otherwise noted.

(2) Observed coverage of lap area of weld bonded specimens.

(3) Calculated from the following formula: $\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$

Therefore, in order to obtain improved thermal stability than reported for the Kerimid 601 resin, a series of resin blends were evaluated. Initial test results (see Table XIV, specimen numbers 21-1-3 and 21-1-6), indicated high promise for the resin blends. In addition, the study indicated that either blend provided the capillary flow and gap-filling characteristics essential for a capillary flow adhesive resin.

TABLE XIV.

RESIN BLEND SCREENING

Panel #	Resin	Cure Temperature[1] K (°F)/min.	Coverage[2] sq.cm. (sq.in.)	Coverage[3] %	Breaking Load N x 10^3 (lbs)	Cohesive Failure %
18-2	NA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (50:50)	505(450)/20 561(550)/960	12.9 (2.0)	100	24.0 (5400)	45-55
18-1	NA/BSDA/*m,m'*MDA & BMPM, BDAS (50:50)	505(450)/20 561(550)/960	12.9 (2.0)	100	24.0 (5400)	35-40
18-4	MA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (50:50)	505(450)/20 561(550)/960	11.61 (1.80)	90	26.7 (6010)	10-15
18-3	MA/BSDA/*m,m'*MDA & BMPM, BDAS (50:50)	505(450)/20 561(550)/960	12.26 (1.90)	95	26.6 (5970)	10-15
21-1-5	NA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (40:60)	505(450)/20 561(550)/960	12.77 (1.98)	99	23.4 (5250)	35-45
21-1-6	NA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (60:40)	505(450)/20 561(550)/960	12.64 (1.96)	98	20.7 (4665)	50-60
21-1-3	NA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (50:50)	477(400)/20 505(450)/20 533(500)/20 561(550)/960	12.9 (2.0)	100	25.0 (5610)	55-65
21-1-4	NA/BSDA/*m,m'*MDA & BDAS Maleimide *m,m'*MDA (50:50)	490(425)/20 505(450)/20 533(500)/20 561(550)/960	12.38 (1.92)	96	25.1 (5640)	35-45
21-1-1	NA/BSDA/*m,m'*MDA (PMR) BDAS Maleimide *m,m'*-MDA (50:50 in MeOH)	505(450)/20 533(500)/20 561(550)/960	12.9 (2.0)	100	20.5 (4600)	35-40
21-1-2	NA/BSDA/*m,m'*MDA, with BDAS Maleimide *m,m'*MDA (50:50 in MEK)	505(450)/20	8.90 (1.38)	69	23.4 (5270)	5

(1) Cure Temperature shown indicates the initial oven temperature unless otherwise noted.

(2) Observed coverage of lap area of weld bonded specimens.

(3) Calculated from the following formula: $\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$

Based on these results, it was decided to proceed with the final capillary flow adhesive development studies using the resin blend approach. It was determined during the primer development studies that the BTDA containing A-type polyimide resin yielded superior adhesive properties to the BSDA containing A-type polyimide resin. In order to corroborate this finding , additional weld bonded specimens were fabricated and tested (see Table XV). These results indicated that the BSDA containing A-type polyimide resin provided slightly better flow characteristics. However, because the BTDA containing resin provided higher adhesive strength (see Section 3.1) further evaluation of this resin was performed. It then was shown that the flow of this resin could be made similar to the BSDA containing resin by process adjustment, therefore , the NA/BTDA/*m*,*m*'MDA A-type resin was selected for detailed evaluation.

TABLE XV.

CAPILLARY FLOW ADHESIVE STUDY

Panel #	Primer Resin	Resin	Cure Temp [1] K(°F)/Min	Coverage [2] sq.cm. (sq.in.)	Coverage [3] %	Breaking Load Nx10^3 (lbs)
33-1-1	A-Type Imide	NA/BSDA/*m*,*m*'MDA (imide) with BDAS maleimide, *m*,*m*'MDA (50 : 50)	477(400)/20 505(450)/20 533(300)/20 561(550)/960	12.90 (2.0)	100	30.9 (6950)
33-1-2	A-Type Imide	Same	505(450)/20 533(500)/20 561(550)/960	12.13 (1.87)	94	31.2 (7025)
33-1-3	A-Type Imide	NA/BSDA/*m*,*m*'MDA amide-acid with BDAS maleimide, *m*,*m*'MDA	505(450)/20 533(500)/20 561(550)/960	8.90 (1.38)	69	34.1 (7660)
33-2-1	A-Type Amide Acid	NA/BSDA/*m*,*m*'MDA imide with BDAS maleimide, *m*,*m*'MDA (50 : 50)	505(450)/20 533(500)/20 561(550)/960	6.84 (1.06)	53	32.1 (7220)
33-2-2	A-Type Amide Acid	NA/BTDA/*m*,*m*'MDA imide with BDAS maleimide, *m*,*m*'MDA	505(450)/20 533(500)/20 561(550)/960	4.90 (0.75)	38	29.5 (6625)

[1] Cure temperature shown indicates the initial oven temperature unless otherwise noted.

[2] Observed coverage of lap area of weld bonded specimens.

[3] Calculated from formula: $\frac{\text{(Coverage area) x 100}}{\text{Lap area of weld bonded specimen}}$

(Note: Unless otherwise noted, all the A-type polyimide resins are formulated at n = 1.)

4. WELD BONDING PROCESS EVALUATION

Weld bonded joints prepared using the weld-through primer system and a capillary flow adhesive, were evaluated statically before and after thermal cycling. Joints bonded with the 50:50 mixture of NA/*m*,*m*'MDA/BTDA and the *bis*maleimide of BDAS/*m*,*m*'MDA blend, as well as weld bonded joints, were tested and the data compared to the welded only specimens prepared and reported in Task III (see Reference 1). Details of fabrication and testing of the adhesive only and the weld bonded specimens are provided below.

4.1 EVALUATION OF WELD-THROUGH PROCESS

Titanium alloy lap shear test specimens prepared using the weld-through primer and capillary flow adhesive were evaluated in order to determine whether properties equivalent to the weld-through weld bonding process are obtained (see Reference 1). Static tests at 219K (-65°F), R.T. and 561K (550°F) were performed in order to determine temperature effects on the strength of the weld bonded and bonded joints. Also, because adhesive-bonded joints are vulnerable to thermal oxidative degradation at certain extreme environmental conditions, both isothermal aging at 561K (550°F) and thermal cycling tests over a temperature range from 219K (-65°F) to 561K (550°F) were performed. These tests were designed to define the effects of isothermal aging and any of the cycle stresses caused by the thermal expansion mismatch between the adherends and adhesives.

4.1.1 Fabrication Procedure

The titanium alloy 6Al4V faying surfaces of the lap shear finger test panels (Reference 1, Figure 10) were solvent cleaned, then immersed in a 355K (180°F) bath containing Turco HTC alkaline cleaner for 15 minutes, washed in hot and then cold water, immersed in a nitric acid-hydrofluoric acid etching solution for 30 seconds, cold water rinsed, and finally immersed in Pasa-Jell 107. After an elapsed time of 15 minutes at 294K (70°F) the lap-shear finger panels were water rinsed and dried for 10 minutes at 339K (150°F). Immediately after drying, the panels were coated

with the conductive adhesive primer, as described in Appendix B. The panels then were assembled, spot welded (Reference 1, Figure 11) and oven cured as described in Appendix B.

Bonded-only panels were prepared using the same primer with the adhesive and press bonding cycles described in Appendix B, *i.e.*, contact pressure at 477K (400°F) for 20 minutes, then 689 KN/m^2 (100 psig) was applied and press temperature was raised to 561K (550°F) and held for 60 minutes followed by 16 hours at 561K (550°F) postcure.

4.1.2 Static Tests

Lap shear test specimens, as described in 4.1.1, were tested in triplicate at room temperature using pin and clevis type test grips and a loading rate of 2720 N (600 lbs) per minute. For the low temperature tests, specimen temperature was stabilized at 219K (-65°F) by preconditioning the specimens for ten minutes in a test chamber cooled to 219K (-65°F) by liquid nitrogen refrigeration. Similarly, specimen temperature was stabilized at 561K (550°F) for elevated temperature tests by preconditioning the specimens for ten minutes in a test chamber heated to 561K (550°F) with circulating air. Additional specimens were submitted to thermal aging and thermal cycling prior to performing the above tests.

Thermal cycling was performed by loading the specimens into a Bemco test chamber cooled with carbon dioxide at 219K (-65°F) for 30 minutes, after which they were removed and immediately loaded into a 561K (550°F) air circulating oven with a horizontal air velocity of 51 cm/sec (100 feet/minute) and an air change rate of 0.19 m^3/sec (400 cubic feet/minute). After 30 minutes the specimens were removed and then recycled 100 times. Isothermal aging of specimens was performed in a similar 561K (550°F) air circulating oven. Results of these tests are provided in Tables XVI, XVII and XVIII, and examples of the observed failure modes are depicted in Figures 31 and 32.

TABLE XVI.

STATIC TESTS AT 219K (-65°F) FOR WELD BONDED SPECIMENS

Specimen Description	Specimen Preconditioning	Load at Failure N x 10^3 (lbs)	Type of Failure[a]
Bonded-Only	As prepared	13.4 (3010)	Cohesive (3)
	500 Hrs/561K (550°F)	7.2 (1610)	Adhesive[b] (3)
	1000 Hrs/561K (550°F)	1.7 (375)	Adhesive[b] (3)
	Thermal cycling	13.3 (3000)	Cohesive
Weld Bonded	As prepared	27.0 (6065)	Nugget (2) [98]
	500 Hrs/561K (550°F)	32.0 (7200)	Nugget (2) [93]
	1000 Hrs/561K (550°F)	27.3 (6130)	Nugget (2) [90]
	Thermal cycling	29.9 (6730)	Nugget (2) [98]

a) See Figures 31 and 32 for illustration of failure modes, ( ) shows number of specimens, [ ] % coverage computed from formula.

$$\% \text{ Coverage} = \frac{\text{Observed Coverage Area}}{\text{Total Area}} \times 100$$

b) Failure was at the primer-titanium interface.

TABLE XVII.

STATIC TESTS AT 295K (72°F) FOR WELD BONDED SPECIMENS

Specimen Description	Specimen Preconditioning	Load at Failure N x 10^3 (lbs)	Type of Failure[a]
Bonded-Only	As prepared	12.2 (2750)	Cohesive (3)
	500 Hrs/561K (550°F)	6.4 (1450)	Adhesive[b] (3)
	1000 Hrs/561K (550°F)	2.6 (590)	Adhesive[b]
	Thermal cycling	13.1 (2950)	Cohesive (3)
Weld Bonded	As prepared	25.8 (5880)	Nugget & Sheet (2) [98]
	500 Hrs/561K (550°F)	28.5 (6400)	Nugget (2) [95]
	1000 Hrs/561K (550°F)	27.3 (6140)	Nugget & Sheet (2) [90]
	Thermal cycling	29.3 (6580)	Nugget (2) [94]

a) See Figures 31 and 32 for illustration of failure modes, ( ) shows number of specimens, [ ] % coverage computed from formula.

$$\% \text{ Coverage} = \frac{\text{Observed Coverage Area}}{\text{Total Area}} \times 100$$

b) Failure was at the primer-titanium interface

TABLE XVIII.

STATIC TESTS AT 561K (550°F) FOR WELD BONDED SPECIMENS

Specimen Description	Specimen Preconditioning	Load at Failure N x 10^3 (lbs)	Type of Failure[a]
Bonded-Only	As prepared	11.8 (2660)	Cohesive (3)
	500 Hrs/561K (550°F)	6.6 (1480)	Adhesive (3)
	1000 Hrs/561K (550°F)	3.0 (680)	Adhesive[b] (2)
	Thermal cycling	11.4 (2560)	Cohesive (3)
Weld Bonded	As prepared	31.6 (7110)	Nugget (2) [96]
	500 Hrs/561K (550°F)	34.6 (7790)	Nugget (2) [94]
	1000 Hrs/561K (550°F)	32.5 (7300)	Nugget (2) [90]
	Thermal cycling	33.0 (7430)	Nugget (2) [98]

a) See Figures 31 and 32 for illustration of failure modes, ( ) shows number of specimens, [ ] % coverage computed from formula.

$$\% \text{ Coverage} = \frac{\text{Observed Coverage Area}}{\text{Total Area}} \times 100$$

b) Failure was at the primer-titanium interface.

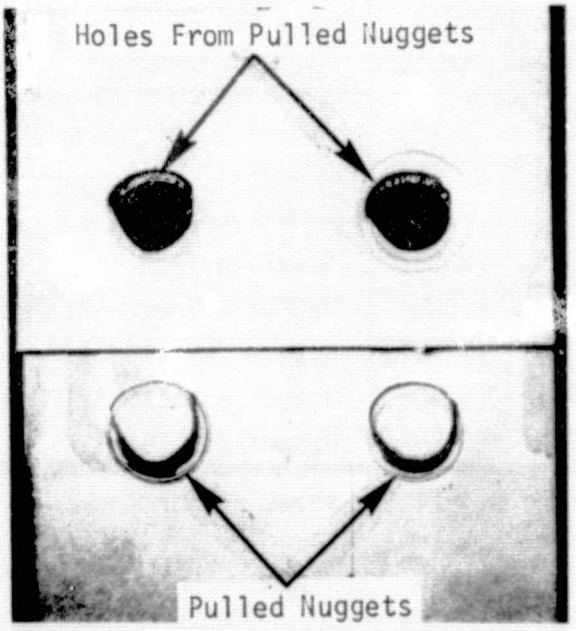

Figure 31. Pulled Nuggets Failure

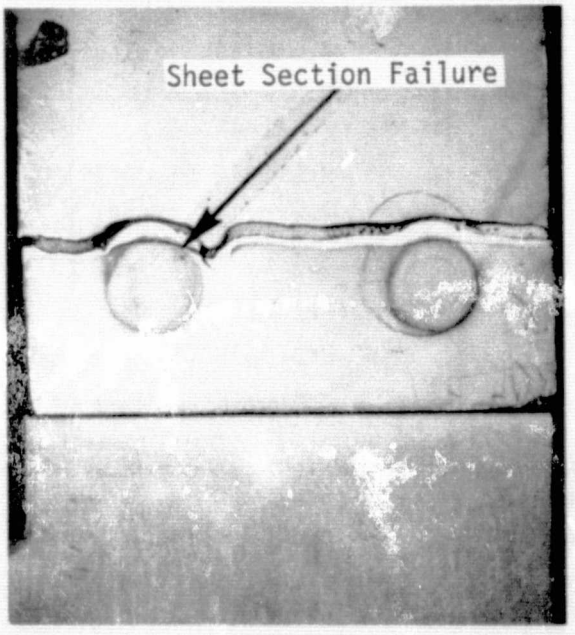

Figure 32. Sheet Section Failure

The average breaking loads at 219K (-65°F), R.T., and 561K (550°F) of the three specimens of each configuration were plotted as a function of aging duration (see Figures 33, 34 and 35). There appeared to be no significant differences between the plot for the welded and weld bonded specimens and neither indicated any property degradation trends. As expected, the bonded-only specimens plot defined a significant strength degradation trend which was not reflected in the weld bonded specimen plot.

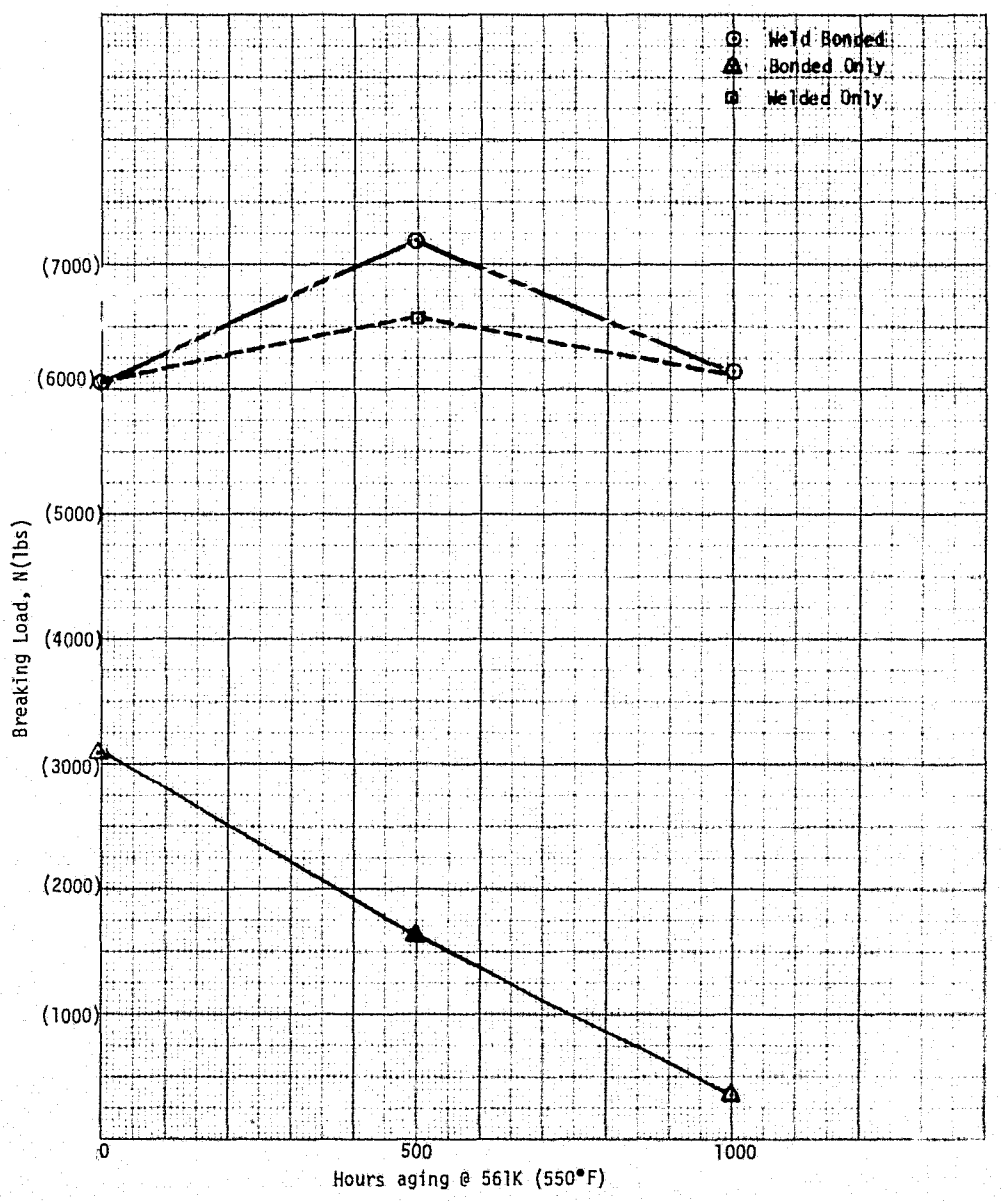

Figure 33. Effects of Thermal Aging on 219K (-65°F) Strength of Weld Bonded Specimens

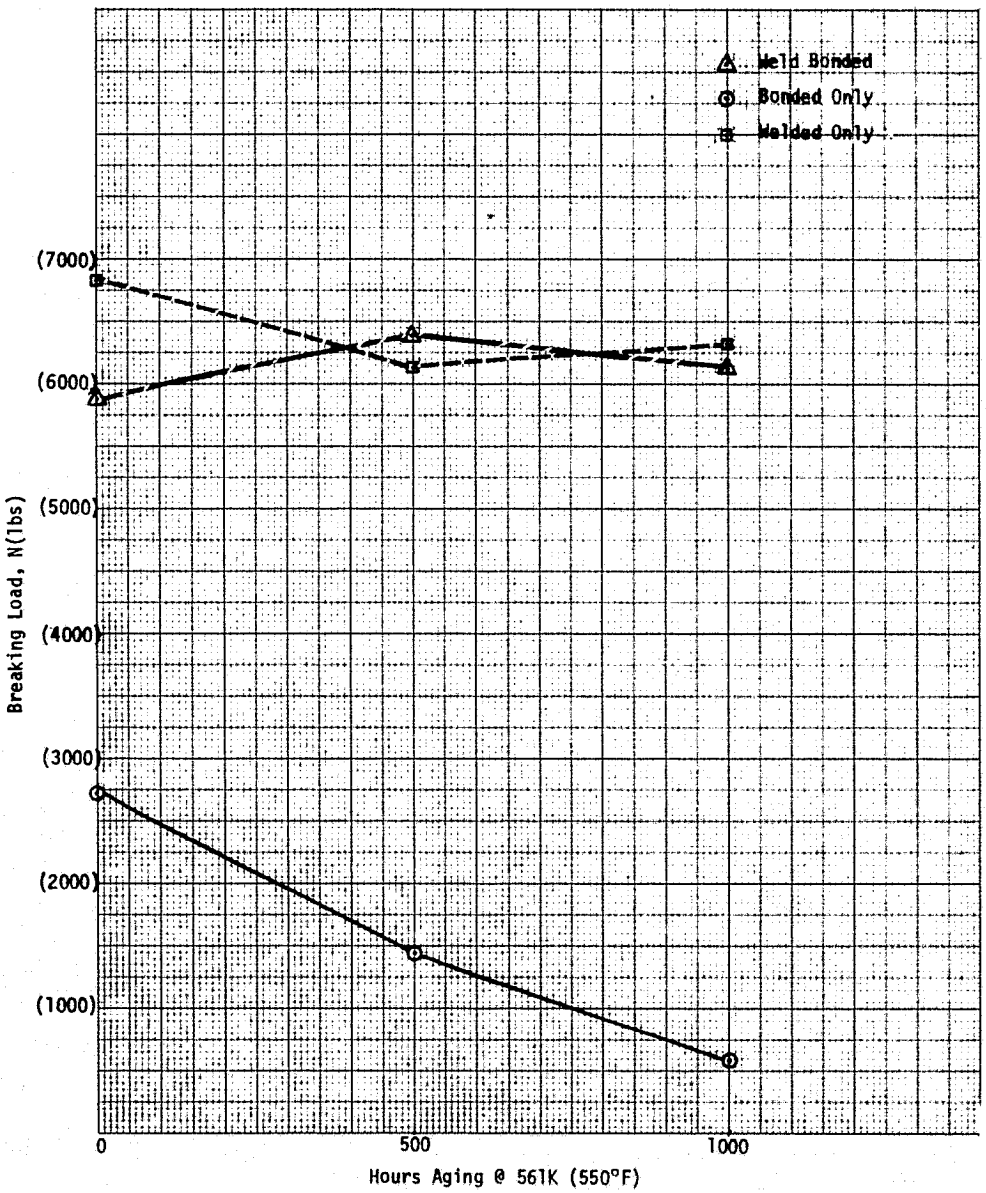

Figure 34. Effects of Thermal Aging on Room Temperature Strength of Weld Bonded Specimens

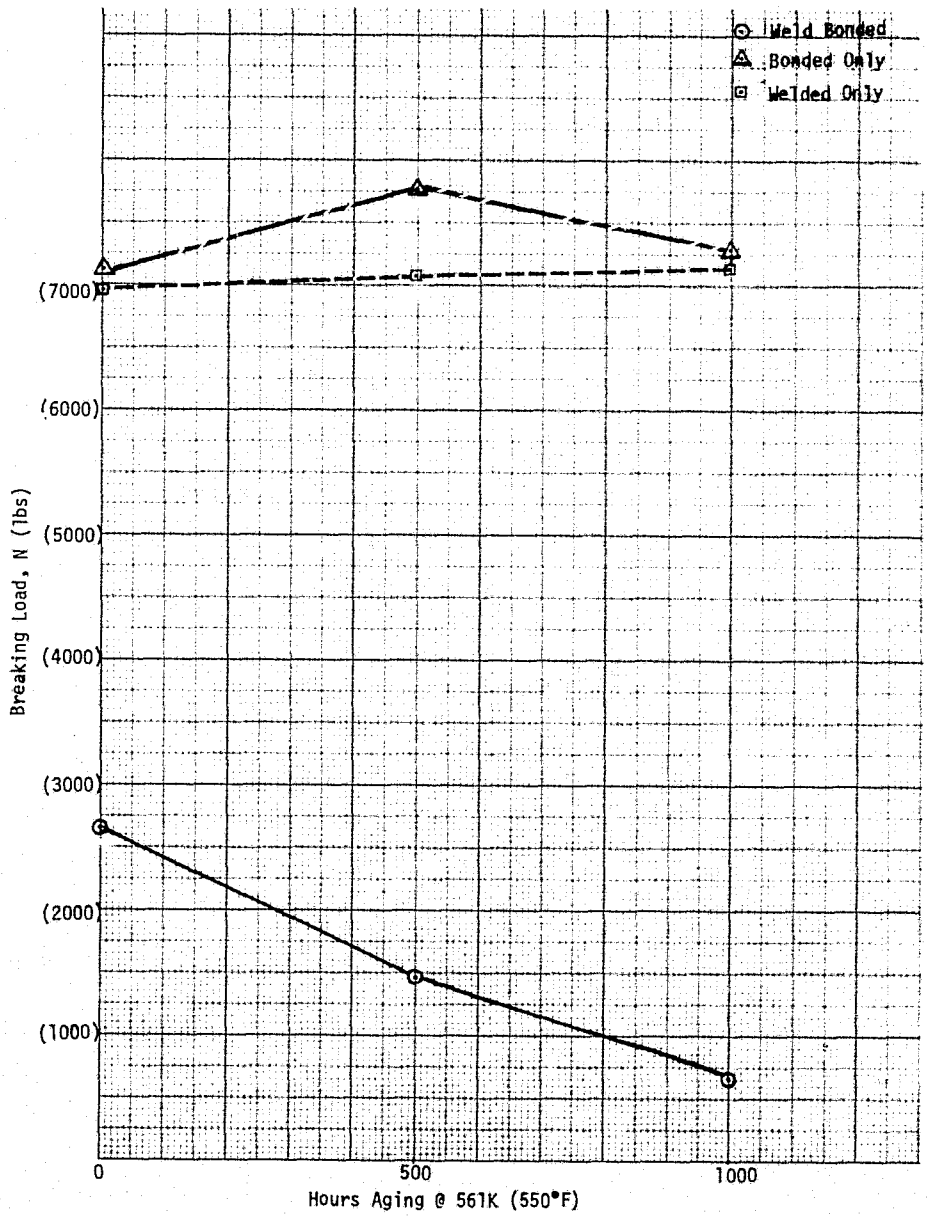

Figure 35. Effects of Thermal Aging on 561K (550°F) Strength of Weld Bonded Specimens

A bar graph was made showing the average breaking load values for specimens tested at 219K (-65°F), R.T., and 561K (550°F) before and after thermal cycling for all three specimen configurations (see Figure 36). It appeared from the results for the bonded-only specimens that thermal cycling had no adverse effects on the load values. The welded-only and weld bonded specimen plots indicated the same trends, *i.e.*, the breaking loads remained essentially the same after thermal cycling.

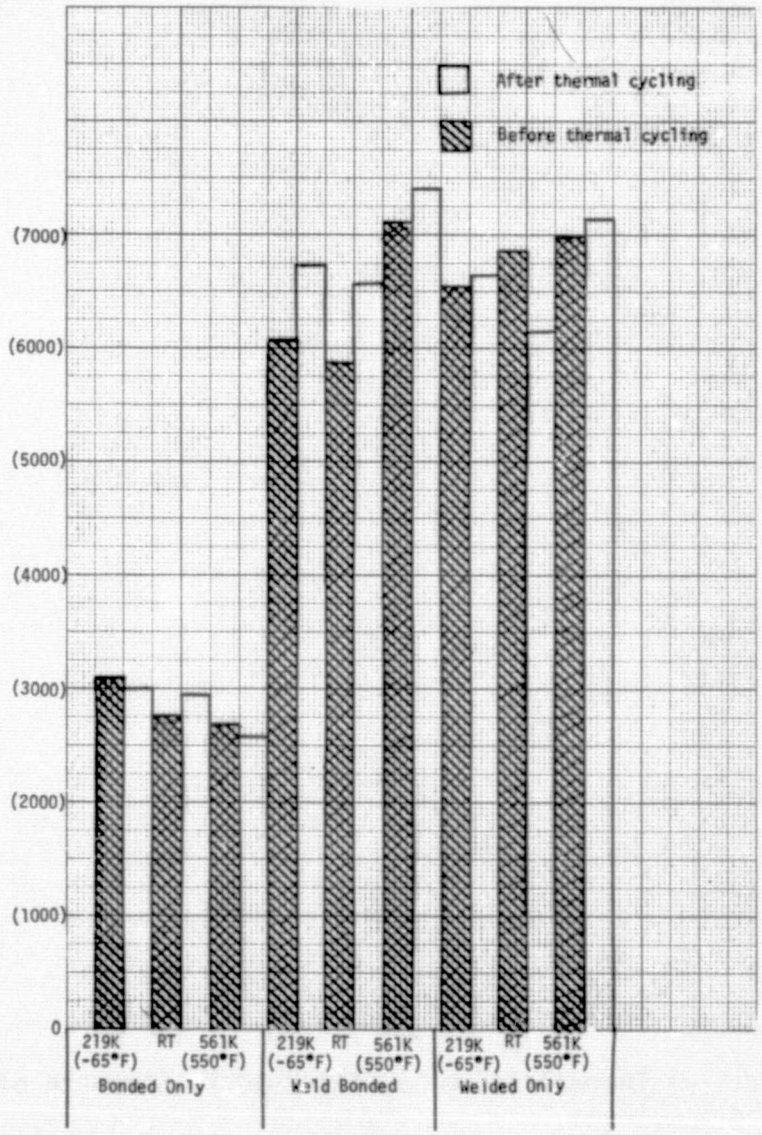

Figure 36. Effects of Thermal Cycling on Strength of Weld Bonded Specimens

Breaking load *vs* test temperature plots were made for specimens of all three configurations after being subjected to thermal cycling (see Figure 37). These plots indicated that the breaking load values for the weld bonded specimens were higher than the room temperature values at both 219K (-65°F) and 561K (550°F), while the welded-only specimens were higher at 219K (-65°F) and slightly lower at 561K (550°F). A plot of strengths for "as fabricated" specimens (see Figure 38) showed higher values at 219K (-65°F) for the welded-only specimens. Higher values at 219K (-65°F) and at 561K (550°F) were shown for the weld-bonded specimens. The plot for the bonded-only specimens showed no change at 561K (550°F), although a plot of strengths for "as fabricated" specimens also showed higher values at 219K (-65°F).

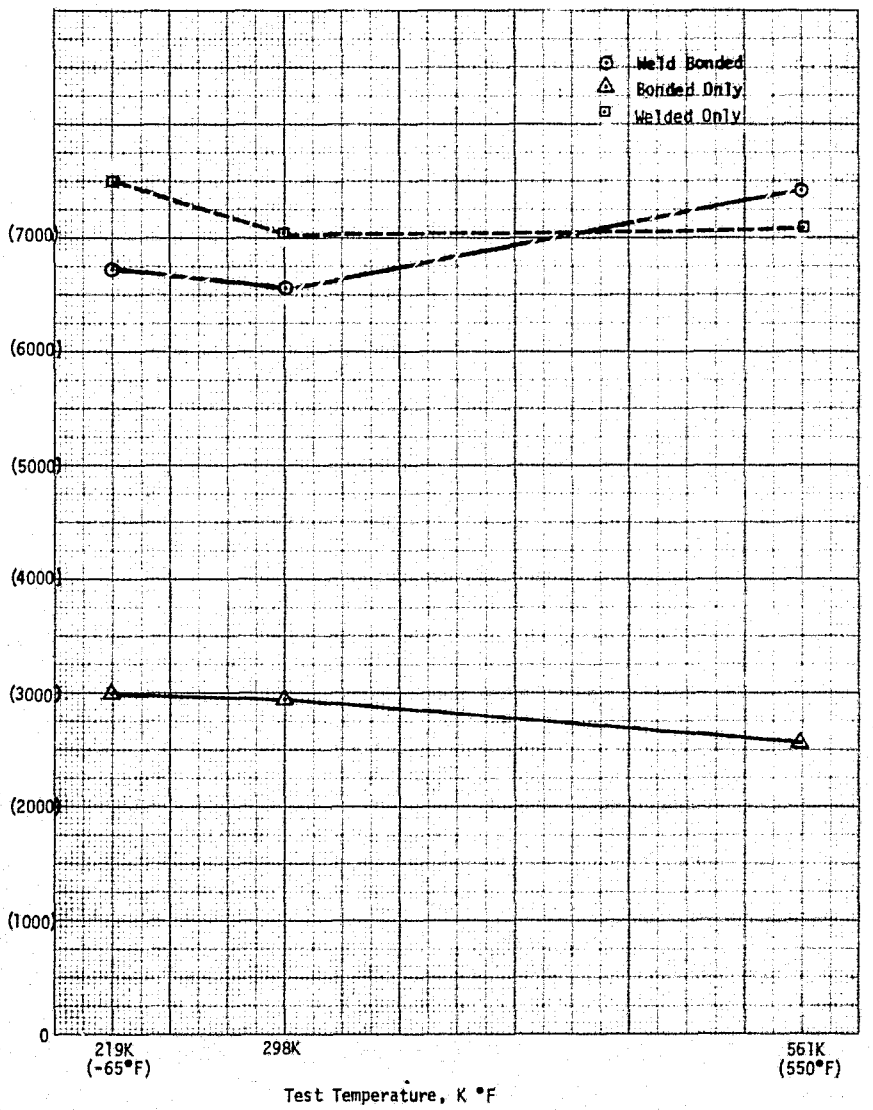

Figure 37. Effects of Test Temperature on Strength of Thermally Cycled Weld Bonded Specimens

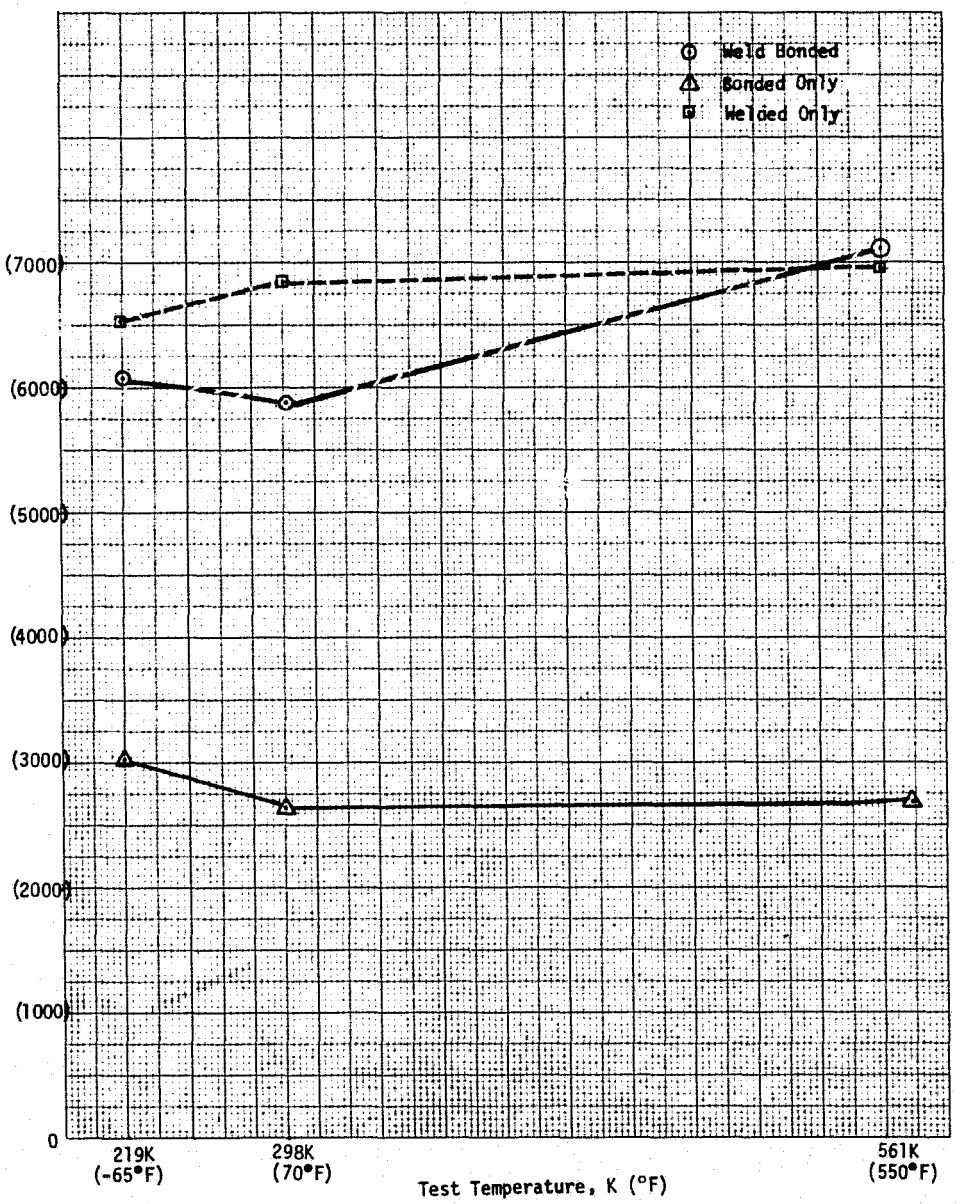

Figure 38. Effects of Test Temperature on Strength of As Prepared Weld Bonded Specimens

5. STRUCTURAL PANEL FABRICATION AND EVALUATION

Utility of the capillary flow weld bonding process for preparing stringer-stiffened skin panels was demonstrated and the efficiency of these joints under static loading was evaluated. Results from these static tests established similar trends to those observed previously (Reference 1).

5.1 FABRICATION AND PREPARATION OF STRUCTURAL TEST PANELS

In order to demonstrate the applicability of the capillary flow weld bonding process for fabricating structural, stringer-stiffened skins, test panels were fabricated consisting of a titanium alloy 6Al4V skin stiffened longitudinally with a hat-section rib. The process used was identical to that employed for preparing lap joints (see Section 4). Bonded-only panels also were prepared in order to provide comparative data. Strain gauges were installed on the completed test panels in preparation for the structural panel tests.

5.1.1 Fabrication of Panels

Components for the structural test panels (Reference 1, Figure 28) were fabricated from titanium alloy 6Al4V sheet. These components were prepared for welding or bonding by the Pasa-Jell process and the weld-through primer then was applied as described in Appendix B (see Figure 39).

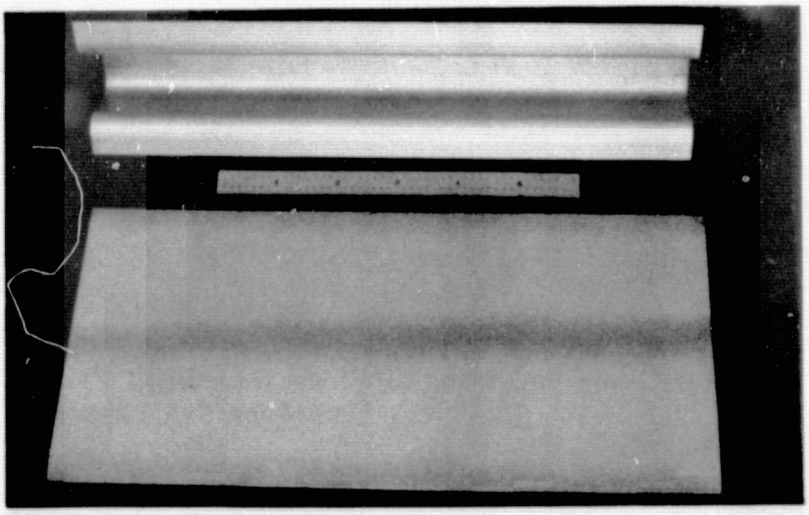

Figure 39. Primed Structural Test Panel

The components then were spot-welded using the same welding jig used previously (Reference 1, Figure 30). Photographs of the components, first after welding and then after the capillary flow adhesive application are provided in Figures 40 and 41, respectively. Bonded-only structural test panels were prepared as described in Appendix B. These test panels were bonded in a press and then collectively postcured 16 hours at 561K (550°F).

Figure 40. Welded Structural Test Panel

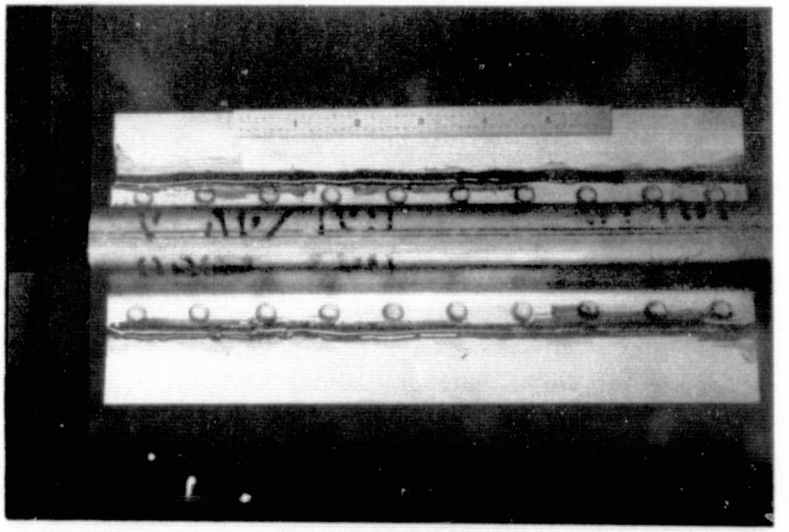

Figure 41. Welded Structural Test Panel with Capillary Flow Adhesive Paste

After the capillary flow adhesive processing cycle was completed, doublers were welded to the test panels along the top and bottom edges as shown in Reference 1, Figure 42. The edges were ground to provide flat and parallel loading surfaces.

5.1.2 Preparation of Panels

The type of panels, number of panels and test environment used in the test program is shown in Table XIX. Procedures for thermal cycling were identical to those employed for the lap-shear test specimens (see Section 4.1.2). Those panels that were subjected to a thermal cycling, were instrumented after the thermal cycling.

TABLE XIX.
STRUCTURAL PANEL TEST SCHEDULE

Type of Panel	Test Condition		
	294K(70°F)	294K(70°F) After Thermal Cycling a)	561K(550°F)
Adhesive Bonded	2	2	2
Weld Bonded[a)]	2	2	2

a) 100 Cycles of 30 minutes at 219K (-65°F) and 561K (550°F).

Five strain gauges were installed on each panel in accordance with Reference 1, Figure 32. The titanium alloy surfaces were prepared for bonding by the Pasa-Jell treatment (see Appendix B). The strain gauges used were Micro-Measurements WK-05-125BT-350 which were nickel-chromium alloy on epoxy-phenolic glass fabric backing and self-temperature compensating. They were bonded onto the test panels using M-Bond 600 adhesive together with CTF-60D Bondable printed Circuit Terminals. All solder joints were made with 570-28R high lead content, resin flux core solder. The strain gauge installation then was coated with Budd GW-1 coating and subjected to a two-stage cure process: 394K (250°F) for 2 hours, plus 533K (500°F) for 2 hours. For those panels that were tested at elevated temperature, the strain gauges also were protected with Bean Gagekote #1 plastic coating.

Three Chromel-Alumel thermocouples (T/C) were used to monitor the panel temperatures for the elevated temperature tests. They were located as illustrated in Reference 1, Figure 33. A fourth thermocouple (#4) was located near T/C #2 and used to control the heat input to the panel. These thermocouples were spot welded to the test specimen and coated with Omega CC High Temperature Cement.

5.2 TEST DESCRIPTION AND EVALUATION OF RESULTS

Structural panel tests were performed in order to provide a comparison between the weld-through and capillary flow weld bonding processes. The test articles, test set-up and instrumentation were identical to the previous study (Reference 1).

5.2.1 Test Instrumentation and Set-Up

Test set-up for room temperature and elevated temperature tests is shown in Reference 1, Figures 34 through 39. The strain gauges were used to identify the load level where the onset of localized elastic buckling (coupling) occurred which leads to eventual failure of the panel. This local buckling is indicated by a strain reversal.

Load *vs* end-shortening data also were monitored to establish the load level where general instability occurred (ultimate load carrying capacity). This general instability load level is indicated by a load drop-off above a given level of end-shortening.

Figures 42 and 43 show typical panel data. For the bonded-only panel, failure was sudden and catastrophic, with the hat section stiffener almost completely delaminating from the plate. As can be seen, there is little or no strain reversal, indicating negligible local buckling and load drop-off once the bond has failed. For panels with spot welds, failure was a more gradual event, with significant localized buckling preceding general instability.

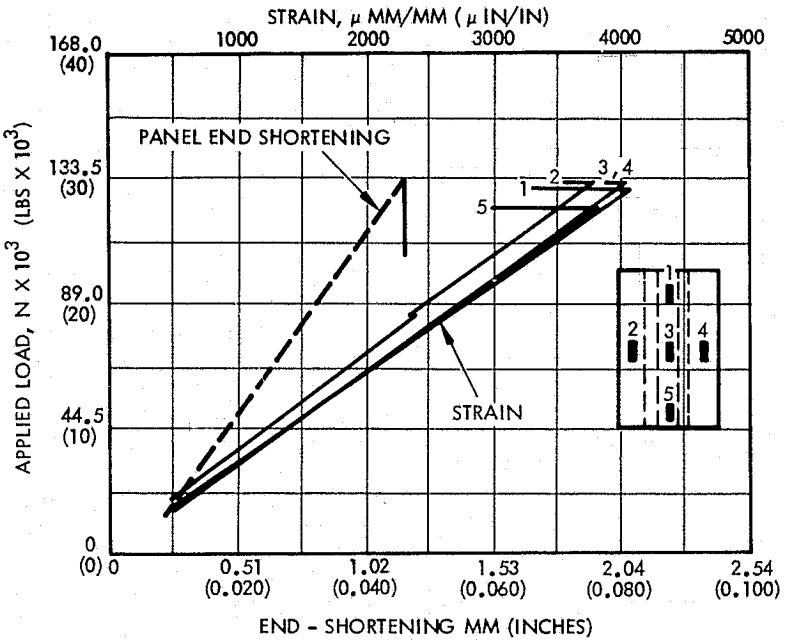

Figure 42. Typical Strain and End-Shortening Data (Bond-Only, Room Temperature Test Panel)

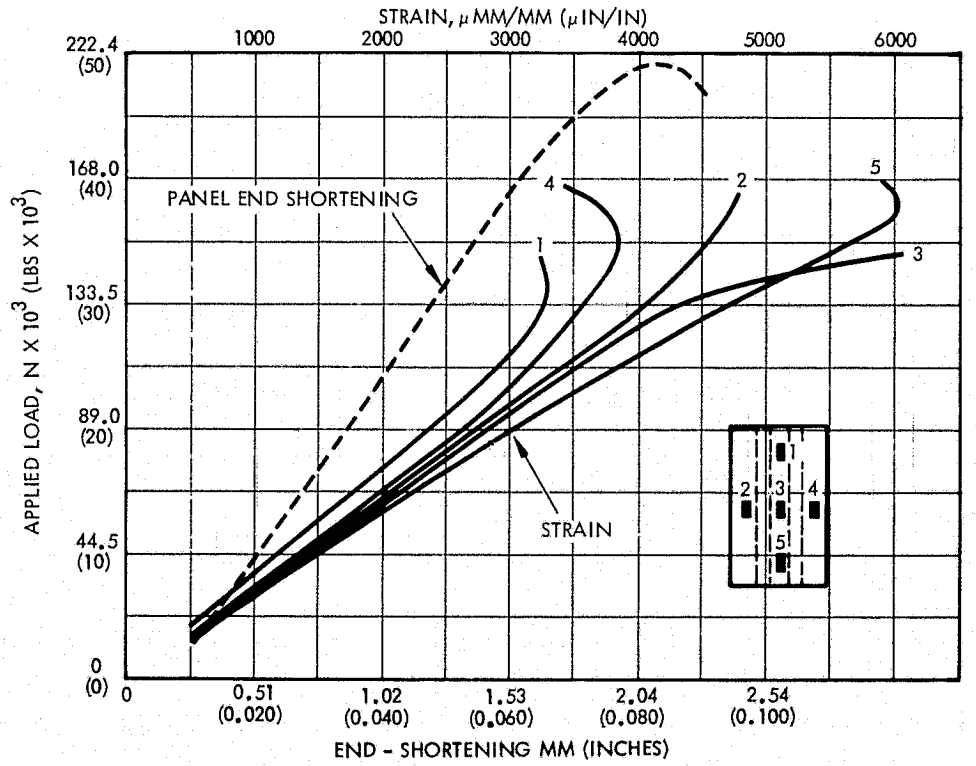

Figure 43. Typical Strain and End-Shortening Data (Weld-Only or Weld Bond Room Temperature Test Panel)

For the elevated temperature tests, four thermocouples were used to monitor panel temperature (see Figure 44). A fifth thermocouple (#5) was located near T/C #3 to control the heat input into the panel from surrounding tungsten/quartz lamps. With proper insulation of the test specimen from the loading machine, temperature levels along the bond or weld line over 80 percent of the length were held to 561K ± 14K (550°F ± 25°F).

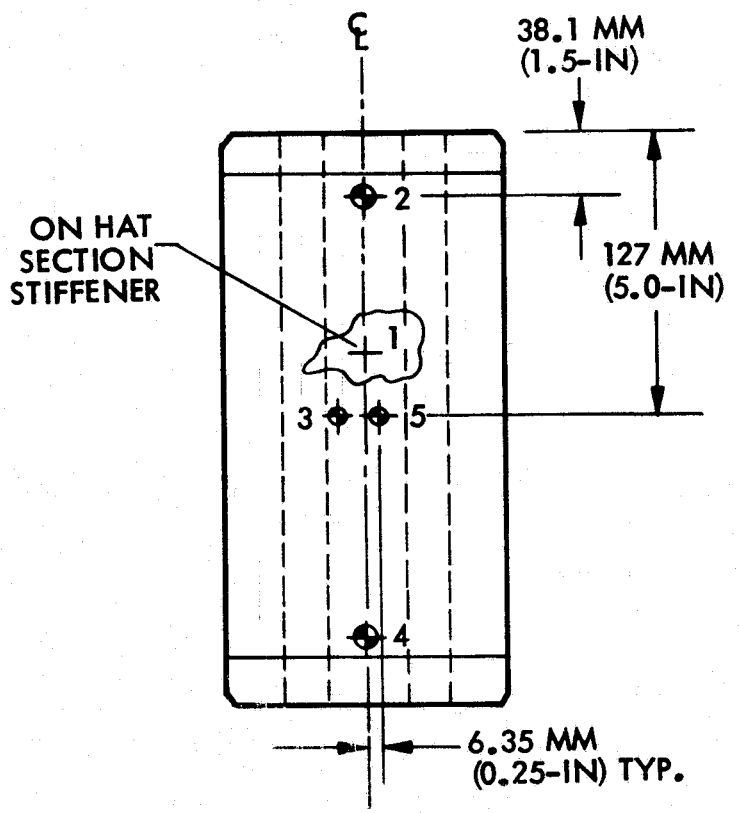

Figure 44. Thermocouple Location For Structural Test Panels

5.2.2 Test Results

The nature of the panel tests and the small number of panels tested precludes a definition and conclusive comparison between the various types of joining processes. The compression panel only indirectly provides a means of testing the joining process since the joint between the hat section stiffener and plate was not directly loaded. Nevertheless, the data generated do provide gross trends concerning joint efficiency.

Table XX presents the test results for the twelve new panels along with the results from Reference 1, for comparison purposes. Figure 45 presents the direct comparison between the current and past fabrication process for room temperature tests. Test results for thermally cycled panels and panels not cycled are combined. Included are the data spread, the average load value and the number of panels tested for each joint process. Based on the limited number of tests, there is no indication that the room temperature characteristics of the two processes are significantly different.

TABLE XX.

STRUCTURAL PANEL TEST DATA SUMMARY

	Specimen (Joint Process)	Room Temp.	Temp. Cycled	Elevated Temp.	Local Crippling Load N x 10^3 (lbs x 10^3)	Ultimate Panel Load N x 10^3 (lbs x 10^3)
WELD-THROUGH PROCESS	Bonded Only -1	x			122.2 (27.5)	130.8 (29.4)
	Bonded Only -2	x			124.6 (28.0)	142.3 (32.0)
	Bonded Only -1[a]		x		48.9 (11.0)	75.6 (17.0)
	Bonded Only -2		x		151.2 (34.0)	160.1 (36.0)
	Bonded Only -1			x	95.6 (21.5)	97.9 (22.0)
	Bonded Only -2			x	108.9 (24.5)	118.8 (26.7)
	Spotweld, 1.57P-1	x			184.6 (41.5)	196.6 (44.2)
	Spotweld, 1.57P-2	x			140.1 (31.5)	177.9 (40.0)
	Spotweld, 1.57P-1		x		146.8 (33.0)	173.5 (39.0)
	Spotweld, 1.57P-2[b]		x		-- (--)	-- (--)
	Spotweld, 1.57P-1			x	129.0 (29.0)	144.6 (32.5)
	Spotweld, 1.57P-2			x	129.0 (29.0)	144.1 (32.4)
	Spotweld, 2.54P-1	x			133.4 (30.0)	151.2 (34.0)
	Spotweld, 2.54P-2	x			120.1 (27.0)	137.9 (31.0)
	Spotweld, 2.54P-1		x		106.8 (24.0)	124.6 (28.0)
	Spotweld, 2.54P-2		x		175.7 (39.5)	193.5 (43.5)
	Spotweld, 2.54P-1[c]			x	-- (--)	-- (--)
	Spotweld, 2.54P-2			x	120.1 (27.0)	141.0 (31.7)
	Bond/Weld, 1.57P-1	x			146.8 (33.0)	184.6 (41.5)
	Bond/Weld, 1.57P-2	x			184.6 (41.5)	210.4 (47.3)
	Bond/Weld, 1.57P-1		x		200.2 (45.0)	217.9 (49.0)
	Bond/Weld, 1.57P-2		x		209.1 (47.0)	220.2 (49.5)
	Bond/Weld, 1.57P-1			x	140.1 (31.5)	143.7 (32.3)
	Bond/Weld, 1.57P-2			x	133.4 (30.0)	157.0 (35.3)
	Bond/Weld, 2.54-1	x			129.0 (29.0)	199.3 (44.8)
	Bond/Weld, 2.54-2	x			133.4 (30.0)	193.5 (43.5)
	Bond/Weld, 2.54-1		x		135.7 (30.5)	194.8 (43.8)
	Bond/Weld, 2.54-2		x		108.9 (24.5)	203.7 (45.8)
	Bond/Weld, 2.54-1			x	120.1 (27.0)	129.0 (29.0)
	Bond/Weld, 2.54-2			x	102.3 (23.0)	140.6 (31.6)
CAPILLARY FLOW PROCESS	Bond Only	x			146.8 (33.0)	146.8 (33.0)
	Bond Only	x			186.5 (41.9)	186.5 (41.9)
	Bond Only		x		87.0 (19.8)	87.0 (19.8)
	Bond Only		x		175.3 (39.4)	175.3 (39.4)
	Bond Only			x	132.5 (29.8)	132.5 (29.8)
	Bond Only			x	133.4 (30.0)	133.4 (30.0)
	Bond/Weld, 2.54P	x			95.5 (21.5)	175.0 (39.3)
	Bond/Weld, 2.54P	x			115.7 (26.0)	175.3 (39.4)
	Bond/Weld, 2.54P		x		118.0 (26.5)	202.0 (45.4)
	Bond/Weld, 2.54P		x		173.5 (39.0)	212.5 (47.8)
	Bond/Weld, 2.54P[d]			x	64.5 (14.5)	133.4 (30.0)
	Bond/Weld, 2.54P[d]			x	114.5 (23.5)	142.3 (32.0)

[a] Damaged bond due to doubler re-work.
[b] Premature failure due to lack of doublers.
[c] Cement-asbestos insulation sheets broke under load.
[d] Specimen bowed 1/16" in center.

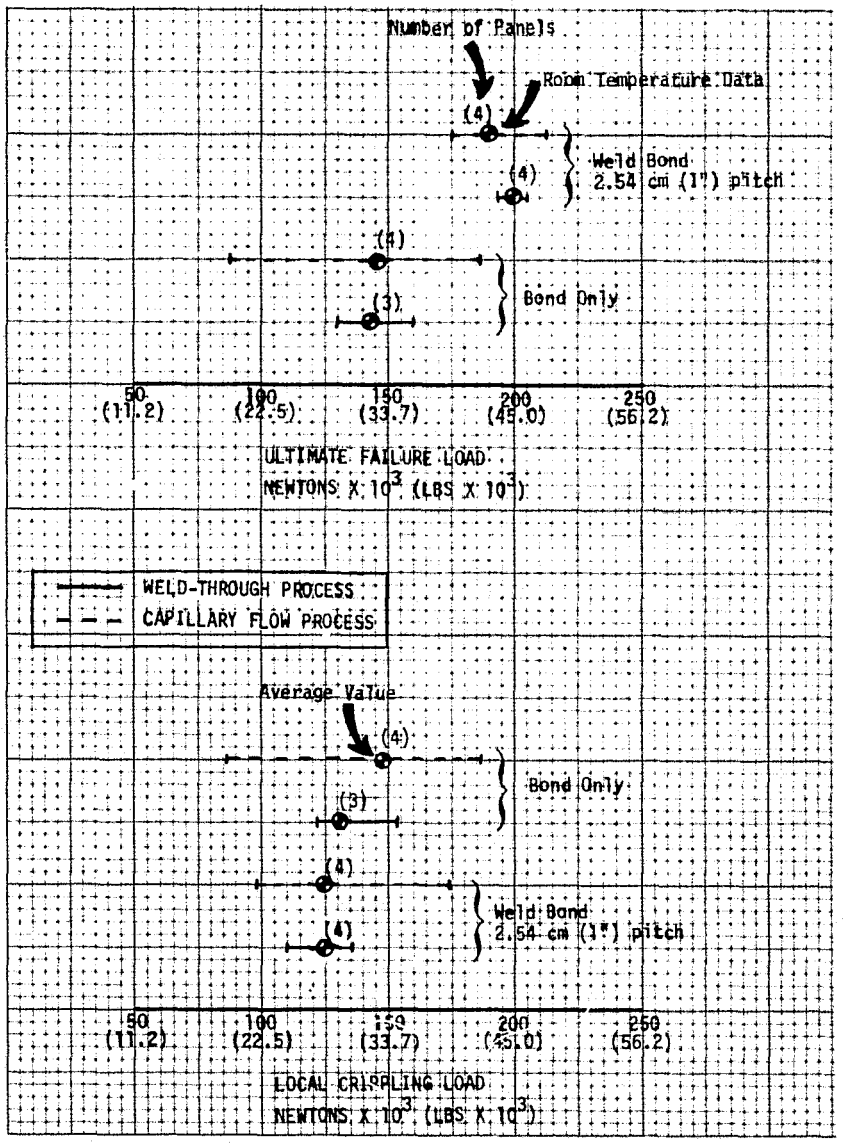

Figure 45. Relative Ranking of Room Temperature Structural Panel Tests

Figure 46 shows the comparative rankings of the elevated temperature tests. Because of the limited number of tests, individual panel data are shown superimposed on the room temperature results of Figure 45. Other than the approximately 20% reduction in load due to thermal reduction on the elastic modulus of the titanium panel material, the other differences are negligible.

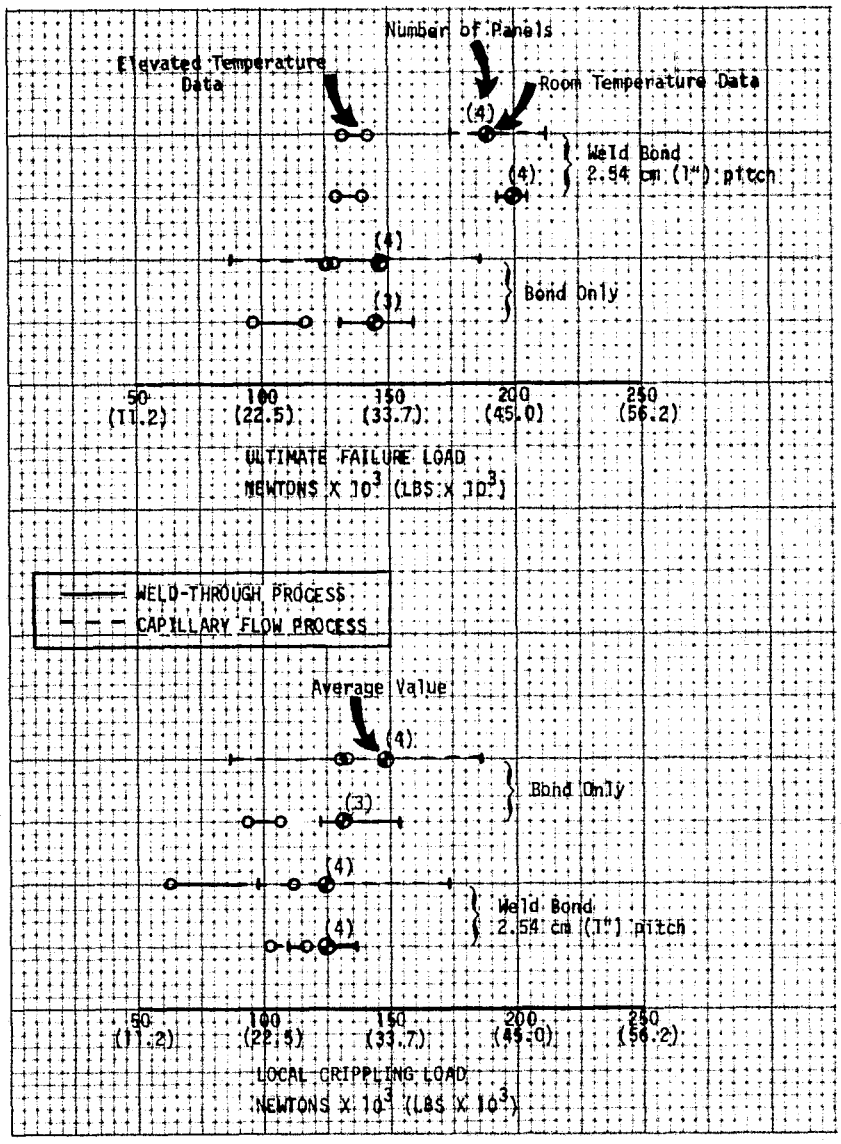

Figure 46. Relative Ranking, Elevated Temperature Structural Panel Tests, Superimposed on Room Temperature Rankings

6. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to develop a capillary flow adhesive formulation and weld bonding process using A-type polyimide resins containing ingredients considered to be non-carcinogenic. Based on these findings, recommendations are given for further developmental activities.

6.1 CONCLUSIONS

- A conductive adhesive primer formulation was developed which was satisfactory for spot welding through. Failure analysis of nuggets formed by the weld through process showed no detrimental effects from use of the conductive primer.

- A capillary flow adhesive formulation was developed which provided weld bonded joints equivalent in load carrying capacity to the weld-through weld bonded joints evaluated previously. Evaluation of bonded joints using the capillary flow adhesive provided lower values than obtained with the weld-through adhesive.

- Equivalent flow to the P11BA resin was obtained with A-type polyimide resins containing ingredients considered to be non-carcinogenic, *i.e.*, *m,m'*MDA instead of MPD and TDA. However, amine chain extended *bis*-maleimide had to be blended with the A-type polyimide in order to obtain satisfactory gap-filling characteristics.

6.2 RECOMMENDATIONS

- Studies to evaluate the conductive adhesive primer as a weld-through adhesive are warranted in order to provide a weld-through process for applications where precise location of the adhesive is not feasible. These studies should include formulation screening, fatigue and static testing.

- Studies to evaluate the A-type polyimide formulations containing ingredients considered to be non-carcinogenic, *i.e.*, *m,m'*MDA, are warranted in order to provide a satisfactory substitute to P11BA used in the P4/A5F adhesive. These studies should include evaluation of bonded-only and weld bonded joints.

- Studies to evaluate the use of the conductive adhesive primer as a surface preparation for titanium alloy prior to welding are warranted. This application of the conductive primer would permit titanium alloy surfaces to be cleaned and then stored or pre-assembled prior to welding. Presently, prepared titanium alloy surfaces have to be welded within four hours of treatment; priming of these surfaces would circumvent this requirement.

APPENDIX A.
MATERIALS PREPARATION PROCEDURES

A.1 Preparation of *Bis*[4-(4-aminophenoxy) phenyl] sulfone (BDAS)

The diamine was prepared by a route similar to that outlined in U.S. Patent 3,514,415 granted to Union Carbide. The diamine then was used to prepare the corresponding *bis*maleimide as described below.

A.2 Preparation of *Bis*[4-(4-maleimidophenoxy) phenyl] sulfone (BDAS-BM)

To a solution of 54.06 g (0.125 mole) of BDAS in 50 ml of dimethylformamide was slowly added a solution of 24.5 g (0.25 mole) of maleic anhydride in 25 ml of dimethylformamide. The temperature of the reaction mixture was maintained at 293K by means of an ice bath. The mixture was stirred at room temperature for one hour after the completion of the maleic anhydride solution and then 30.6 g (0.3 mole) of acetic anhydride and 2.46 g (0.03 mole) of sodium acetate were added. The reaction mixture then was heated at 338K for 2 hours during which time a precipitate formed. The reaction was added to 2-l. of water and the yellow precipitate was collected by filtration, washed with water and dried to give 70 g of crude *bis*maleimide. Recrystallization from a benzene/hexane mixture afforded 52 g of *bis*maleimide; mp 481-484K. The infrared spectrum of this compound is shown in Figure A-1.

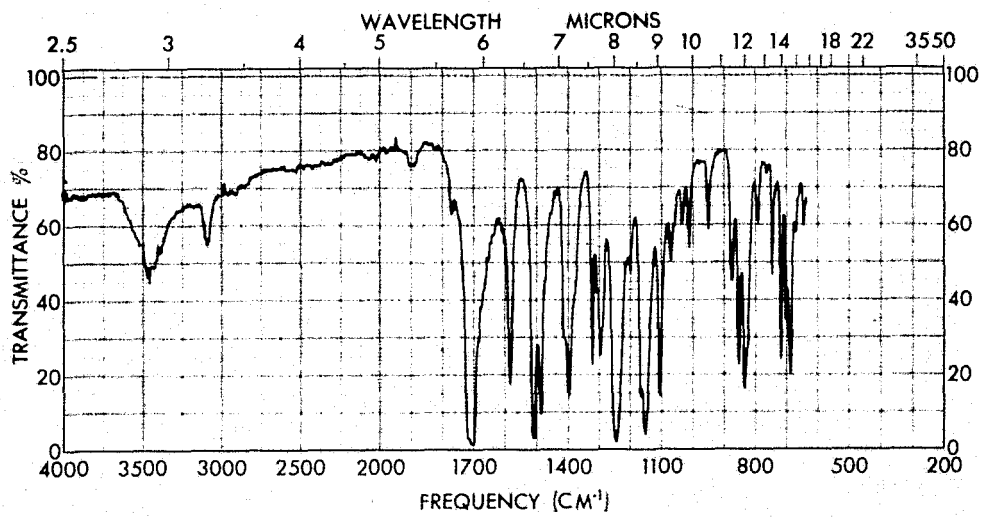

Figure A-1. Infrared Spectrum (KBr) of *Bis*[4-(4-maleimideophenoxy) phenyl] sulfone
Concentration: 3.1 mg/g KBr

A-3 Preparation of Prepolymer from BDAS-BM and *m,m'*MDA

To 2.22 g (0.0112 mole) of *m,m'*-MDA heated to 393K under a nitrogen atmosphere was added portionwise 11.85 g (0.020 mole) of BDAS-BM. After 5 g of BDAS-BM had been added, 8 ml of DMF was added to improve the mixing action. After all of the *bis*maleimide had been added, the mixture was stirred for 30 minutes at 393K and then the temperature was raised to 423K and maintained for 15 minutes. Most of the DMF was removed during the last 15 minutes of heating by sweeping the flask with nitrogen. After cooling, the yellow resin was powdered and dried *in vacuo* to give 13 g of prepolymer.

A-4 Preparation of Modified P13N Prepolymer

To a cooled solution (ice bath) of 7.94 g (0.040 mole) of *m,m'*-methylene dianiline in 30 g of dry dimethylformamide was slowly added 4.93 g (0.030 mole) of Nadic anhydride under a nitrogen atmosphere. The mixture was stirred for 30 minutes after the addition was complete and then 8.07 g (0.025 mole) of BTDA was added as a slurry in 17 g of DMF. The mixture was stirred an additional 3 hours before isolation of the amide acid form of the prepolymer or preparation of the imide prepolymer, both procedures are described below.

The amide acid form of the prepolymer was isolated by slowly adding the DMF solution of the prepolymer to cold methylene chloride. The resulting precipitate was collected by filtration and dried *in vacuo* at <323K.

The imidized prepolymer was prepared by thermally dehydrating the amide acid prepolymer which was isolated by removing DMF *in vacuo* at 373K. The material so isolated then was heated at 433K *in vacuo* for 4 hours to complete dehydration.

A-5 Preparation of *Bis*(2-Furfuryl) Benzophenone Tetracarboxylic Imide (BFBI)

To a solution of 258 g (0.8 mole) of BTDA in 600 ml DMF was slowly added 150 g (1.6 mole) of furfurylamine. The mixture was stirred an additional twenty minutes after the amine was added and then 1000 ml of xylene was added. The mixture was refluxed for 12 hours during which time the water of imidization was removed with a Dean-Stark trap. The reaction mixture was allowed to cool and the resulting precipitate was collected by filtration. Recrystallization of the filter cake from xylene afforded 261 g (68%) of *bis*imide; mp 506-508°K (233-235°C).

A-6 Preparation of *Bis*(4-Maleimidophenyl) Methane (BMPM)

To a solution of 158 g (0.8 mole) of methylenedianiline in 480 ml of dimethylformamide was added a solution of 157 g (1.6 moles) of maleic anhydride in 240 ml of dimethylformamide at such a rate as to keep the temperatures below 343K (158°F). After stirring the mixture for an additional 15 minutes, it was cooled to room temperature and 204 g (2 moles) of acetic anhydride followed by 16 g (0.2 moles) of sodium acetate were added. The resulting mixture was heated to 323K (122°F) and maintained there for 3 hours. The crude product was precipitated by pouring the reaction mixture into 4000 ml portions of water. The precipitate was collected by filtration, washed twice with 4000 ml portions of water and dried. Crystallization from methanol afforded 203 g (71%) of *bis*imide, mp 429-432K (312-319°F).

APPENDIX B.
DETAILED PROCESS PROCEDURES

B-1 Preparation of 6Al4V Titanium Alloy

Step 1 - Solvent clean faying surfaces with methyl ethyl-ketone (MEK)

Step 2 - Alkaline clean at 355K (180°F) for 15 minutes in a solution of Turco HTC (90-120 g/liter)

Step 3 - Rinse in hot tap water 339K (150°F) then cold tap water 295K (72°F)

Step 4 - Immerse in an aqueous bath of nitric acid 15% w/w and hydrofluoric acid 3% w/w at room temperature for 30 seconds

Step 5 - Rinse in tap water at 295K (72°F).

Step 6 - Immerse faying surfaces in Pasa-Jell 107 for 15 minutes at room temperature

Step 7 - Rinse in distilled water at 295K (72°F)

Step 8 - Dry in an air circulating oven at 339K (150°F)

B-2 Capillary Flow Adhesive Formulations

B-2.1 Capillary Flow Adhesive Formulation

pbw	Constituents
40.0	NA/BTDA/*m*,*m*'MDA (polyimide with n = 1)
40.0	BDAS maleimide/*m*,*m*'MDA
20.0	Dimethylformamide

B-2.2 Primer Formulation

pbw	Constituents
3.2	NA/BTDA/*m*,*m*'MDA amide acid (n = 1)
3.2	BDAS maleimide/*m*,*m*'MDA
6.4	Amoco AI 1137 amide imide resin
39.6	Silflake 135 silver flake
47.6	Dimethylformamide

B-2.3 Bonded-Only Adhesive Formulation

pbw	Constituents
15.7	NA/BTDA/*m*,*m*'MDA (Imide with n = 1)
15.7	BDAS maleimide/*m*,*m*'MDA
55.0	Aluminum powder, Grade 101
13.6	Dimethylformamide

B-3 Capillary Flow Adhesive Process

B-3.1 Primer Process

Spray primer formulation onto titanium alloy faying surfaces pre-treated with Pasa-Jell with a pressure gun and dry as follows:

60 minutes at 292K (R.T.)
60 minutes at 337K (150°F)
45 minutes at 407K (275°F)
5 minutes at 448K (350°F)

B-3.2 Capillary Flow Adhesive Process

Apply the capillary flow adhesive paste along welded joint edge then process as follows in an air circulating oven:

60 minutes at 292K (R.T.)
60 minutes at 337K (150°F)
20 minutes at 477K (400°F, 505K(450°F), 533K (500°F)
16 hours at 561K (550°F)

B-4 Bonded-Only Adhesive Process

Coat primed specimens with adhesive and dry as follows:

60 minutes at 292K (R.T.)
60 minutes at 337K (150°F)
45 minutes at 407K (275°F)
5 minutes at 448K (350°F)

Assemble lap shear panels on the bonding fixture which has been preheated to 477K (400°F). Insert assembly into press preheated to 477K (400°F) and stage for 20 minutes under contact pressure. After staging apply 689 KN/m^2 (100 psig) pressure, raise press temperature to 561K (550°F) and hold for 60 minutes. Remove pressure and cool assembly to ambient conditions. Postcure panel in an air circulating oven for 16 hours at 561K (550°F).

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