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TANTALUM AND MOLYBDENUM BRAZING TECHNIQUES.

TECHNICAL DOCUMENTARY REPORT NO. ML-TDR-64-270

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AF MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
US AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Northrop
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(Prepared under Contract No. AF 33(657)-11227
by Northrop Corporation, Norair Division,
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FOREWORD

This report was prepared by the Materials Research Group of Northrop Corporation, Norair Division, under USAF Contract No. AF 33(657)-11227. The research activities related herein represent the total program effort covering the period of 1 June 1963 through 30 June 1964.

The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, with Mr. R. E. Bowman serving as project engineer.

This report has been assigned number NOR 64-156 for internal control.

ABSTRACT

Brazed molybdenum and tantalum alloy honeycomb structures offer good potential for structural and heat shield applications in the 2500-3500 F range. However, molybdenum is seriously embrittled at braze temperatures above approximately 2500F. Tantalum alloys are not embrittled by high braze temperatures, but there are serious production problems associated with braze temperatures above 3200F. The purpose of this program was to develop molybdenum and tantalum braze systems which braze at relatively low temperatures, but develop high remelt and service temperatures. Some attention was also directed to the development of braze alloys for tantalum that braze several hundred degrees above the expected service temperature. Most of the effort was based on TZM molybdenum alloy and Ta-10W alloy. Some work was performed using Ta-8W-2Hf and Ta-30Cb-7.5V.

The most promising method of developing high remelt temperatures involved the diffusion sink brazing approach. This concept relied on the reaction of a braze alloy with the base material and/or refractory metal powder placed at the fillets, during the brazing cycle and during a post braze diffusion treatment at low temperatures. This diffusion reaction resulted in a new alloy in the joint with a higher melting temperature.

A Ti-25Cr-13Ni diffusion sink braze alloy which melted at 2200F produced the highest remelt temperatures on TZM. Remelt temperatures of tee joints exceeded 3100F under a 120 psi stress. Lap joint remelt temperatures exceeded 3200F and shear strength exceeded 250 psi at 3000F. Remelt temperatures as high as 3180F were attained on honeycomb specimens. In all cases, acceptable room temperature ductility was maintained.

Pure titanium, Ti-30V, and 33Zr-34Ti-33V diffusion sink braze alloys produced the highest remelt temperatures on Ta-10W. Remelt temperatures of lap and honeycomb specimens exceeding 3800F were achieved with Ti and Ti-30V following a diffusion treatment of 2850F for 24 hours. Lap shear strengths at 3500F were 3800 to 4270 psi and 2160 to 3050 psi with Ti and Ti-30V, respectively. In addition, brazed honeycomb specimens loaded to a 1.2 psi flatwise tensile stress withstood a one hour exposure with no failure. The lower melting (2480F) 33Zr-34Ti-33V braze alloy produced good remelt increases and high strengths for service to approximately 3000F. A Cb-1.3B conventional braze alloy (braze temperature 4200F) for either vacuum or argon brazing of Ta-10W exhibited lap shear strengths of approximately 4000 psi at 3500F. Brazed honeycomb specimens loaded to a 1.2 psi flatwise tensile stress withstood a one hour exposure at 3500F with no failure.

Pure titanium, Ti-30V, and 33Zr-34Ti-33V diffusion sink braze alloys as well as the conventional alloy Cb-1.3B were evaluated on the Ta-8W-2Hf and Ta-30Cb-7.5V alloys. In general, tee and lap joint strengths were equivalent to those achieved on Ta-10W. Room temperature ductility of all tantalum alloys and brazed lap joints was adequate based on transition temperature tests.

Coating-braze alloy compatibility was poor except for Ta-10W brazed with Cb-1.3B and coated with an unmodified silicide. In most cases coating-braze alloy interactions resulted in formation of low melting non-protective reaction products.

Development of high remelt temperatures using the diffusion sink brazing approach has been demonstrated on TZM and tantalum alloys. Remelt temperature increases of at least 1000F have been attained.

Application of the laboratory established brazing procedures and techniques was demonstrated by the fabrication of a completely ductile, typical, 5 x 5 x ½ inch TZM honeycomb panel, complete with edge enclosures. This panel, manufactured using the Nortobraze quartz lamp process, was brazed at 2300F and is expected to exhibit a remelt in excess of 3000F.

This technical documentary report has been reviewed and is approved.

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I INTRODUCTION

The general goal of this program was to develop braze alloys and techniques for the fabrication of molybdenum and tantalum alloy honeycomb panels for high temperature service.

Specific program goals for the program were established as follows:

Molybdenum Alloy: Mo-.5Ti-.08Zr (TZM)

1. Development of braze alloys and techniques for brazing below the recrystallization temperature of TZM, with joint remelt capability up to 3300F.
2. Development of braze alloys and techniques for brazing closed cell honeycomb panels which will withstand a single exposure at 3000F for one hour with a 1.2 psi flatwise tensile stress on the panel face sheets.
3. Determination of braze system - coating compatibility under an exposure of one hour at 3000F in a 1.2 psi air atmosphere.
4. Demonstration of the manufacturing applicability of the brazing alloys and techniques developed during the program, using the Nortobraze process.[1]

Tantalum Alloys: Ta-10W, Ta-8W-2Hf, Ta-30Cb-7.5V

1. Development of braze alloys and techniques for brazing in the 2000-3150F range with a 3800F joint remelt temperature.
2. Development of braze alloys and techniques for brazing closed cell honeycomb panels which will withstand a one-hour exposure at 2500-3500F with a 1.2 psi flatwise tensile stress on the panel face sheets. A temperature of 2500-3000F was required for the Ta-30Cb-7.5V alloy.
3. Development of conventional braze alloys which flow 200-300F above the intended service temperatures and can meet the requirements of goals 2 and 4.
4. Determination of braze system - coating compatibility under conditions of one hour at 2500-3500F in a 1.2 psi air atmosphere.

Approaches for achieving a high temperature brazing system include (1) volatilization of the melting point depressant element, (2) formation of intermetallic compounds with the melting point depressant element (reactive brazing), (3) brazing at temperatures from 200 to 300F above the service temperature (conventional brazing), and (4) diffusion of the melting point depressant element into a high melting solid solution (diffusion sink brazing).

In the first method, the addition of a volatile element strongly depresses the initial melting point of the braze alloy. After brazing, the braze joint may be held at a temperature somewhat below the braze temperature in a dynamic vacuum. As the volatile element is evaporated from the joint the remelt temperature is increased. This approach does not appear to be feasible for lap joints or closed-cell honeycomb structures.

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The second approach is based on the use of a braze alloy containing a strong melting temperature depressant. The depressant is selected to react with the base material or a suitably placed second component, to form a high melting intermetallic compound during a post-braze diffusion treatment. By removing the depressant in this manner, the joint remelt temperature is increased.

The concept of reactive brazing offers some potential for increasing joint remelt temperatures. However, successful application of this concept is highly dependent upon controlling the intermetallic compound reaction to form discrete particles. If continuous intermetallic compound films are present in grain boundaries or along the base metal-braze alloy interfaces, joint ductility will be seriously impaired.

The third concept is employed for the majority of brazements made today. However, a service temperature of 200-300F below the recrystallization temperature would be required for TZM. Above this critical temperature very rapid recrystallization, grain growth, and severe embrittlement would render the base alloy useless as a structural material.

Since tantalum alloys are not embrittled by recrystallization and grain growth, conventional brazing may be employed. However, this approach requires the use of cold-wall vacuum furnaces which generally are small and expensive.

Finally, in the diffusion sink concept, the braze alloy is placed so as to flow and fillet properly at the required braze temperature. The diffusion sink may be a powder concentrated at the needed areas and/or the base metal itself. A subsequent diffusion treatment will permit the braze alloy and diffusion sink to interact in the joint to form a new alloy with a higher melting temperature.

The braze alloy and diffusion sink powder should form solid solutions with one another. In addition, all possible interactions between braze alloy, sink powder, and base material should result in solid solution formation, thus avoiding brittle joints.

Because of these considerations, the diffusion sink approach to achieving high service temperature braze alloys was adopted in this program as the principal guide. However, some attention was directed to the development of brazing alloys for conventional brazing of the Ta base alloys.

II MATERIALS

Most of the braze systems selected contained substantial amounts of reactive metals such as Ti, V, Zr, Cb, Mo, and Ta. Mechanical properties of these metals are greatly influenced by their interstitial content. Therefore, commercially available metals of the highest purity were used as starting materials for braze alloy preparation.

Available chemical analyses and processing histories of the molybdenum and tantalum base alloys used in this program are recorded in Tables I and II, respectively.

Government-furnished closed cell TZM core (3/16 cell x .002 foil x .50 inch thick) was used in this program. The core was produced by Martin-Marietta Corporation, under Contract No. AF 33(657)-7276, using an electron beam welding technique.

Tantalum brazing studies employed closed cell, diffusion bonded, Ta-10W core (1/4 cell x .002 foil x .50 inch thick). This core was diffusion bonded by Hexcel Products Incorporated, using a node intermediate consisting of .002 inch Cb 752 foil coated on both sides with 60-100 micro-inches of titanium. The majority of core was fabricated from portions of the two foil lots listed in Table II.

TABLE I

CHEMICAL ANALYSIS AND PROCESSING HISTORY OF TZM MATERIALS

SOURCE	GAGE (In.)	HEAT NO.	(1) PROCESSING HISTORY	YIELD STRENGTH (KSI)	UTS (KSI)	% El.	CHEMICAL ANALYSIS
Universal Cyclops	.002	KDTZM936A	VAC, CR,	-	-	-	Percent C-.028, Si-.0035, Ni-.002, Ti-.46, Zr-.121, Fe-.0015, Mo-bal (Ingot Analysis
Fansteel	.013	32705-4	-	-	-	-	PPM C-120, 0-50, N-20, H-2, Ti-5800, Zr-890, Si-50, W-100, Ca-10, Cr-10, Cu-10, Fe-10, Mg-10, Ni-10, Mo-bal (Sheet Analysis)
Universal Cyclops	.040	KDTZM971A	VAC, HR, SR, Descaled	Trans. 120 Long. 108	131 125	10.9 12.3	Percent C-.031, Ti-.41, Zr-.12, Mo-bal (Ingot Analysis)

(1)	VAC	Vacuum Arc Cast
	HR	Hot Rolled
	SR	Stress Relieved
	CR	Cold Rolled

TABLE II

CHEMICAL ANALYSIS OF TANTALUM ALLOY MATERIALS

ALLOY	SOURCE	GAGE (In.)	HEAT NO.	CHEMICAL ANALYSIS (PPM)
Ta-10W	National Research Corp.	.002	2354	C-23, 0-16, N-14, Fe-10, Cr-5, Ni-10, Si-100, Cb-100, Al-50, Cu-1, Ti-10, Mo-10, W-9.8 x 10^4, Ta-bal (Ingot Analysis)
Ta-10W	National Research Corp.	.002	2798	C-19, 0-46, N-22, Fe-5, Cr-2, Ni-10 (Ingot Analysis)
Ta-10W	Fansteel	.010	22437-2	C-30, 0-50, N-30, Cb-930, Mo-230, Fe-50, Si-100, Ti-100 W-9.0 x 10^4, Ta-bal (Ingot Analysis)
Ta-10W	Fansteel	.040	22437-1	C-30, 0-50, N-30, Cb-930, Mo-230, Fe-50, Si-100, Ti-100, W-9.0 x 10^4, Ta-bal (Ingot Analysis)
Ta-8W-2Hf	Wah Chang	.010	4.5-30753	Al-20, B-1, C-60, Cb-315, Cd-5, Co-10, Cr-20, Cu-40, Fe-40, H-6, Mg-20, Mn-20, N-80, Ni-20, 0-60, Pb-20, Si-40, Sn-20, Ti-50, V-20, W-8.15 x 10^4, Hf-1.65 x 10^4, Ta-bal (Ingot Analysis)
Ta-8W-2Hf	Wah Chang	.040	4.5-30753	Same composition as .010 inch Ta-8W-2Hf (Ingot Analysis)
Ta-30Cb-7.5V	AF Materials Lab.	.013	5.58-7037A-TCV #3	
Ta-30Cb-7.5V	AF Materials Lab.	.030	5.58-7037A-TCV #3	

III PROCEDURES

PRE-BRAZE CLEANING

All TZM and tantalum alloy base materials were chemically cleaned prior to brazing. A number of cleaning procedures were evaluated; final selection was based on surface appearance, etching weight loss data, metallographic analysis for intergranular corrosion and braze alloy flow tests.

A TZM pre-braze cleaning procedure reported in the literature[1] produced excellent results on .013 inch TZM sheet. However, the .002 inch TZM foil for this program contained a surface contamination layer which was clearly visible after a recrystallization treatment as shown in Figure 1. Therefore, it was necessary to remove about 20% of the original thickness of the foil.

Table III outlines the two TZM cleaning procedures adopted for materials with heavy and light surface contamination. Only the .002 inch foil required the procedure for heavy surface contamination. Nevertheless, most of the TZM sheet was cleaned using the procedure for heavy contamination to assure surface cleanliness.

The tantalum alloys were cleaned using the procedures outlined in Table IV. While the $25HF-25HNO_3-50H_2O$ etchant produced excellent results on Ta-10W, light smut formation was observed on the Ta-8W-2Hf and Ta-30Cb-7.5V alloys. However, the $12.5HF-25HNO_3-62.5H_2SO_4$ etchant eliminated this problem.

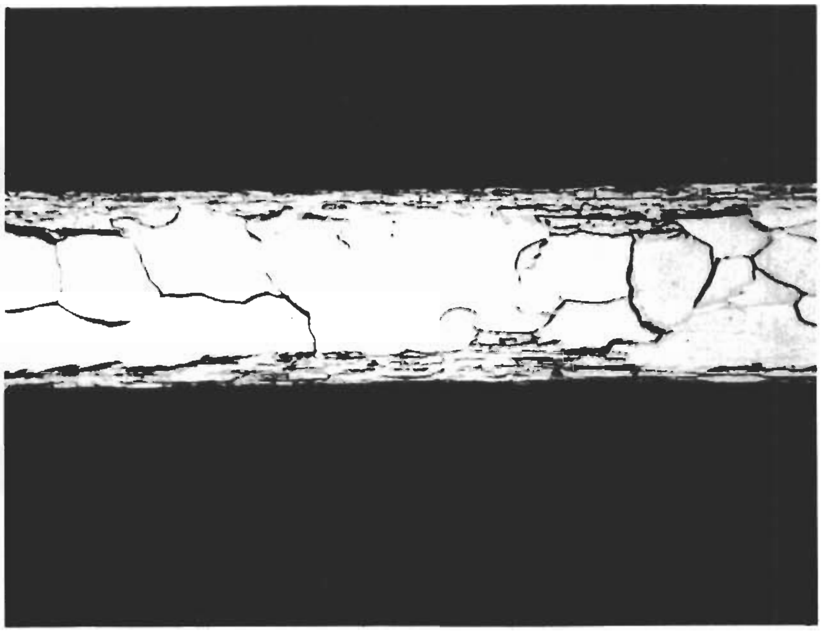
BRAZE SYSTEM PLACEMENT

Development of procedures for placing braze alloys and diffusion sink powders on honeycomb specimens was based on the following assumptions:

1. Sink powder is undesirable between the edges of the core and the face sheets.
2. Sink powder should be placed only at the fillets and nodes of the core.
3. Braze alloys should be placed on the face sheets only.

A number of sink powder placement methods were investigated. The most effective procedure involved dipping both edges of the core into a shallow (.005-.020 inch) low viscosity suspension of -400 mesh powder suspended in clear nitrocellulose lacquer. After the suspension flowed up the nodes by capillary action, the core was placed between glass or teflon plates and slowly rotated to maintain even distribution of the sink powder in the nodes until the lacquer dried. Any excess powder on the dipped edges of the core was removed by a flat scraper. Powder loading in nodes was determined by weight measurements.

Each side of the core was again dipped into a more viscous lacquer-powder suspension to deposit powder at fillets. Excess powder along the core edges was removed by a flat scraper. The fillet loading on each side of the core edges was determined individually by weight measurements. Total lineal distances of nodes and fillets were approximately equal in the core configurations that were employed. Therefore, approximately 50 percent of the desired sink powder quantity was placed in nodes and the balance divided equally between the fillet areas on both sides of the core.



NOTE SURFACE
CONTAMINATION

MAG: 500X ETCHANT: MURAKAMI'S

RECRYSTALLIZED AT 2600F FOR 1 MIN. IN 300 TORR ARGON

FIGURE 1 MICROSTRUCTURE OF RECRYSTALLIZED .002 INCH TZM FOIL

TABLE III

TZM PRE-BRAZE CLEANING PROCEDURE

1. Vapor Degrease.
2. Alkaline clean - 6-10 oz/gal Wyandotte Nuvat at 180F ± 10F for five to ten minutes or equivalent alkaline cleaner.
3. Cold tap water rinse.

Heavy Surface Contamination	Light Surface Contamination
4. Alkaline Etch 10 wt. % NaOH 5 wt. % $KMnO_4$ 85 wt. % H_2O Use fifteen minutes at 220F ± 10F	4. Alkaline etch 10 wt. % NaOH 5 wt. % $KMnO_4$ 85 wt. % H_2O Use five minutes at 90F ± 10F
5. Cold tap water rinse.	5. Cold tap water rinse
6. Smut Removal 15cc H_2SO_4 (96%) 15cc HCl (38%) 70cc H_2O 12 gm Chromic Acid Use ten minutes at 220F ± 10F	6. Smut removal 15cc H_2SO_4 (96%) 15cc HCl (38%) 70cc H_2O 12 gm Chromic Acid Use five minutes at 120 F ± 10F
7. Cold tap water rinse	7. Cold tap water rinse
8. One minute in alkaline etch (same composition as Step 4)at room temperature	8. Distilled water rinse
9. Cold tap water rinse	9. Alcohol dip (optional)
10. Thirty seconds in smut remover (Step 6) at 220F ± 10F	10. Air dry
11. Cold tap water rinse	
12. Distilled water rinse	
13. Alcohol dip (optional)	
14. Air dry	
Typical Weight Loss .002 Inch TZM Foil 15-20% .013 Inch TZM Sheet 3-4% .040 Inch TZM Sheet 1-2%	Typical Weight Loss .002 Inch TZM Foil 2% .013 Inch TZM Sheet .5% .040 Inch TZM Sheet .2%

NOTE: For heavily contaminated TZM core,clean in accordance with procedure for Heavy Surface Contamination, but modify steps 4 and 6 immersion times to 5 minute steps to yield a total of 15 minutes in each solution. Example: 5 minutes in alkaline etch, rinse, 5 minutes in smut remover, rinse, 5 minutes in alkaline etch . . . . . Typical weight loss 15-20%

TABLE IV

PRE-BRAZE CLEANING PROCEDURE FOR TANTALUM BASE ALLOYS

1. Vapor degrease.
2. Alkaline clean - 6-10 oz/gal Wyandotte Nuvat at 180 F ± 10F for five to ten minutes or equivalent alkaline cleaner.
3. Cold tap water rinse.

Ta-10W	Ta-8W-2Hf (T-111) and Ta-30Cb-7.5V
4. Acid Etch	4. Acid Etch
25 Vol. % HF (49%) 25 Vol. % HNO_3 (70%) 50 Vol. % H_2O Use five minutes at room temperature	12.5 Vol. % HF (49%) 25 Vol. % HNO_3 (70%) 62.5 Vol. % H_2SO_4 (98%) Use five minutes at room temperature

5. Cold tap water rinse.
6. Distilled water rinse.
7. Alcohol dip (optional on sheet, preferable on core).
8. Air dry.

Typical Weight Losses

Ta-10W	Ta-8W-2Hf (T-111) and Ta-30Cb-7.5V
5-7% on .002 Inch Foil 2% on .010 Inch Sheet	1.2% on .010-.012 Inch Sheet

In all cases sink powder quantities and distribution were maintained within ± 15 percent of the desired amount. The minimum amount of sink powder that could be placed on the core in a reproducible manner was approximately .003 cm^3 per square inch of core. Figure 2 shows a typical honeycomb specimen with sink powder placed at fillet and node areas. The procedure for placing sink powder on tee joint specimens was similar to that used for honeycomb specimens.

Braze alloy powder placement on tee and honeycomb specimens was accomplished by screening the material onto suitably masked base sheets. A fine-mesh screen was loaded with powder and then vibrated and rotated over the base sheets to provide an even distribution of braze alloy. Powder loading rate was controlled by weighing each base sheet before and after placement. Once the desired loading was attained, several drops of lacquer were used to anchor the powder in place.

Braze alloy powder was hand placed on lap joints involving small faying areas. A fixed quantity of powder was weighed out, spread over the desired area with the aid of a metal mask, and anchored in place with lacquer. Lap joints with large faying areas required use of the above-mentioned screening technique for braze alloy placement.

In cases where foil braze alloys were used, the foil was simply cut to the desired size, positioned on the particular specimen and held in place with lacquer or by spot-welding.

BRAZE ALLOY FABRICATION

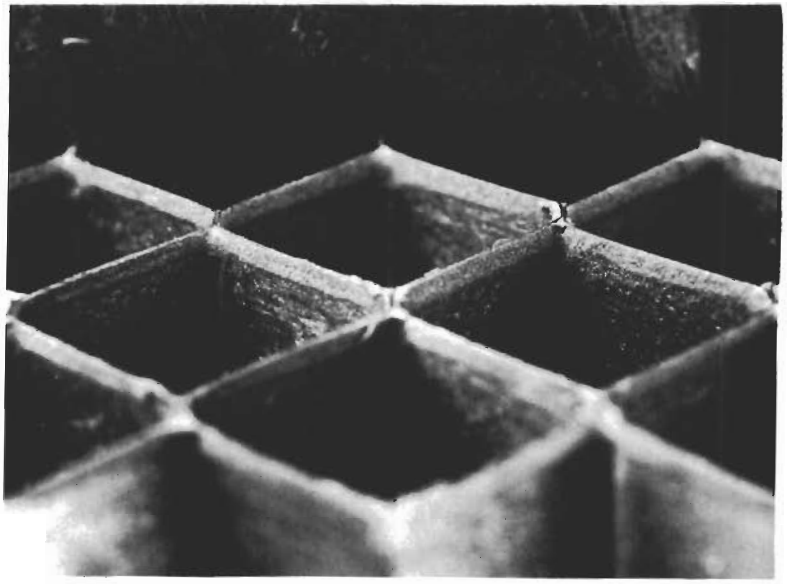
Experimental braze alloys were produced by conventional, non-consumable tungsten-arc melting in a water-cooled copper hearth. Each alloy was melted six times in a 400 torr high purity argon atmosphere. The alloys were weighed before and after melting and the compositions assumed to be correct if no appreciable weight changes were noted. A qualitative measure of ductility was obtained by chiselling a chip from each alloy. The following designations were used to rate ductility:

Ductile	Substantial chip curling or deformation.
Slightly Ductile	Some chip curling or deformation.
Brittle	No visible deformation.
Very Brittle	Button fractured when struck with chisel.

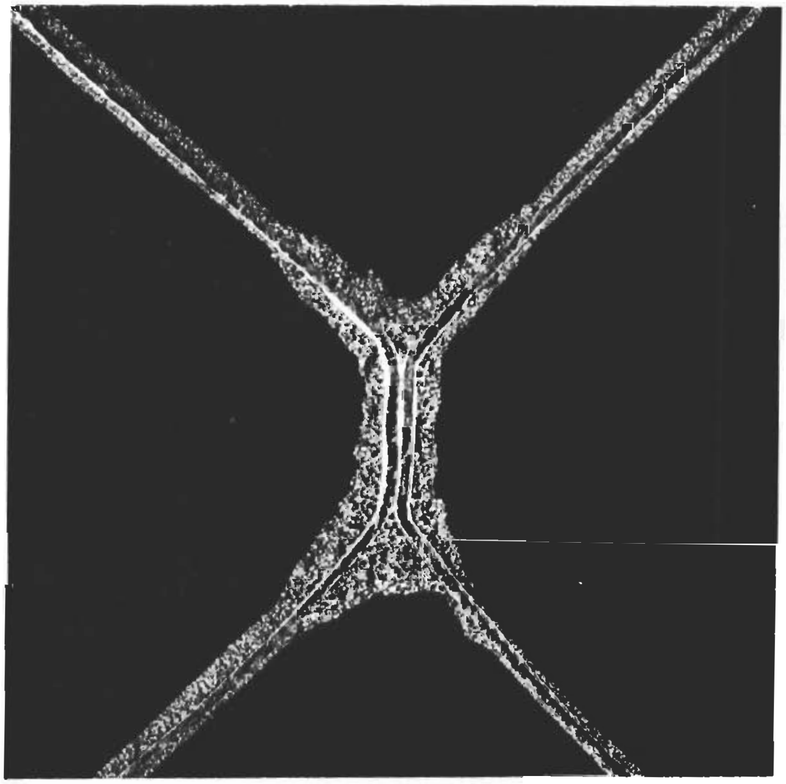
Melting temperatures were determined on sections cut from each alloy. These sections were placed on refractory metal sheets, heated in a 300 torr high purity argon atmosphere and melting temperatures determined visually. Temperatures to 3050F were measured by Pt/Pt-10Rh thermocouples; W/W-26Re couples or a micro-optical pyrometer were used at higher temperatures. Accuracy of melting temperature determinations was estimated to be within ± 20F to 3050F and ± 40F at higher temperatures.

In most cases, Rockwell "C" hardness and density of as-melted alloys were measured. Density values were determined by the Jolly balance technique.

A number of braze alloys were reduced to powder to provide an economical and convenient form for brazing. To facilitate powdering, the alloys were embrittled by hydriding for 30 to 90 minutes at 500-1000F in pure hydrogen flowing at approximately 30 CFH. The hydrogen gas used was a high purity grade which was passed through a platinum catalyst and a titanium-chip getter, operating at 1550F, to assure a clean gas.



FILLET AND NODE AREAS
MAGNIFICATION 5X



NODE AREA
MAGNIFICATION 25X

FIGURE 2 HONEYCOMB SPECIMEN WITH DIFFUSION SINK POWDER PLACED AT FILLETS AND NODES

After hydriding, the alloys were wet-crushed to -100 mesh in a steel mortar and pestle. Perchlorethylene was used to prevent oxidation of the powder during the crushing operation.

The liquidus temperatures of as-hydrided and powdered alloys were determined and compared to as-melted liquidus temperatures as a quality control measure. The ductility of the melted powder was also compared to as-melted ductility as a further quality control measure. Ductility was determined by the chisel ductility test. It was found that this ductility test and particularly liquidus temperature determinations were quite sensitive measures of contamination.

SPECIMEN BRAZING

A number of .002-.013 inch TZM and .002-.010 inch Ta-10W "S" type tee joints were brazed. A typical specimen is shown in Figure 3. This same configuration was used to braze tee joints with .010 inch Ta-8W-2Hf and .013 inch Ta-30Cab-7.5V. Edges of the tee sections were machined flat and parallel before precision bending to the "S" shape. Corner areas of the tees were machined out to prevent vertical braze alloy flow. A constant volume of braze alloy (.025 cm^3 for TZM and .030 cm^3 for the tantalum alloys) was placed on each base sheet along a 3/16 inch wide zone running along the tee section. This placement approach simulated the condition existing in a honeycomb panel with braze alloy evenly applied to base sheets.

The .002 inch tee sections were held in a Ta-10W jig to prevent buckling and to maintain close alignment and joint fit during brazing. Brazing was performed in a cold-wall tantalum furnace operating at 10^{-4} - 10^{-5} torr vacuum. Initial heating was limited by the rate of outgassing of lacquer and hydrogen from the braze alloys. Outgassing was completed at approximately 1200F. Then the heating rate was increased to approximately 500F/min. until the braze temperature was reached. This was followed by a one minute hold time at the brazing temperature. Several specimens were also brazed in argon. However, they were outgassed to approximately 1200F in vacuum before backfilling with argon to 300 torr.

Temperatures to approximately 3050F were measured and controlled by Pt/Pt-10Rh thermocouples. A micro-optical pyrometer or W/W-26Re couples were used for higher temperatures.

Lap shear specimens were brazed using 2.0 x .50 inch blanks positioned in a tantalum jig and overlapped .120 - .140 inch. Base metal thickness was .040 inch except for Ta-30Cb-7.5V which was .030 inch. In general, a constant volume (.002 cm^3) of braze alloy was placed in the faying plane of each specimen. In some cases braze alloy was placed outside the joint and allowed to flow in by capillary action. All specimens were dead-weight loaded to approximately 2 psi on the faying planes to maintain joint contact during brazing. Brazing procedures were the same as those used on tee joints.

Lap joint specimens for coating compatibility studies were brazed with the same gages of materials used for lap shear specimens. However, the coating laps were shaped like sheet tensile specimens with a joint overlap of 3/8 x 1-15/16 inches in the reduced section. A constant braze alloy volume of .025 cm^3 was used on Ta-10W specimens and .012 cm^3 on TZM specimens. Brazing procedure was the same as that used for lap shear specimens.

Each lap joint for bend transition temperature determination was brazed using two 2.5 x 2.5 inch squares of .010-.013 inch sheet. Braze alloy was centered on a 2 x 2 inch area between the sheets. A constant braze alloy volume of .20 cm^3 was used on tantalum alloys and .10 cm^3 used on TZM. Each joint was dead-weight loaded

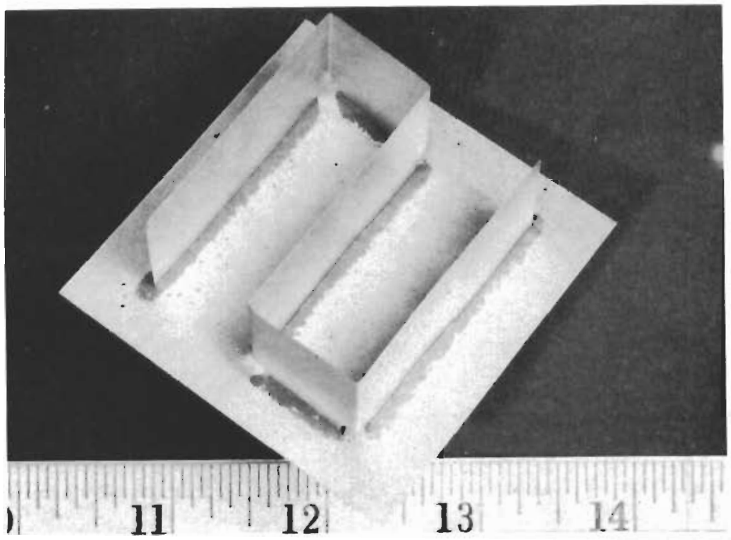


FIGURE 3 TYPICAL .002 - .013 INCH BRAZED TEE JOINT SPECIMEN

at 0.5 psi during brazing. Then the joints were sectioned into the required number of bend transition temperature specimens. The 2 x 2 inch and 1 x .75 inch honeycomb specimens were fabricated in a similar manner. The TZM specimens were brazed with .013 inch face sheets and 3/16 cell x .0016 foil x .50 inch thick closed cell electron beam welded core. Original foil thickness of the core was .002 inch but it was necessarily reduced to .0016 inch by chemical cleaning to remove surface contamination. The Ta-10W specimens were similar to TZM specimens except that .010 inch face sheets were used and the closed cell diffusion bonded core configuration was 1/4 cell x .002 foil x .50 inch thick.

Length and width dimensions of face sheets were cut approximately 1/2 inch larger than the length and width of the core. Braze alloy placement on each face sheet was limited to an area slightly larger than the area covered by core. Braze alloy loading on TZM honeycomb specimens was .046 $cm^3/in.^2$ on each face sheet. Loading on Ta-10W specimens was maintained at .033 $cm^3/in.^2$ on each face sheet. All specimens were dead weight loaded to 0.5 psi during brazing. Brazing cycles and procedures followed those used for tee joint brazing.

DIFFUSION TREATMENT

Most of the diffusion treatments were conducted in a tantalum cold-wall vacuum furnace with the specimens exposed to the vacuum system. In some cases specimens were placed in a small rigid F82 (Cb-33Ta-.7Zr) retort which was sealed by electron beam welding. The retort was placed in the furnace for diffusion treating. Temperatures were measured and controlled by a W/W-26Re thermocouple. Furnace vacuum level was approximately 5×10^{-4} torr at the beginning of a diffusion run and increased to approximately 2×10^{-6} torr within a few hours.

METALLOGRAPHIC

Metallographic polishing of TZM and Ta-10W braze joints was relatively straightforward. It was necessary to use two different etchants on TZM specimens to develop braze alloy and base metal microstructures. However, no troublesome interactions were encountered with this double etching procedure.

Metallographic etching of Ta-10W braze joints posed some problems. All etchants rapidly attacked most of the braze alloys before base metal structure could be developed. Therefore, it was necessary to etch and photograph the braze alloy and base metal independently. Then a paste-up of these photographs was prepared and re-photographed to represent joint microstructure.

HIGH TEMPERATURE TEST

Remelt temperatures were determined on TZM and Ta-10W tee joints using the jig arrangement shown in Figure 4. Remelt test specimens, cut from the "S" tees previously discussed, were 1/2 inch wide. A 42 gm. tantalum weight was hung from a hole drilled through the foil leg of each tee. This load produced a tensile stress of approximately 120 psi on the foil which was equivalent to a flatwise tensile stress of 1.2 psi on a panel using a core configuration of 3/16 cell x .0016 inch foil.

The testing jig was positioned in a tantalum furnace and heated at approximately 600 F/minute in a 10^{-4} to 10^{-5} torr vacuum. Temperatures were measured by an optical pyrometer sighted on the base of the tee. Remelt temperature was recorded as the temperature at which the joint failed.

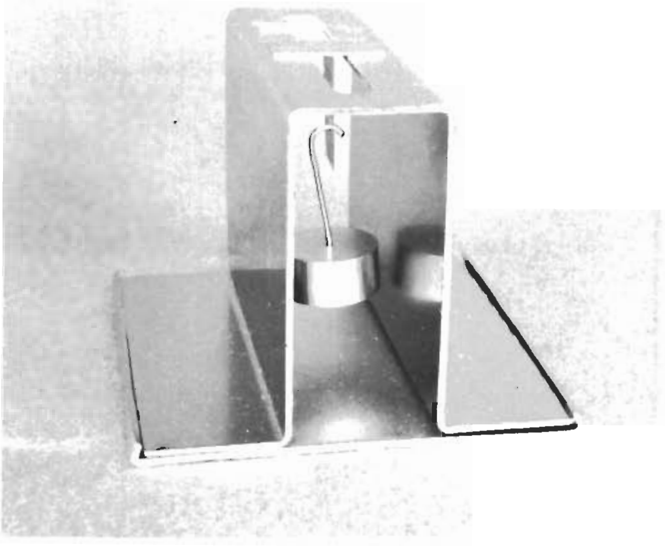


FIGURE 4 TEE JOINT TESTING JIG

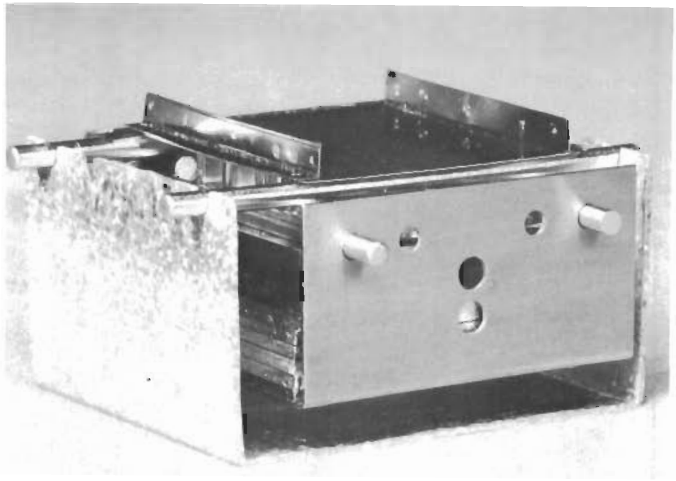


FIGURE 5 HONEYCOMB SPECIMEN TESTING JIG

Strength tests on TZM and Ta-10W tee joints were conducted using the specimen configuration and jig arrangement discussed above. However, the tantalum weight was increased to achieve a maximum foil tensile stress of 650 psi. Similarly the same 650 psi base metal tensile stress was maintained on the Ta-8W-2Hf and Ta-30Cb-7.5V tees which were made from .010 and .013 inch sheets, respectively. These strength tests were conducted in the same manner as remelt tests. Applied stress and failure temperature were recorded for each specimen.

Remelt tests on honeycomb specimens were conducted using the jig arrangement shown in Figure 5. The top face sheet of the panel was supported by two 1/4 inch diameter tungsten rods. Two similar rods were placed across the lower face sheet, rotated 90 degrees from the top rods. Doublers, spot welded or clipped to the face sheets, were used to evenly distribute the load and minimize bending. A load pan containing tungsten plates was suspended from the bottom rods. Honeycomb specimens were dead weight loaded to produce up to 1.2 psi flatwise tensile stress on the panel. Remelt testing procedure was similar to that used on tee joints. This same approach was used to determine the effects of a 1.2 psi stress on a specimen during elevated temperature exposure for one hour.

Remelt and high temperature strength tests on lap joints were conducted in a double gun electron beam testing furnace positioned in a tensile testing machine. The electron beam was adjusted to limit heating rates in the lap area to 600F/minute. Temperatures were measured by a two-color optical pyrometer calibrated against a Pt/Pt-10Rh thermocouple to 3000F. For the remelt tests, the specimens were dead weight loaded to 2.4 pounds. This load produced a tensile stress of approximately 120 psi on the base material and 40 psi shear stress on the joint. For the strength tests the specimens were heated to the test temperature, under no load, followed by immediate loading at a head speed of .05 inch/minute.

TRANSITION TEMPERATURE TEST

Base Metal

Ductile-to-brittle transition temperatures of .010-.020 inch TZM and tantalum alloys were determined by transverse bend testing. All transverse bend transition samples were sheared with the width dimensions parallel to the sheet rolling direction. These specimens were machined to finish dimensions of 0.5 x 1.0 inch by grinding at least .025 inch from each edge.

The bend jig shown in Figure 6 was positioned in an insulated container which could be filled with various fluids to attain test temperatures ranging from 212 to -320F. Temperatures from 212F to room temperature were achieved using water heated by a resistance element. Temperatures to -125F were produced by filling the container with acetone and pumping liquid nitrogen through a copper cooling coil immersed in the acetone. Temperatures from -125 to -250F were produced in a similar manner by replacing the acetone with 2-methylbutane. A temperature of -320F was produced by filling the container with liquid nitrogen. In all cases temperatures were measured and controlled by an iron-constantan thermocouple positioned on the bend jig adjacent to the sample.

The jig and container assembly were positioned on a compression load cell in a tensile test machine. Deflection was determined by running the tensile machine at a head speed of .05 inch/minute. A load versus time curve was made for each run using a chart speed of 10 inches/minute. Thus, each inch of chart travel corresponded to .005 inch deflection. Specimen fracture was detected by a sharp drop in load.

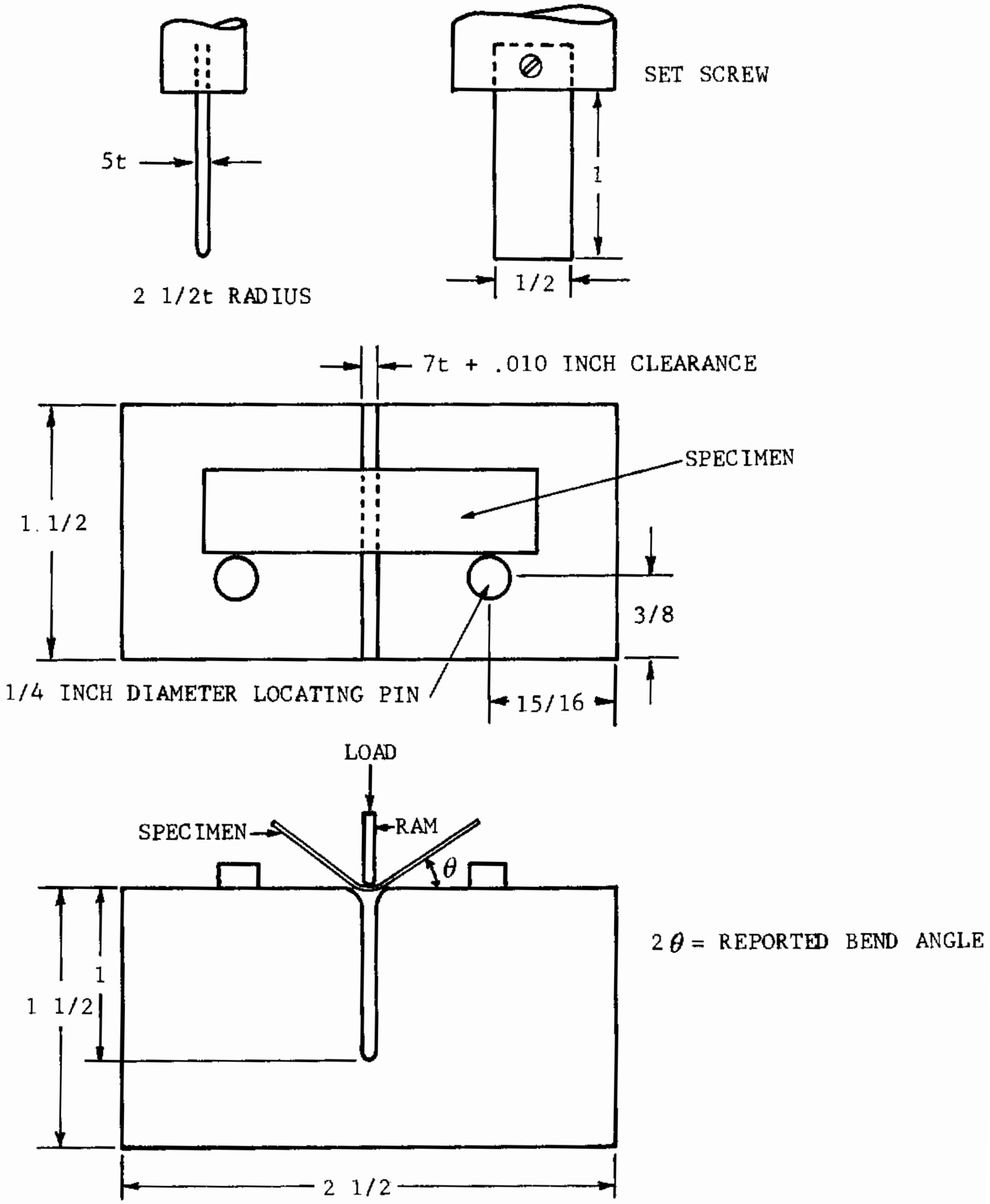


FIGURE 6 TEST JIG FOR BEND TRANSITION TEMPERATURE DETERMINATION

In many cases bend angle values represent a more meaningful measure of joint ductility than deflection values. Therefore, several calibration tests were conducted on representative specimens to provide a direct correlation between bend angle and bend deflection data. Bend deflection and bend angle at fracture were plotted as a function of test temperature to determine the bend transition temperature.

Transverse notched tensile test specimens with dimensions as shown in Figure 7, were used to determine transition temperatures of .002 inch TZM and Ta-10W foils. Test temperatures below room temperature were achieved using an environmental chamber cooled with liquid or gaseous nitrogen. Temperatures above room temperature were produced by a portable recirculating air heater. An iron-constantan thermocouple was clipped to the reduced section of each test specimen for temperature measurement and control.

The specimens were positioned in a tensile testing machine by shear pin loading in doubler-type grips to prevent buckling. Testing was conducted at a head speed of 0.1 inch per minute to failure. Notched tensile strengths were plotted as a function of test temperature to determine the ductile to brittle transition temperatures.

Braze Joints

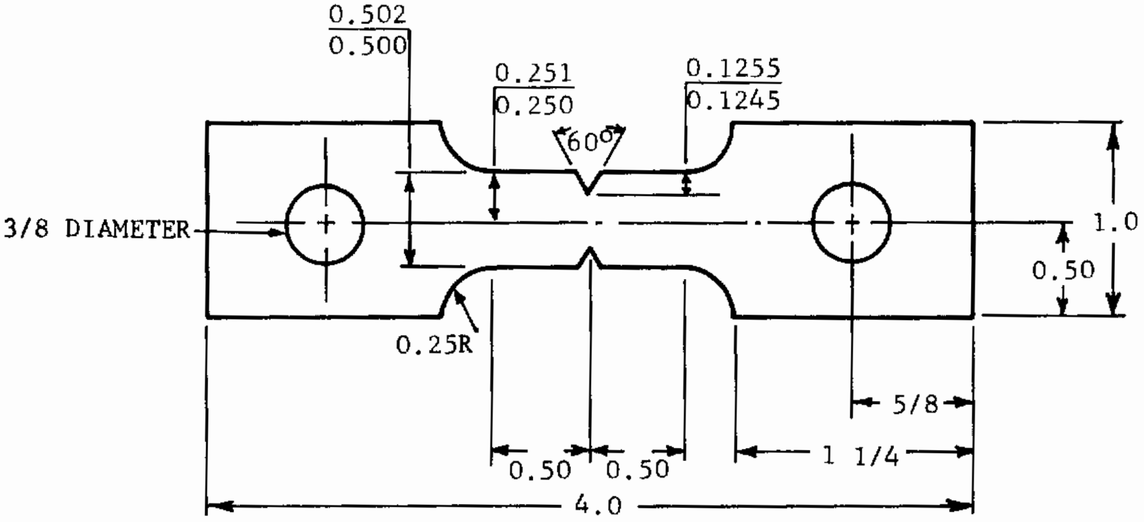
Transverse bend transition temperature tests on brazed lap joints were conducted using the same basic procedures, equipment, and specimen geometry used for base metal bend tests. In some cases these specimens failed by braze joint cracking alone. This type of failure could not be detected from load versus deflection curves. Therefore, it was necessary to metallographically examine selected samples after testing to determine presence and magnitude of cracking.

Bend transition tests were conducted on 3/8 inch wide brazed tee specimens cut from the "S" tee joints previously described. The vertical leg of each specimen was bent .040 inch above the base sheet using a flat ram with an edge radius of 1/64 inch and a head speed of .05 inch per minute. Bend deflection and bend angle at fracture were recorded at several test temperatures. These tests were conducted using the same basic procedures used for bend testing. However, the bend test jig was replaced with a jig specifically designed for this type of test.

COATING COMPATIBILITY TEST

Brazed lap joint specimens of the configuration shown in Figure 8, were employed for coating-braze alloy compatibility tests. After brazing and suitable diffusion treatments, specimen edges were rounded to a minimum radius of 0.005 inch prior to coating.

An unmodified silicide coating for Ta-10W and PFR-6 coating for TZM were applied by Pfaudler Company using the pack cementation process. A Sn-25Al coating for Ta-10W was applied at Northrop Norair by lacquer spraying a 75Sn-25Al mixture of -200 + 325 mesh powder. After spraying, these specimens were heated to 1925 ± 25F for 15 minutes in flowing argon to remove the lacquer and diffuse the coating.



NOTCH ROOT RADIUS: 0.001 INCH MAXIMUM
STRESS CONCENTRATION FACTOR: 11.2

FIGURE 7 NOTCHED TENSILE TRANSITION TEMPERATURE SPECIMEN

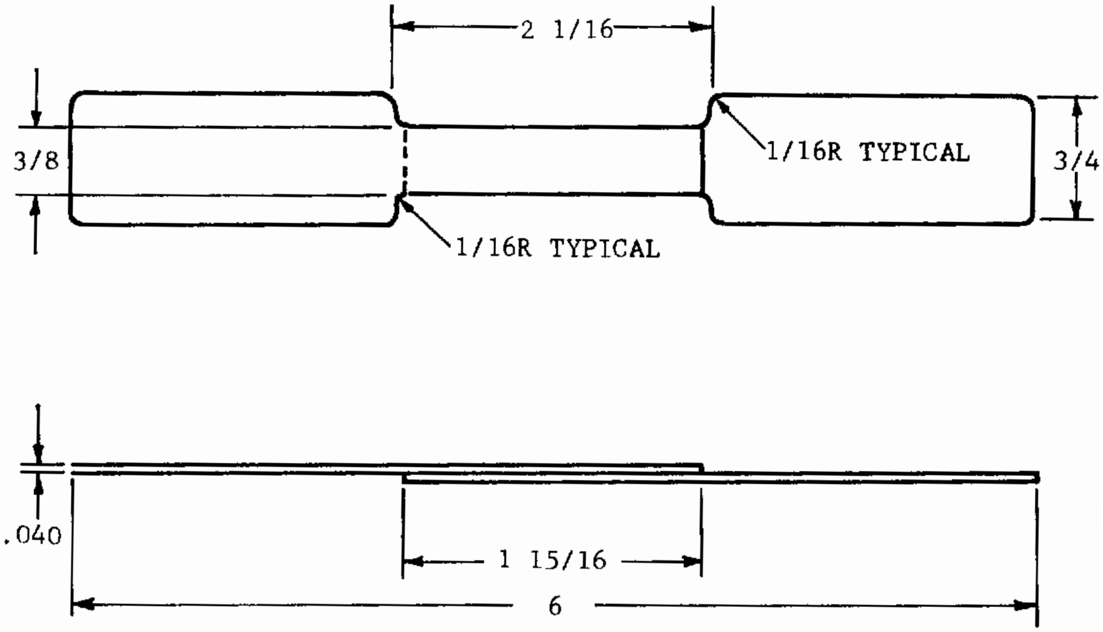


FIGURE 8 LAP JOINT SPECIMEN FOR COATING COMPATIBILITY TESTS

The specimens were tested at temperatures between 2500F and 3500F by direct resistance heating. All tests were conducted in a 1.2 psi air atmosphere using an air flow of approximately 5 cubic feet per hour. Temperature was measured by sighting a micro-optical pyrometer on the reduced section of the specimen. In these tests, brightness temperatures are reported since the emissivities of the coatings under the reduced pressure conditions used were unknown. Specimens were observed during testing and any visible coating-braze alloy or coating-base metal interactions noted.

After testing, the specimens were sectioned at the center and the faying plane-coating area examined by metallographic analysis and microhardness traverses.

IV RESULTS AND DISCUSSION

LITERATURE SURVEY

A comprehensive literature survey and analysis, included in Appendix A, was conducted during this program. Relatively little information was found concerning conventional or high remelt temperature brazing of refractory alloys. However, it was established that among the low temperature brazing approaches employed, diffusion sink and, to a lesser extent, reactive brazing concepts offered greatest potential for developing high remelt temperatures, together with good joint ductility.

Diffusion sink brazing involves reaction of a braze alloy with the base material and/or refractory metal powder additions after proper filleting and flow have occurred. The reaction initiates during the braze cycle and is completed during a post-braze diffusion treatment. The diffusion reaction produces a new alloy in the joint with a higher melting temperature. Reactive brazing is based on using a braze alloy containing a strong melting temperature depressant. The depressant is selected to react with the base metal and/or powder additions to form a high melting intermetallic compound during a post-braze diffusion treatment. By removing the depressant in this manner, the joint remelt temperature is increased.

During the literature survey, several binary and ternary phase diagrams were found for systems offering good braze alloy development potential. The following systems appeared most promising for molybdenum brazing.

Ti-Co
Ti-Ni
Ti-Co-Cr
Ti-Ni-Cr
Ti-Fe-Cr
Ti-Cr
Ti-Ni-Si
Ti-Zr-V
Zr-V-Cb

Further, it was determined that alloys in these systems should be formulated to permit brazing at temperatures no higher than 2400F because of the recrystallization behavior of .002 inch TZM foil.

The most promising conventional brazing systems for tantalum were Cb-V, Cb-Ti, Ta-B, and Cb-B. For high remelt temperature brazing of tantalum, the following systems offered the most promise:

Ti-Zr
Ti-V-Si
Ti-V-Fe
Zr-V-Ti
Ta-B
Cb-B
Ti-V-Fe-(Cb, Ta, or Mo)
Ti-V-Si-(Cb, Ta, or Mo)
Ti-Zr-(Cb, Ta, or Mo)

Additions of Cb, Mo, and Ta were the most promising diffusion sink powders for tantalum as well as molybdenum diffusion sink brazing.

TZM BRAZING

Braze System Development

In general, published data were not available for predicting effects of refractory metal (diffusion sink) additions on ductility and liquidus temperature of candidate braze alloy compositions. Therefore, a number of braze systems were alloyed with suitable refractory metals to simulate diffusion sink additions.

It was assumed, conservatively, that the base metal would contribute a 10 weight percent Mo addition to a braze fillet. If complete base metal-braze alloy diffusion occurred in a typical core to base sheet joint (.002 inch core-.010 inch face sheet -.010 inch fillet radius) a 60 percent Mo concentration would be produced in the fillet. It was further assumed that sink powder additions representing 15 percent of the braze fillet weight could be incorporated into a joint. Thus, simulated diffusion sink additions to each braze alloy were standardized at 10 percent base metal - 15 percent diffusion sink powder.

Braze alloy development was based primarily on Ti as a matrix because it forms a complete series of solid solutions with Mo. However, it was necessary to depress the melting temperature of titanium to permit brazing at 2400F or less. There are no Ti alloys which can meet this requirement and still be completely soluble in Mo. Therefore, it was necessary to use "incompatible" depressants and obtain the best possible optimization between braze temperature, depressant content, alloy ductility, and joint ductility.

Table V summarizes the ductility and liquidus temperature data obtained on candidate TZM braze systems. It was believed that alloys rated ductile or slightly ductile possessed adequate ductility for use as braze alloys. Applicability of alloys rated brittle was questionable while those rated very brittle were considered unsuitable. Thus, alloy #31, Zr-30V-20Cb and alloy #29, Ti-10Co-25Cr were eliminated from further considerations as braze alloys. Alloy #24, Ti-13Fe-13Cr and alloy #30, Ti-10Ni-25Zr were eliminated because (1) they were rated brittle and (2) they did not meet the 2400F maximum braze temperature requirement. The latter problem could have been eliminated by increased solute additions, but only at the expense of a further reduction in ductility.

The data on Ti-20Co, alloy #26, and Ti-21Ni, alloy #27, showed that both alloys possessed equivalent ductility. However, Ti-21Ni was more promising because of the combination of equivalent ductility and greater melting temperature depression produced by Ni. Similarly for the Ti-Ni-Si compositions, Ti-8Ni-7Si, alloy #45, possessed the best combination of ductility and liquidus temperature. Of the Ti-Cr-Ni systems, Ti-25Cr-10Ni, alloy #176, and Ti-15Cr-13Ni, alloy #34, appeared equally promising.

A Ti-35Cr, alloy #20, braze alloy was considered because it is close to the minimum melting temperature of the Ti-Cr system. In addition, Ti and Cr form solid solutions with Mo. The high liquidus temperature precluded use of this alloy on TZM honeycomb. However, it offered potential for brazing heavier gage TZM which possesses greater resistance to recrystallization.

Several Zr-V-Ti alloys were formulated. These included alloys for brazing at approximately 2400F and 2550-2600F. The higher braze temperature was desired to determine ductility after brazing above the recrystallization temperature of TZM core but below the recrystallization temperature of the base sheets. The 46Zr-34V-20Ti, alloy #162, and 33Zr-34Ti-33V, alloy #102, alloys were the preferred compositions.

TABLE V

CANDIDATE TZM BRAZE SYSTEMS

Alloy No.	Composition Weight Percent	Liquidus Temp. F	* Ductility	Increase In Liquidus Temp. F
31	Zr-30V-20Cb	2340	VB	
29	Ti-10Co-25Cr	2340	VB	
24	Ti-13Fe-13Cr	2420	B	
30	Ti-10Ni-25Zr	2460	B	
26	Ti-20Co	2220	SD	
27	Ti-21Ni	2070	SD	
46	75(Ti-21Ni)-25Mo	2700	B	630
47	80(Ti-21Ni)-8Mo-12Ta	2490	B	420
180	Ti-10Ni-6Si	2160	B	
177	Ti-11Ni-6Si	2160	B	
90	Ti-7Ni-7Si	2320	SD	
45	Ti-8Ni-7Si	2250	SD	
50	75(Ti-8Ni-7Si)-25Mo	2690	B	440
58	75(Ti-8Ni-7Si)-10Mo-15Ta	2610	VB	360
176	Ti-25Cr-15Ni	2120	B	
179	Ti-25Cr-13Ni	2190	B	
28	Ti-25Cr-10Ni	2300	SD	
34	Ti-15Cr-13Ni	2290	SD	
59	75(Ti-25Cr-10Ni)-15Mo-10Ta	2900	VB	600
60	75(Ti-25Cr-10Ni)-25Mo	3060	B	760
49	75(Ti-15Cr-13Ni)-10Mo-15Ta	2745	B	455
48	75(Ti-15Cr-13Ni)-25Mo	2780	B	490
20	Ti-35Cr	2600	SD	
56	75(Ti-35Cr)-25Mo	3130	VB	530
57	75(Ti-35Cr)-10Mo-15Cb	2960	VB	360
36	75(Ti-35Cr)-25Ta	2740	B	140
32	38Zr-31V-31Ti	2370	D	
42	40Zr-30V-30Ti	2335	D	
65	42Zr-29V-29Ti	2340	D	
115	43Zr-32V-25Ti	2350	D	
162	46Zr-34V-20Ti	2250	D	
178	50Zr-32V-18Ti	2120	D	
43	75(36Zr-35V-29Ti)-25Mo	2960	SD	560
35	75(36Zr-35V-29Ti)-10Mo-15Cb	2810	SD	460
86	30Zr-35Ti-35V	2570	SD	
102	33Zr-34Ti-33V	2480	SD-D	
93	75(30Zr-35Ti-35V)-25Mo	3010	SD	440
94	75(30Zr-35Ti-35V)-10Mo-15Ta	2990	SD	420

* D = Ductile
SD = Slightly Ductile
B = Brittle
VB = Very Brittle

The Mo diffusion sink additions to Ti-Ni, Ti-Ni-Cr, and Ti-Ni-Si braze alloys produced the largest liquidus temperature increases and minimum reductions in ductility. The severe embrittlement of Ti-35Cr by Mo additions was unexpected based on phase diagram considerations. The Ti-25Cr-10Ni braze alloy showed the highest remelt potential of these systems and was selected for evaluation on tee joints. Although Ti-8Ni-7Si alloy exhibited less remelt potential, it was still considered attractive for two reasons. First, it was a lower melting modification of the Ti-8.5Si alloy which has shown large remelt temperature increases in brazing TZM [2]. Secondly, it represented an approach based on a metal-metalloid braze alloy.

Data for the Zr-Ti-V alloys presented in Table V are based on diffusion sink brazing alone. A Mo diffusion sink addition to the lower melting Zr-Ti-V alloys produced the largest liquidus temperature increase. Another brazing approach with this alloy involved a combination of diffusion sink and reactive brazing using carbon additions. This approach could not be evaluated by additions to alloy melts but required experiments on actual joint configurations. This was necessary because carbon must be added to the diffusion sink powder as discrete particles to avoid embrittling compound films.

The higher melting Zr-V-Ti alloy showed somewhat less remelt potential than the lower melting modifications. Nevertheless, the alloy was still promising because the sink additions of Ta and Mo produced essentially equivalent increases in the liquidus temperature. Since Ta exhibits a higher density than Mo, it offered potential for placing more sink powder in a braze joint. Therefore, Ta was selected as the diffusion sink for this braze alloy.

With the exception of the Zr-Ti-V alloys, diffusion sink additions reduced braze alloy ductility to the brittle or very brittle classifications. It was believed systems rated brittle by the chisel test might still possess sufficient ductility for honeycomb brazing applications. The Rockwell C hardness of a number of alloys was measured to determine if (1) hardness could be correlated with chisel test ductility and (2) if there were any differences between systems rated brittle. This hardness data showed poor correlation with ductility as measured by the chisel test.

A summary of the final TZM braze systems selected for further evaluation is given in Table VI. Estimates of the amount of diffusion sink required for a 3300F remelt temperature are also included. These estimates were based on the data of Table V and phase diagram considerations.

All final braze alloys were reduced to powder for subsequent studies. Pertinent braze alloy properties and powdering parameters are included in Table VII. The Ti-25Cr-13Ni and Ti-10Ni-6Si are included for reasons discussed in subsequent sections of this report.

Diffusion Sink Powder Parameters

In actual practice, remelt temperature produced by diffusion sink powder additions will depend upon (1) the remelt increase per unit amount of sink powder added, and (2) the maximum amounts of various sink powders that can be incorporated into a joint without affecting braze alloy behavior. Therefore, several .002-.013 inch TZM tee joints were vacuum brazed with 33Zr-34Ti-33V to determine the following sink powder parameters:

TABLE VI

FINAL TZM BRAZE SYSTEMS

Braze Alloy	Liquidus Temp. F	Diffusion Sink Powder	Estimated % Diffusion Sink Req'd. For Remelt Temperature of 3300 F
46Zr-34V-20Ti	2260	Ta	45
46Zr-34V-20Ti	2260	Mo+BorC	45 (Mo alone)
Ti-8Ni-7Si	2250	Mo	55
Ti-25Cr-10Ni	2320	Mo	35
33Zr-34Ti-33V	2480	Ta	35

TABLE VII

TZM BRAZE ALLOY PROPERTIES

Braze Alloy	Liquidus(F) & Ductility As Cast	Hardness As Cast (Rc)	Density gm/cm^3	Hydride Treatment	Liquidus(F) -100 Mesh Powder	Ductility of Melted Powder Patch
46Zr-34V-20Ti	2260-D	33	5.88	1000F-½ hr	2260	D
Ti-8Ni-7Si	2250-SD	53	4.69	850F-1 hr	2260	SD
Ti-25Cr-10Ni	2320-SD	39	5.40	700F-½ hr	2300	SD
33Zr-34Ti-33V	2480-SD	33	5.58	1000F-3/4 hr	2480	D
Ti-25Cr-13Ni	2200-B	40	5.47	700F-½ hr	2200	B
Ti-10Ni-6Si	2160-B	44	4.76	-	-	-

1. The optimum diffusion sink powder particle size.
2. The maximum quantity of diffusion sink powder that can be placed at fillets without impeding braze alloy filleting and flow.
3. The mechanism responsible for impeded braze alloy filleting and flow in the presence of high sink powder concentrations.

The test data from this study are recorded in Table VIII. Comparison of specimens M-5 and M-17 indicated that the -400 mesh Cb sink powder permitted better braze alloy filleting than -100 +140 mesh Cb powder. These limited results suggested that use of finer mesh sink powders was more desirable than coarser particle sizes. However, it was impractical to use sink powders finer than -400 mesh. Therefore, -400 mesh powders were used for all subsequent diffusion sink brazing.

Specimens M-5, M-6, and M-7 were brazed with essentially constant volume percentages (15-17) of -400 mesh Cb, Mo, and Ta, respectively. All of these specimens exhibited unacceptable braze alloy filleting. The braze alloy appeared to have sponged into the sink powder leaving very small, starved fillets. Specimen M-5 which used Cb sink powder exhibited better filleting than the joints employing Mo and Ta. Specimen M-7, employing the Ta sink, exhibited the poorest filleting. Specimen M-8 brazed with 9 volume percent Ta sink exhibited fair but unacceptable filleting. These data indicated that various sink powder additions cannot be made on a constant volume basis. The maximum amounts of -400 mesh diffusion sink powders that could be successfully employed were: (1) 15 wt. percent Cb, (2) 10 wt. percent Mo, and (3) 15 wt. percent Ta. Later tee joint brazing confirmed these values for several braze systems. Therefore, these percentages were standardized for all subsequent brazing with diffusion sink powders.

Estimated diffusion sink quantities required for a 3300F remelt temperature (Table VI) were reviewed with respect to the above data. This showed that allowable sink powder additions represented a relatively small percentage of the total diffusion sink requirement. Thus, the major portion of the diffusion sink must be supplied by the base material.

Impeded braze alloy filleting and flow caused by high sink powder concentrations were believed to be produced by one or both of the following mechanisms:

1. "Trapping" of the braze alloy in the sink powder due to capillary forces.
2. Rapid braze alloy-sink powder diffusion which raised the braze alloy liquidus above the braze temperature before proper filleting and flow took place.

Alloy melting data of Table V indicated that an alloy of the approximate composition 75(33Zr-34Ti-33V)-25Mo, alloy #93, should melt at approximately 3000F. This braze alloy-diffusion sink combination was used to braze specimen M-18 (see Table VIII) at 3100F which was about 200F above the liquidus of alloy #93. Excellent filleting was observed. Specimen M-20 was brazed with the same alloy, #93, at 2800F which was about 100F below the liquidus temperature of the system. This specimen exhibited fair but unacceptable filleting.

Metallographic examination of other as-brazed tee joints employing sink powders showed relatively homogeneous fillets with no evidence of unreacted sink powder. This confirmed the fact that the braze alloy-sink powder diffusion reaction was quite rapid and indicated that the second mechanism for limiting the amount of sink powder additions predominated.

TABLE VIII

SINK POWDER PARAMETER DATA

Tee No.	Diffusion Sink Metal	Diffusion Sink Volume %	Diffusion Sink Weight %	Braze Temp. (F)	Notes
M-17	Cb	17	24	2580	-100 + 140 mesh powder used - poorer filleting than M-5
M-5	Cb	17	24	2580	Unacceptable filleting, but better than M-6 and M-7
M-6	Mo	15	25	2580	Poor filleting - heavy sponging of braze alloy
M-7	Ta	15	34	2580	Very poor filleting - heavy sponging of braze alloy
M-8	Ta	9	21	2580	Fair filleting - slight sponging of braze alloy
M-18	Mo	15	25	3100	Excellent filleting
M-20	Mo	15	25	2800	Fair filleting but unacceptable

Base Material - TZM

Diffusion Sink Powder - 400 Mesh

Brazing Parameters: a) Braze Alloy: 33Zr-34Ti-33V (Liquidus = 2480F)

Brazed one minute in vacuum

Diffusion Treatment

An analysis was conducted to determine the optimum diffusion treatment for TZM braze joints. The allowable total thermal exposure involving brazing, diffusion and coating processes was limited by recrystallization behavior of the .002 inch TZM foil. Several tests were conducted to establish recrystallization behavior of .002 and .013 inch TZM used during the program. These tests were conducted in vacuum using a heating rate of 600F/minute and a cooling rate of approximately 1500F/minute. Results were as follows:

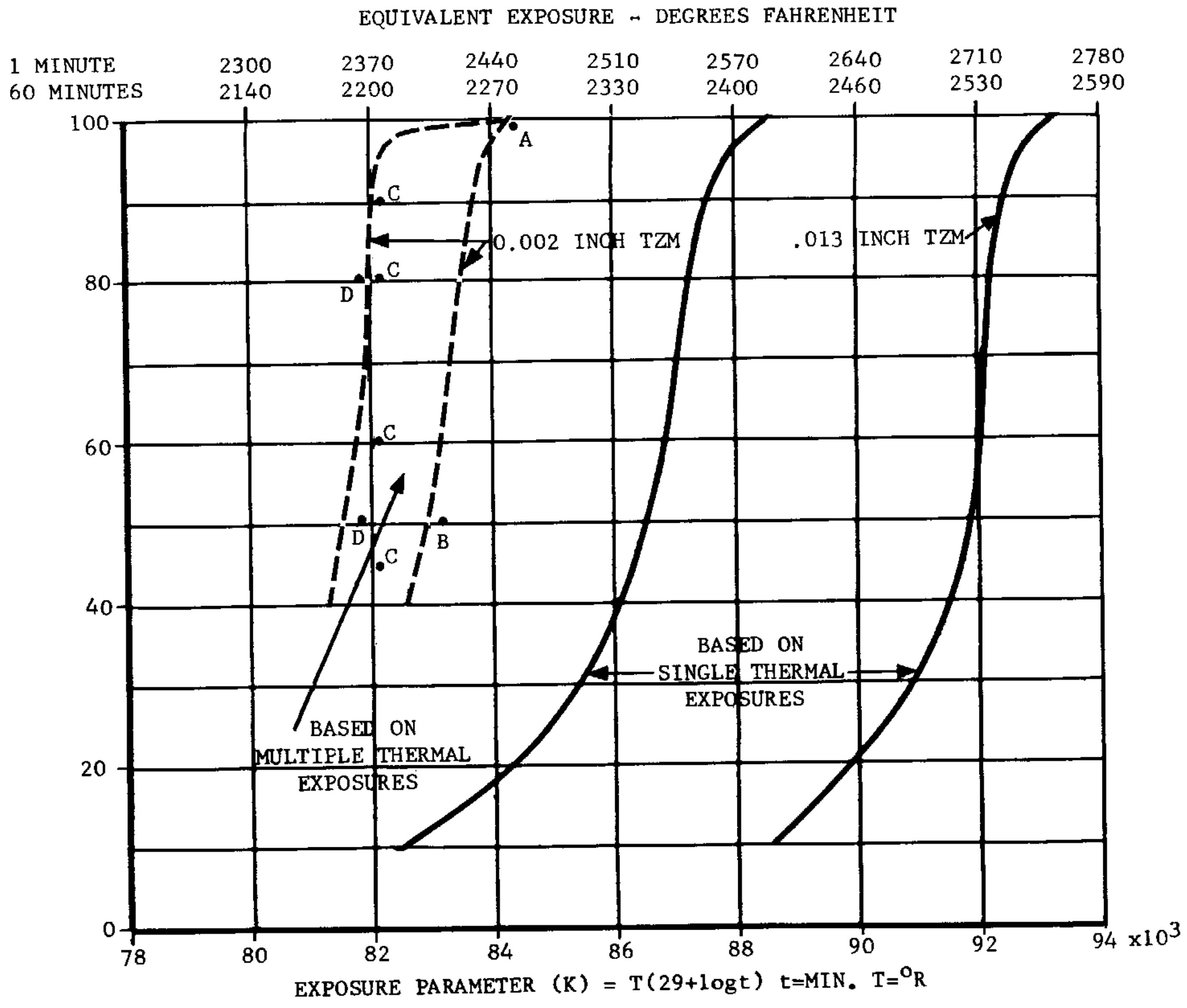
	% Recrystallization	
Single Thermal Exposure	.013 Inch TZM Sheet	.002 Inch TZM Foil
2475F - 1 minute		25
2520F - 1 minute		50
2550F - 2 minutes	10	
2600F - 1 Minute		100
2675F - 1 minute	30	
2750F - 1 minute	100	

The above data were used to plot percent recrystallization versus a Larson-Miller type time-temperature parameter as shown in a portion of Figure 9. This figure shows that the recrystallization temperature range for the foil is about 175F (5000 time-temperature parameter units) lower than for the sheet.

Figure 9 further shows that the foil can withstand a single thermal exposure of about 86,500 units based on a criterion of 50 percent maximum recrystallization. However, multiple thermal exposures using different times and temperatures produced more recrystallization than predicted by the parameter. A brazing cycle followed by a diffusion cycle represents a multiple exposure. Therefore, it was estimated that the total thermal exposure associated with brazing and diffusion treating should be limited to K = 83,000 - 85,000.

A variety of time-temperature combinations equaling the desired parameter values could be employed for the diffusion treatment as shown in Figure 10. A sample calculation of data used to plot this curve is shown in Appendix B. These data are primarily based on a braze cycle of one minute at 2400F prior to the diffusion treatment. One curve is included to show the marked increase in diffusion time which is permitted by reducing the braze temperature to 2300F.

Several diffusion calculations were made to approximate the optimum diffusion times and temperatures to produce the largest degree of braze alloy-base metal diffusion for a given K value. These calculations were based on a simple Ti-Mo diffusion couple. The results are shown in Figure 11 and sample calculations are included in Appendix B. These data show that for a given K value, long time, lower temperature diffusion treatments should produce greater diffusion than short time, higher temperature treatments. It follows that the long time, lower temperature diffusion cycles should produce more braze alloy-base metal diffusion for a fixed amount of TZM recrystallization.



A. 2400F FOR 1 MINUTE +
2130F FOR 40 HOURS

B. 2400F FOR 1 MINUTE +
2040F FOR 20 HOURS

C. 2300F FOR 1 MINUTE +
2050F FOR 85 HOURS

D. 2300F FOR 1 MINUTE +
1900F FOR 16 HOURS +
1950F FOR 8 HOURS +
2000F FOR 40 HOURS +
2050F FOR 56 HOURS

FIGURE 9 THERMAL EXPOSURE PARAMETER VS PERCENT RECRYSTALLIZATION FOR TZM

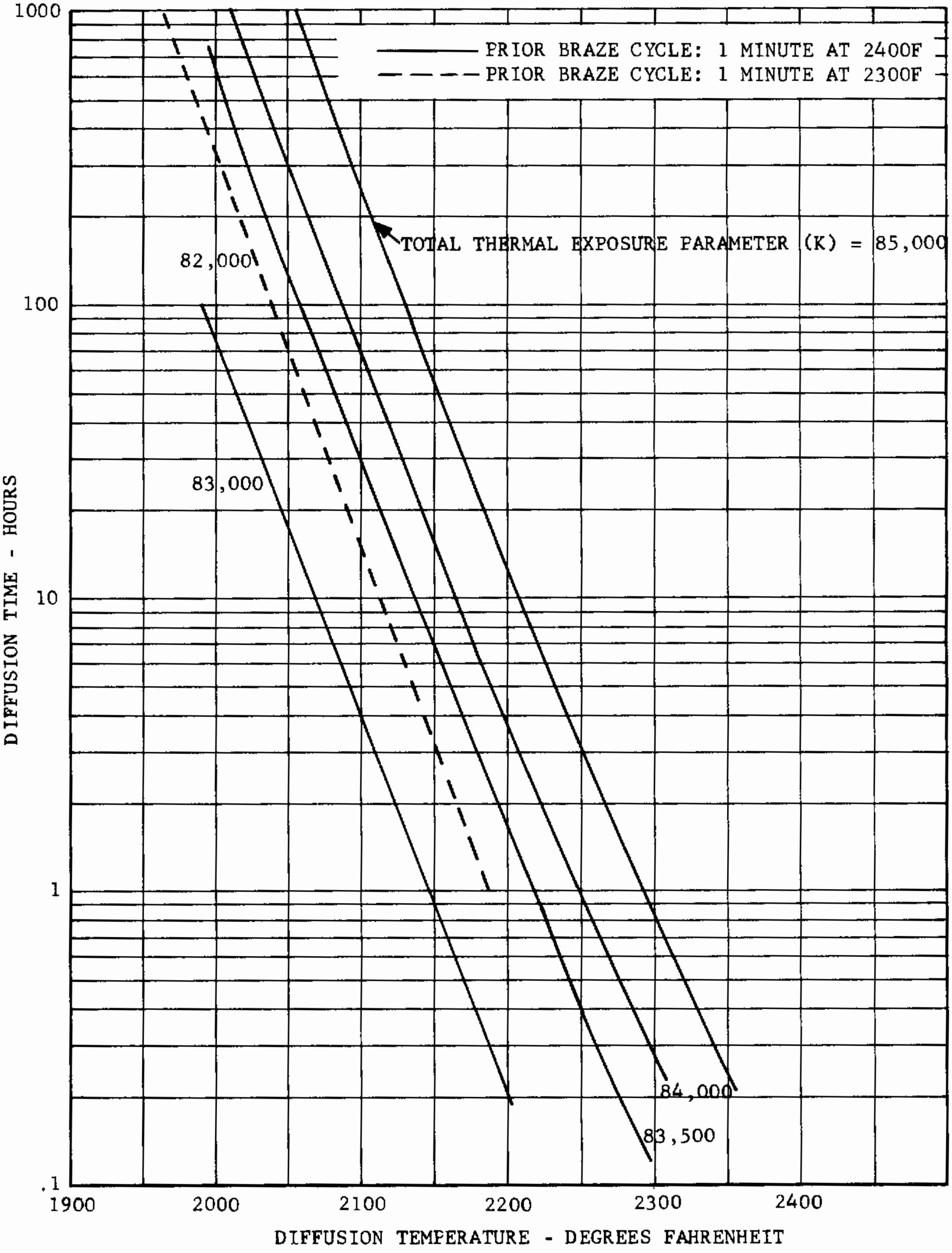


FIGURE 10 ALLOWABLE POST BRAZE DIFFUSION CYCLES FOR .002 INCH TZM FOIL

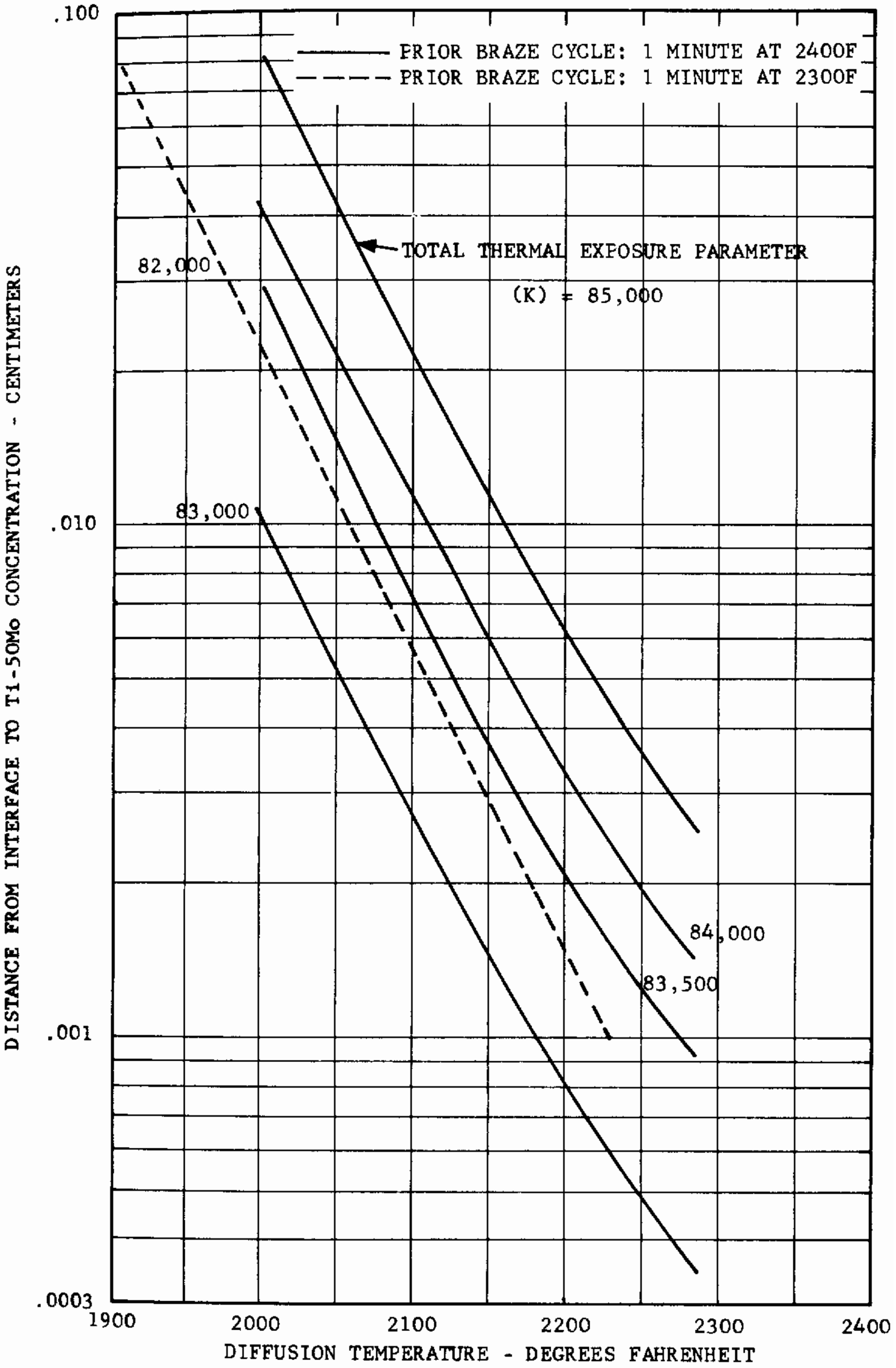


FIGURE 11 DIFFUSION VERSUS TEMPERATURE FOR A Ti-Mo DIFFUSION COUPLE

Tee Joint Evaluation

Initial evaluation of the TZM braze systems listed in Table VI was conducted on .0016-.013 inch tee joints. No significant differences in braze alloy filleting and flow behavior were observed when brazing in either a 10^{-4} torr vacuum or 300 torr high purity argon atmosphere. The 46Zr-34V-20Ti and 33Zr-34Ti-33V alloys exhibited marginal filleting and flow; whereas, excellent filleting and flow occurred with Ti-25Cr-10Ni and Ti-8Ni-7Si.

Metallographic analysis was conducted on as-brazed and diffused tee joints. A post braze diffusion treatment of 40 hours at 2130F was investigated first. This corresponded to a total time-temperature parameter (K) value of 84,300 based on a prior braze cycle of 1 minute at 2400F. The total thermal exposure produced unacceptably severe foil recrystallization and embrittlement. The .013 inch base sheets showed no significant recrystallization or embrittlement.

From a foil recrystallization standpoint, a diffusion treatment of twenty hours at 2040F was the maximum allowable treatment, resulting in 50 percent foil recrystallization and no sheet recrystallization; however, foil and sheet remained ductile. The total K value was 83,100 based on a prior braze cycle of 1 minute at 2400F.

Both diffusion treatments produced similar microstructural effects except for the larger amount of diffusion produced by the higher temperature treatment. Microstructure and microhardness results of as-brazed and diffused (20 hours at 2040F) tees are shown in Figures C1 through C10 and discussed in detail in Appendix C.

These microstructures showed that the sink powders alloyed completely, or at least substantially, with the braze alloys during the short braze cycles employed. Since relatively small amounts of sink powders could be incorporated into the fillets, it was necessary to utilize the base metal as the major diffusion sink. However, most of the braze systems showed less braze fillet-base metal diffusion when sink powder was present. This effect was observed in as-brazed as well as diffusion treated joints. Thus, benefit of sink powder additions was partially offset by the reduced rate of fillet-base metal diffusion. While this effect may not be desirable in diffusion sink brazing, it does offer excellent potential for reducing erosion in conventional brazing as was shown in a recent investigation.[3]

The reduced fillet-base metal diffusion observed in joints containing sink powder is explainable, since the driving force for diffusion is dependent in part upon the difference in Mo (TZM) concentration between the braze fillet and base metal. Initially, this difference was 100 percent for joints containing no sink powder. For a typical joint containing 10 percent molybdenum powder, the initial difference between Mo concentration in the fillet and base metal was only 90 percent. Thus, the rate of fillet-base metal diffusion was reduced in this case.

The metallographic data suggested that only Ti-25Cr-10Ni offered excellent potential for attaining high remelt temperatures. The Ti-8Ni-7Si system appeared to offer remelt potential if the degree of diffusion could be increased somewhat. Remelt temperatures determined on tee joints which were vacuum diffused 20 hours at 2050F are shown in Table IX.

Relatively small remelt temperature increases of 180-330F were attained with the 46Zr-34V-20Ti braze systems. A 15 percent Ta diffusion sink addition produced the highest remelt temperature increase. Specimen M14-1H, brazed with 46Zr-34V-20Ti alone, was given a much greater diffusion treatment which actually embrittled the TZM

TABLE IX

TZM TEE JOINT REMELT TEMPERATURES

SAMPLE NO.	BRAZE ALLOY	SINK POWDER AND AMOUNT	DIFFUSION TREATMENT	*REMELT TEMP.	REMELT TEMP. MINUS BRAZE ALLOY LIQUIDUS
M14-1E	46Zr-34V-20 Ti	-	2050F - 20 hrs	2480F	220F
M15E	46Zr-34V-20 Ti	15%Ta	↓	2590	330
M16-1E	46Zr-34V-20 Ti	1.67% C		2460	200
M19E	46Zr-34V-20 Ti	9.5% Mo +.5% C		2510	250
M10E	Ti-8Ni-7 Si	-		2350	100
M11E	Ti-8Ni-7 Si	8.5% Mo		2300	50
M12E	Ti-25Cr-10 Ni	-		3180 +	860 +
M12G	Ti-25Cr-10 Ni	-		3200 +	880 +
M12F	Ti-25Cr-10 Ni	-		3150	830
M13E	Ti-25Cr-10 Ni	10% Mo		3200 +	880 +
M13F	Ti-25Cr-10 Ni	10% Mo		3130	810
M3F	33Zr-34Ti-33V	-		2670	190
M14-1H	46Zr-34V-20Ti	-	1900F, 16 hrs + 1950F, 8 hrs + 2000F, 40 hrs + 2050F, 56 hrs	2440	180
M23E	Ti-25Cr-13Ni	-	↓	3150	950
M23F	Ti-25Cr-13Ni	-		3100	900
**M27-1E	Ti-25Cr-13Ni	-		3800 +	1600 +
M25E	Ti-10Ni-6Si	-		2600	440
M25G	Ti-10Ni-6Si	-		2680	520
**M28E	Ti-10Ni-6Si	-		3800 +	1640 +
**M28F	Ti-10Ni-6Si	-		3150	990

NOTE: All specimens brazed with approximately .015 - .020 inch radius fillets unless otherwise noted.

* Remelt temperature determined with 120 psi tensile stress on foil leg of tee and a heating rate of approximately 600F/min.

** Specimen brazed with approximately .010 inch radius fillets.

foil. Nevertheless, this treatment produced no further increase in remelt temperature, confirming the limited fillet-base metal diffusion observed with this system.

The Ti-8Ni-7Si system showed the lowest remelt temperature increase. However, the system was actually more promising than indicated by remelt data alone, based on the diffusion potential exhibited by the microstructures.

Excellent remelt temperature increases of 800F or more were attained with the Ti-25Cr-10Ni system. Joints with or without sink powder showed no significant differences in remelt temperature. Additions of Mo sink powder were offset by the reduced fillet-base metal diffusion. Joints without sink powder exhibited greater fillet-base metal diffusion. Apparently, these operating mechanisms resulted in similar Mo concentrations in both types of joints and thus similar remelt temperatures.

Remelt temperature increase obtained with 33Zr-34Ti-33V was 190F which was not surprising based on metallographic results. Therefore, this braze system showed little promise both from a remelt standpoint and the excessive braze temperature required.

Considering both the remelt and metallographic data, the Ti-25Cr-10Ni system was clearly the most promising. The Ti-8Ni-7Si also offered promise if diffusion could be increased. Lap joint remelt results, discussed in a later section of this report, showed that greater diffusion was required for both braze alloys to attain desired remelt temperatures in this configuration. Longer diffusion treatments could not be employed because of foil recrystallization limitations. Therefore, it was necessary to reduce brazing temperatures in order to permit longer diffusion treatments.

The above mentioned brazing effort was based on a total exposure parameter of 83,000 which permitted a diffusion treatment of 20 hours at 2040F after a one minute braze cycle at 2400F. Figure 10 shows that reducing the braze temperature to 2300F and the K value to 82,000 still permitted a diffusion treatment of 70 hours at 2050F.

The Ti-25Cr-10Ni and Ti-8Ni-7Si were modified to permit brazing in the 2250-2300F range. The modified compositions and melting ranges are as follows:

Composition	Approximate Solidus	Liquidus
Ti-25Cr-13Ni	1950F	2200F
Ti-10Ni-6Si	1950F	2160F

These alloys were evaluated on tee joints without sink powder because previous results showed no remelt advantage of sink powders in the basic systems.

Initial diffusion treatment at 2040F caused partial fillet melting and run-off, leaving small, starved fillets. Therefore, several "stepped" diffusion treatments were investigated. The following treatment prevented this problem and was adopted for all diffusion treatments with both braze alloys:

16 hours at 1900F + 8 hours at 1950F + 40 hours at 2000F + 56 hours at 2050F

In terms of the time-temperature recrystallization parameter, this diffusion treatment was equivalent to 70 hours at 2040F. A braze cycle of one minute at 2300F preceding this diffusion treatment resulted in a total exposure of 82,000 parameter units.

Figure 12 shows the as-brazed and diffused microstructures and microhardness data obtained with Ti-25Cr-13Ni. Microhardness data were similar to that obtained with Ti-25Cr-10Ni. However, the diffusion treatment produced substantially more fillet-base metal diffusion. Most of the TZM foil diffused into the fillet.

Figure 13 shows the results obtained with Ti-10Ni-6Si. Both as-brazed and diffused joints show somewhat lower braze alloy and diffusion zone hardnesses than obtained with Ti-8Ni-7Si. The diffusion treated joint also shows a substantial increase in fillet-base metal diffusion. However, some low melting phase remained in the critical area just below the foil tee.

Remelt data on the tee joints brazed with Ti-25Cr-13Ni are included in Table IX. Remelt temperatures on Ti-25Cr-13Ni tee joints were almost equivalent to those obtained on Ti-25Cr-10Ni. However, the actual remelt temperature increase for the former was somewhat higher because of its lower liquidus temperature. One specimen (M27-1E), brazed with smaller fillets, exhibited a remelt temperature above 3800F. Since the amount of Mo available from the tee was constant, the smaller filler apparently contained more Mo after diffusion treating and, thus, a higher remelt temperature.

Table IX shows that remelt temperatures of tees brazed with Ti-10Ni-6Si ranged from 2600 to above 3800F. Here again, smaller fillets produced higher remelt temperatures. The Ti-25Cr-13Ni system clearly showed more promise than Ti-10Ni-6Si, on the basis of remelt temperature results. Therefore, further studies concentrated on this system.

Two Ti-25Cr-13Ni tee joints were brazed with approximately .010 inch radius fillets, diffusion treated, and tested to determine joint strength. The first specimen withstood a 120 psi tensile stress on the foil for one hour at 3000F with no failure. The second specimen was apparently defective and failed above the fillet at 2740F during heat-up under the same stress.

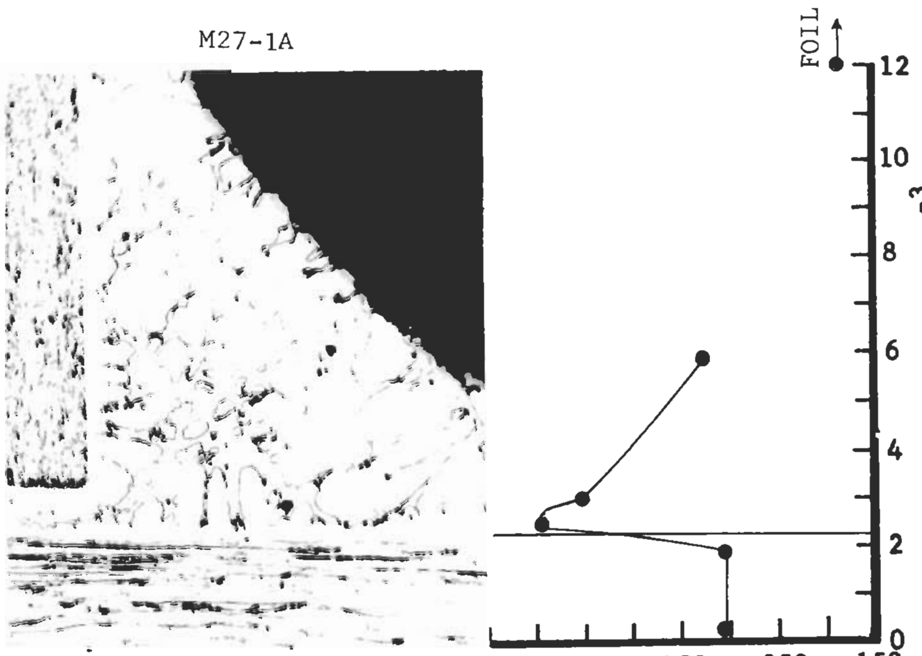
Lap Joint Evaluation

Microstructures of lap joints brazed with the initial braze alloys and vacuum diffused 20 hours at 2050F are shown in Figure 14. Braze alloy-base metal diffusion effects were similar to those observed in the tee joint evaluation. Both 46Zr-34V-20Ti and 33Zr-34Ti-33V exhibited minimal diffusion with the TZM. The greatest degree of diffusion was observed in the Ti-25Cr-10Ni system followed by Ti-8Ni-7Si.

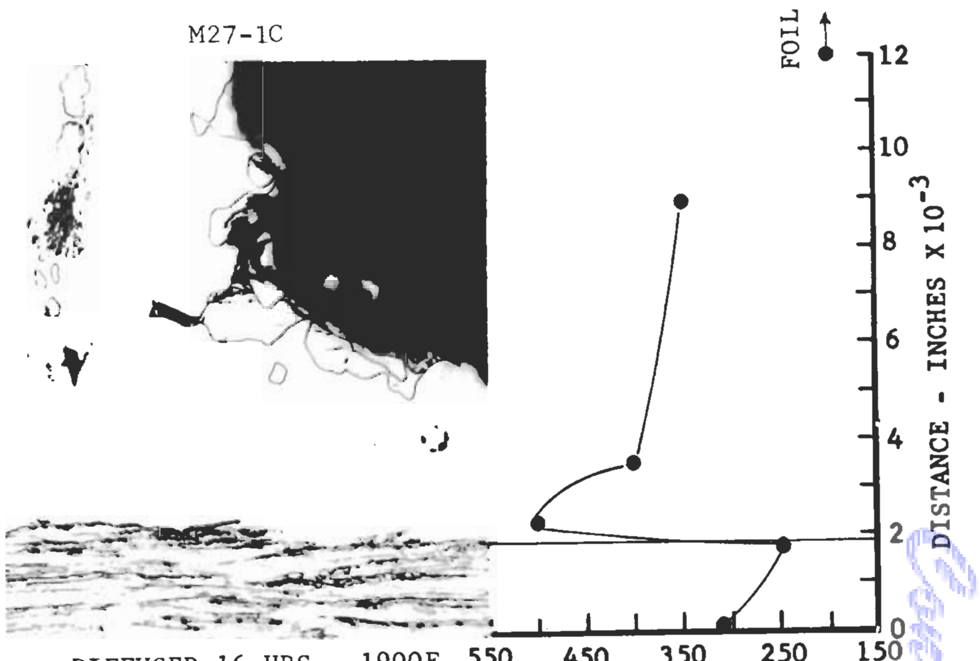
These results showed that only the Ti-25Cr-10Ni joint possessed some remelt potential because the low melting phase at the center of the joint was somewhat discontinuous. Remelt tests were run on 33Zr-34Ti-33V (ML-19) and Ti-25Cr-10Ni (ML-9) joints to confirm the metallographic observations. The results are shown in Table X. Both joints exhibited little or no remelt temperature increase. Figure 15 shows the microstructures of these specimens after remelt testing. These specimens failed by melting of the phases at the center of the joints.

Since the modified Ti-25Cr-13Ni and Ti-10Ni-6Si alloys permitted longer diffusion treatments, it was expected that lap joints brazed with these alloys would show more diffusion. Most of this effort was concentrated on Ti-25Cr-13Ni because it was the more promising system.

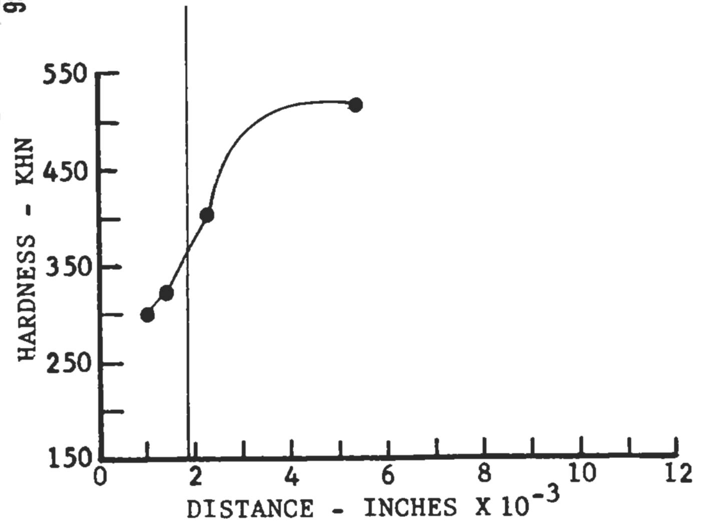
Initial Ti-25Cr-13Ni lap joints were brazed with the alloy powder distributed over the faying plane. Microstructures of as-brazed and vacuum diffused joints produced in this manner are shown in Figure 16. Diffusion treating resulted in partial



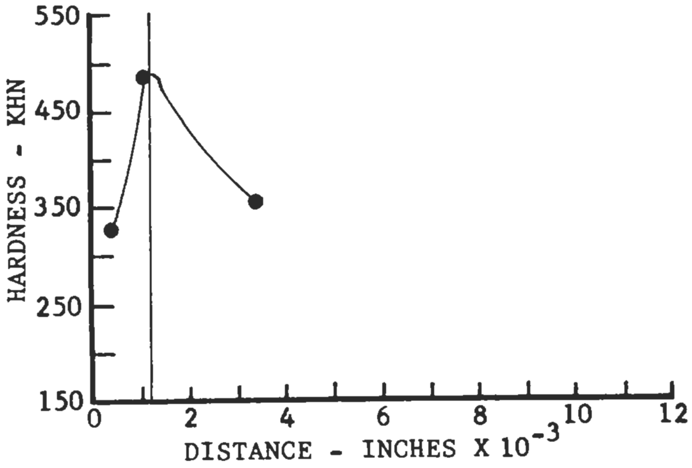
AS-BRAZED



DIFFUSED 16 HRS., 1900F + 8 HRS., 1950F + 40 HRS., 2000F + 56 HRS., 2050F



BRAZE CYCLE: 2260F - 1 MIN.



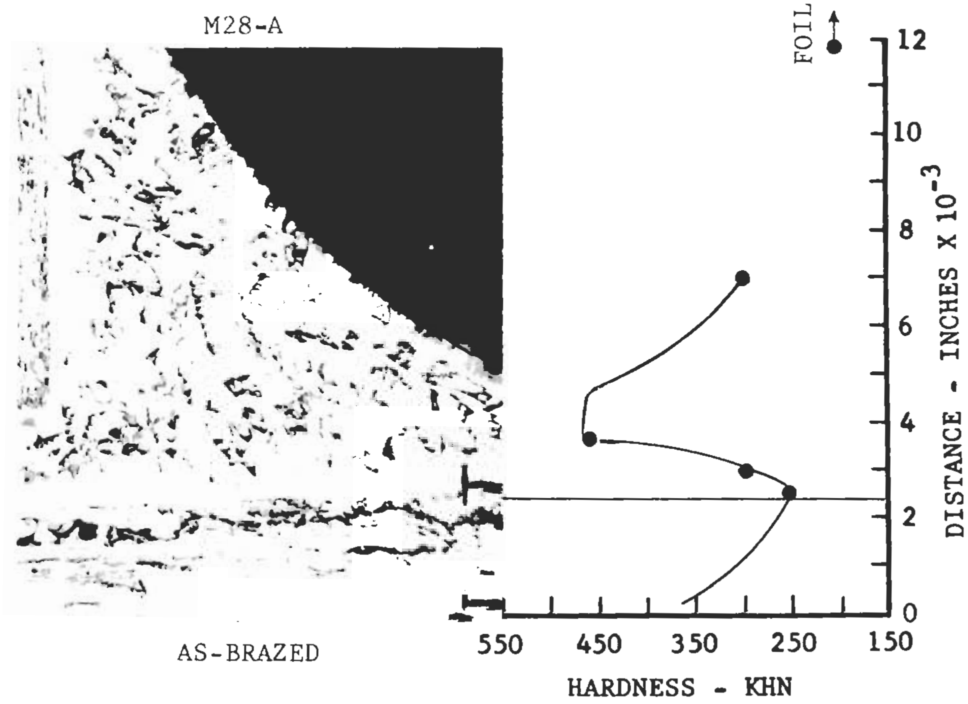
BRAZE CYCLE: 2260F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

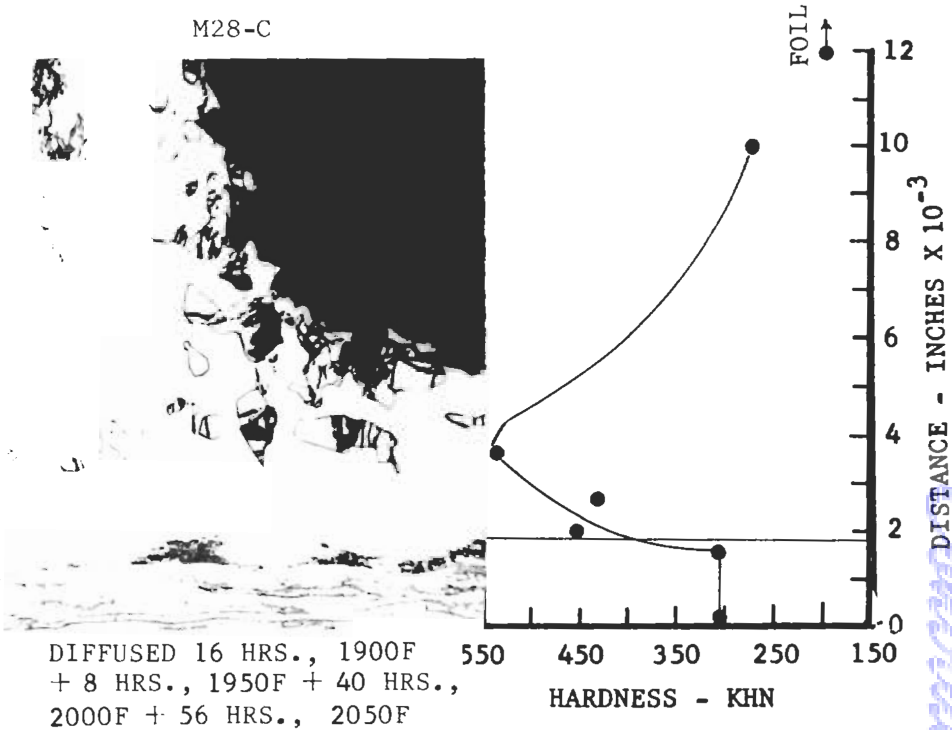
FIGURE 12 TZM TEE JOINTS BRAZED WITH Ti-25Cr-13Ni

M28-A

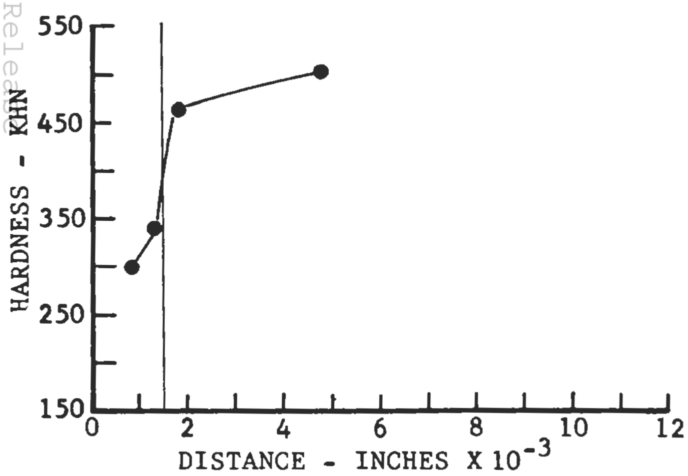


AS-BRAZED

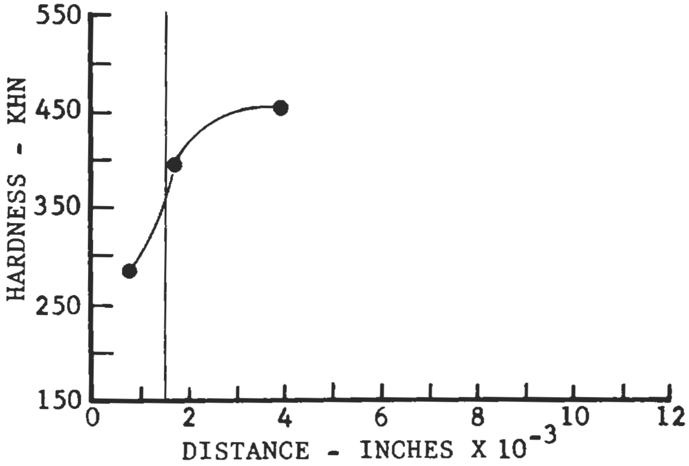
M28-C



DIFFUSED 16 HRS., 1900F
+ 8 HRS., 1950F + 40 HRS.,
2000F + 56 HRS., 2050F



BRAZE CYCLE: 2260F - 1 MIN.

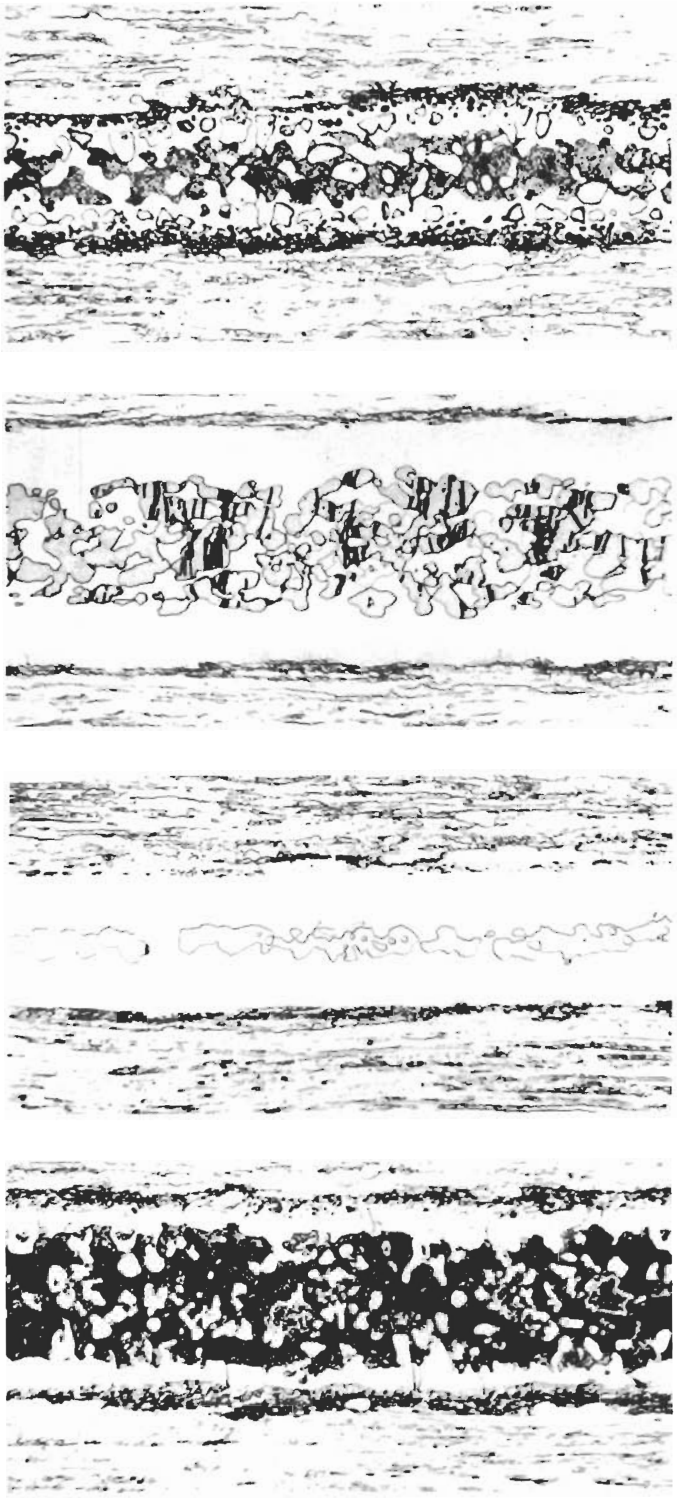


BRAZE CYCLE: 2260F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE 13 TZM TEE JOINTS BRAZED WITH Ti-10Ni-6Si



ML-5

BRAZE ALLOY: 46Zr-34V-20Ti
BRAZE CYCLE: 2400F-1 Min.

ML-11

BRAZE ALLOY: Ti-8Ni-7Si
BRAZE CYCLE: 2360F-1 Min.

ML-7

BRAZE ALLOY: Ti-25Cr-10Ni
BRAZE CYCLE: 2400F-1 Min.

ML-14

BRAZE ALLOY: 33Zr-34Ti-33V
BRAZE CYCLE: 2580F-1 Min.

MAG. 250X

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE 14 TZM LAP JOINTS DIFFUSED 20 HRS AT 2050F

TABLE X

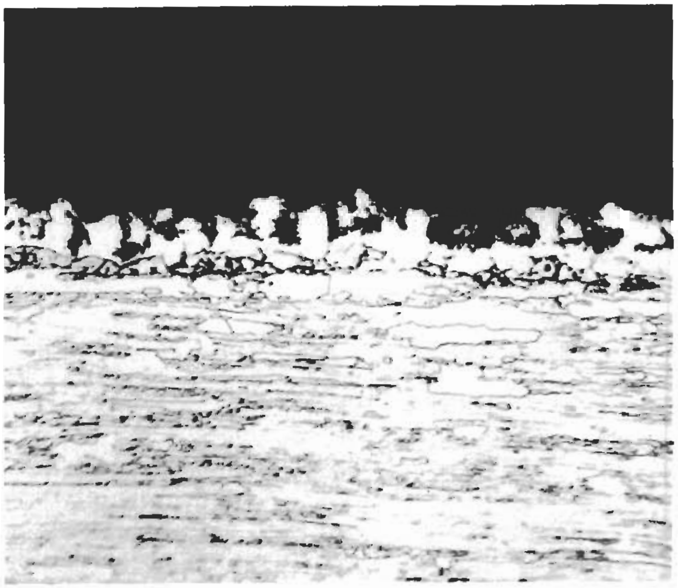
TZM LAP JOINT REMELT TEMPERATURES

Sample No.	Braze Alloy	* Braze Alloy Placement	Approx. Joint Thickness	Diffusion Treatment	Remelt Temp.F	Remelt Temp. Minus Braze Alloy Liquidus F
ML-19	33Zr-34Ti-33V	A	.003 inch	2050F, 20 hrs.	2320	-160
ML-9	Ti-25Cr-10Ni	A	.0016	2050F, 20 hrs.	2440	120
ML-34	Ti-25Cr-13Ni	A	.002	1900F, 16 hrs.+ 1950F, 8 hrs.+ 2000F. 40 hrs. + 2050F, 56 hrs.	<2600	<400
ML-35	Ti-25Cr-13Ni	A	.002		<2600	< 400
ML-49	Ti-25Cr-13Ni	A	.0016		2680	480
ML-50	Ti-25Cr-13Ni	A	.0016		2770	570
ML-41	Ti-25Cr-13Ni	B	.001		3470	1270
ML-55	Ti-25Cr-13Ni	C	.001		3220	1020
ML-46	Ti-25Cr-13Ni	A	.0016	Same as ML-34 + repeat	3780	1580
ML-37	Ti-25Cr-13Ni	B	.001	1900F, 16 hrs.+ 1950F, 8 hrs. + 2000F, 40 hrs. + 2050F, 24 hrs.	3150	950
ML-59	Ti-25Cr-13Ni	C	.001		3600	1400
ML-39	Ti-10Ni-6Si	B	.001	Same as ML-34	3425	1265

Notes: All specimens were .040 inch thick with a .120-.140 inch overlap. Remelt tests conducted with 120 psi tension on base metal (40 psi shear stress on lap joint). All specimens failed in braze joint.

* A = powdered braze alloy placed over lap.
B = particle of braze alloy placed at edge of lap.
C = powdered braze alloy placed at edge of lap.

ML-9
BRAZE ALLOY: Ti-25Cr-10Ni
BRAZE CYCLE: 2400F-1 Min.
REMELT TEMP: 2320F



ML-19
BRAZE ALLOY: 33Zr-34Ti-33V
BRAZE CYCLE: 2580F-1 Min.
REMELT TEMP: 2440F

MAG. 250X
BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE 15 TZM LAP JOINTS DIFFUSED 20 HRS AT 2050F AND REMELT TESTED

ML-45B

BRAZED 1 MIN. AT 2300F

ML-45A

BRAZED 1 MIN AT 2300F

DIFFUSED 16 HRS., 1900F+8 HRS., 1950F+
40 HRS., 2000F+56 HRS., 2050F

MAG. 250X	BASE MATERIAL ETCHANT:	10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
	BRAZE ALLOY ETCHANT:	1 HF, 2 HNO_3, 97 H_2O

FIGURE 16 MICROSTRUCTURES OF AS-BRAZED AND DIFFUSED Ti-25Cr-13Ni LAP JOINTS

solution of the semi-continuous low melting phase at the center of the joint. Remelt temperatures for specimens fabricated in this manner are represented by the data on specimens ML-34, ML-35, ML-49 and ML-50, shown in Table X. Remelt temperatures ranged from less than 2600F up to 2800F depending upon joint thickness.

Several lap specimens were brazed with the braze alloy placed outside the joint and allowed to flow in by capillary attraction. This technique reduced joint thickness and thereby reduced the diffusion distance. After diffusion treating, the low melting phase at the center of the joint showed more solution and significantly less continuity. Table X shows that remelt temperature of joints prepared in this manner (ML-41 and ML-55) was increased to 3200-3470F.

Specimen ML-46, brazed with Ti-25Cr-13Ni powder placed over the faying plane, was given a double diffusion treatment. The remelt temperature was increased to 3780F. While this treatment would embrittle TZM foil, it could be satisfactorily employed on .013 inch TZM sheet. Specimens ML-37 and ML-59 were given a modified diffusion treatment in which the time at 2050F was reduced from 56 to 24 hours. The large spread in remelt temperatures (3150-3600F) made it difficult to correlate effect of this shorter treatment on remelt temperature.

One lap specimen (ML-39) was brazed with Ti-10Ni-6Si placed outside the joint. After diffusion, the remelt temperature was 3425F.

These results on the Ti-25Cr-13Ni alloy indicate that joint thicknesses must be .001 inch or less to develop remelt temperatures above 3000F. Laboratory results have shown that it is difficult to maintain this joint thickness when braze alloy is placed over the faying plane. However, placement of braze alloy outside the joint easily and reproducibly maintains desired joint thickness.

Lap shear strength results on diffusion treated specimens brazed with Ti-25Cr-13Ni are shown in Table XI. Each of these specimens was fabricated by placing the braze alloy at the edge of the lap area. Shear strengths of 833 and 270-310 psi were noted at 2600 and 3000F, respectively, after the standard diffusion treatment. Specimens ML-60 and ML-61 were given a modified diffusion treatment in which the time at 2050F was reduced from 56 to 24 hours. This reduced lap shear strength to 73-95 psi at 3000F.

Honeycomb Evaluation

The objective in the honeycomb evaluation series of tests was to establish the validity of the high remelt results obtained with tee joint samples on specimens having a more complex makeup. The remelt and stress test results on brazed TZM honeycomb panels employing the Ti-25Cr-13Ni alloy are shown in Table XII. Remelt tests on a small (1 x 3/4 inch) honeycomb sample, SCM-7, were consistent with the tee joint remelt tests previously discussed. However, when larger panels were made in the laboratory (2 x 2 inch) relatively little remelt was achieved regardless of the braze alloy loading employed as shown in Table XII. When 2 x 2 inch honeycomb samples were brazed in the Nortobraze quartz lamp process, the remelt temperatures improved considerably, as shown in the last four rows of Table XII.

TABLE XI

SHEAR STRENGTHS OF TZM LAP JOINTS BRAZED WITH Ti-25Cr-13Ni

Sample No.	Approx. Joint Thickness	Diffusion Treatment	Test Temp. F	Shear Strength	Base Metal Stress
ML-57	.0006 inch	1900F, 16 hr. + 1950F, 8 hr. + 2000F 40 hrs. + 2050F 56 hrs.	2600	833 psi	2500 psi
ML-58	.0008		3000	310	920
ML-56	.001		3000	270	910
ML-60	.001	1900F, 16 hrs. + 1950F, 8 hrs. + 2000F, 40 hrs. + 2050F, 24 hrs.	3000	95	300
ML-61	.001		3000	73	220

Notes: All specimens brazed with powder placed at edge of lap. Specimens were .040 inch thick with a .120-.140 inch overlap. Shear strength tests conducted at .05 inch/min. head speed. All specimens failed in braze joint.

TABLE XII

REMELT TEMPERATURES OF TZM HONEYCOMB BRAZED WITH Ti-25Cr-13Ni

Sample No.	Braze Alloy Loading	Flatwise Tensile Stress on Panel	Remelt Temp.	Remelt Temp. Minus Braze Alloy Liquidus
*SCM-7	.35 gm/in^2	1.2 psi	3050F	850F
HM-6	.25	1.2	2540	340
HM-8	.25	1.2	2520	320
**HM-7	.25	1.2	2560	360
HM-16	.125	1.2	2400	200
HM-8A	.125	0.6	2400	200
HM-1	.35	0.3	2740	540
HM-9	.075	0.01	4000+	1800
HM-14	.25 + 8% Mo Sink Powder	1.2	2200	0
MRD-5	.25	1.2	2640	440
MRD-3	.25	0.3	3180	980
MRD-4	.25	1.2	2550	350
MRD-2	.25	0.3	3130	930

Heating Rate Approximately 600F/minute.

All specimens brazed 1 minute at 2250-2300F in vacuum and diffused 16 hours at 1900F, + 8 hours at 1950F, + 40 hours at 2000F, + 56 hours at 2050F.

MRD-2 and 4 diffused 16 hours at 1900F, + 8 hours at 1950F + 40 hours at 2000F, + 24 hours at 2050F.

Specimens were 2 x 2 inches except as noted.

---

* Specimen was approximately 3/4 x 1 inch.

** Specimen was a single cell cut from a 2 x 2 inch specimen.

It is believed that the explanation for these anomalous remelt temperature results is as follows:

The tee joints were diffusion treated with the fillet areas exposed to a hard vacuum. The 1 x 3/4 inch specimens represented a configuration that had a large portion of the total number of fillets exposed to the vacuum. With both of these configurations, good remelt characteristics were obtained. However, the 2 x 2 inch honeycomb specimens made under laboratory conditions had the smallest number of fillets exposed to the vacuum relative to the total number of fillets in the panel. This configuration resulted in low remelt temperatures. The effects of vacuum exposure on typical brazed fillets after standard diffusion treatments are shown in Figure 17. The tee joint microstructure shows a substantial solid solution diffusion zone near the TZM interfaces with a second phase located at the extremities of the fillets. Electron probe analysis has shown that the former phase consists of 60% Ti-25% Mo-10% Cr-4% Ni; whereas, the latter phase was identified as a low melting nickel-rich phase of the Ti_2Ni type. The microstructure and composition of the fillets analyzed from the 1 x 3/4 inch honeycomb samples (SCM-9) were similar to the tee joint results. The microstructure of the honeycomb specimen produced under laboratory conditions (HM-15) exhibits a concentration of the same nickel-rich phase on both the fillet extremities as well as at the base of the vertical core member. Thus, in spite of the extensive diffusion zone, a discontinuous, low melting bridge existed between the core and face sheet. Concentration of nickel in this region was probably caused by inability of the material to evaporate from the closed cell.

The microstructure of a honeycomb sample brazed by the quartz lamp process (MRD-1) showed no evidence of the low melting phase between the core and face sheet. The close core-to-face sheet tolerances maintained in these samples probably reduced diffusion distances in this region, thereby suppressing formation of the low melting phase. In addition, the thicker core foil also contributed to a high Mo concentration in the fillet.

Based upon these observations, it appears that the success of the Ti-25Cr-13Ni braze alloy in achieving high remelt temperature depends upon the control of the nickel-rich phase either by suppressing its formation or controlling its distribution. Nickel evaporation is one way in which this can be accomplished as demonstrated by the contrasting remelt results on the tee joints and 2 x 2 inch honeycomb samples made under laboratory conditions.

Transition Temperatures

Figure 18 shows the transverse bend transition temperature data obtained on .013 inch base metal and .013-.013 inch brazed lap joints. Transition temperature was defined as the temperature at which the first decrease in bend deflection to fracture was noted.

As-received sheet exhibited a transition temperature of -175 F. After a simulated braze cycle and standard diffusion treatment, the transition temperature increased to -125F. However, the sheet still exhibited sufficient ductility to permit a 130 degree bend at -125F with no fracture.

Lap bend samples brazed with Ti-25Cr-13Ni and given the standard diffusion treatment exhibited a transverse bend transition temperature of 0F. Two types of fracture were observed with these specimens. In some cases the entire joint fractured. In other cases, metallographic analysis showed braze alloy cracking perpendicular to the faying plane with no base metal cracking. One specimen bent three degrees at 0F, showed no evidence of braze alloy or base metal cracking.

M27-1C

TEE JOINT

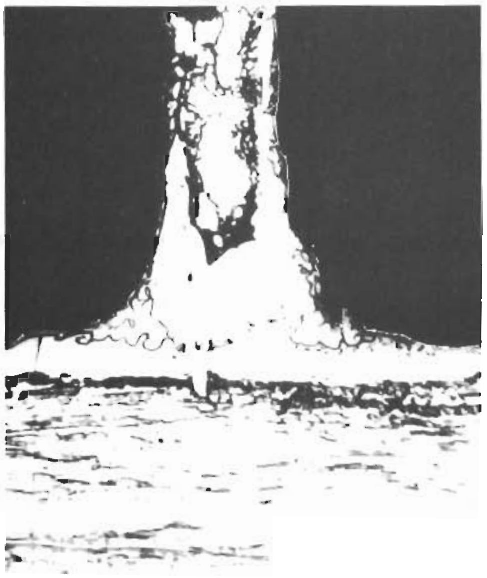
REMELT TEMPERATURE 3150F

SCM-9

1 X 3/4 INCH HONEYCOMB SPECIMEN

REMELT TEMPERATURE 3050F

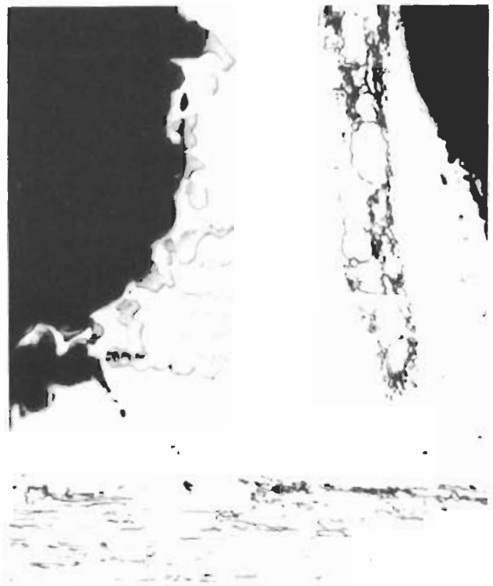
HM-15



2 X 2 INCH HONEYCOMB SPECIMEN

REMELT TEMPERATURE 2540F AT 1.2 psi
2740F AT .3 psi

MRD-1

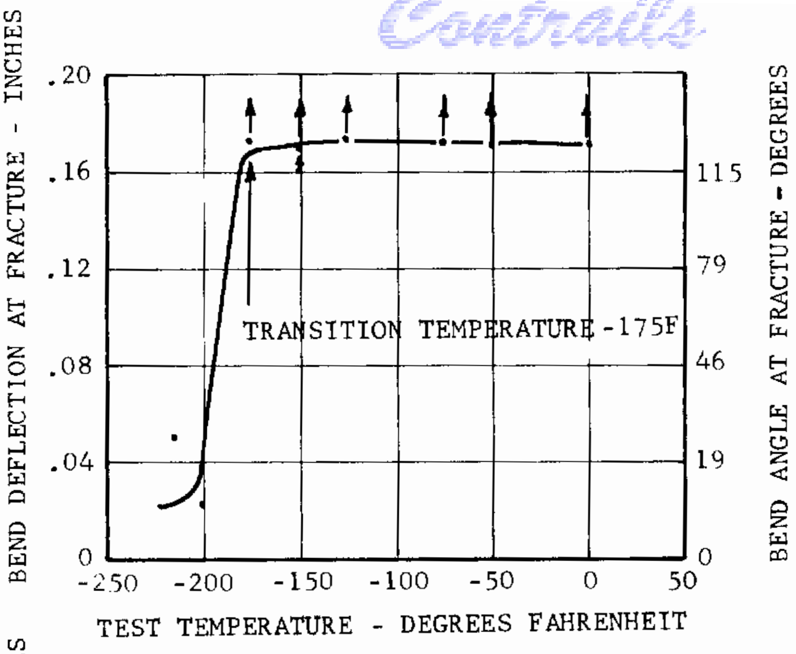


2 X 2 INCH QUARTZ LAMP BRAZED HONEYCOMB SPECIMEN

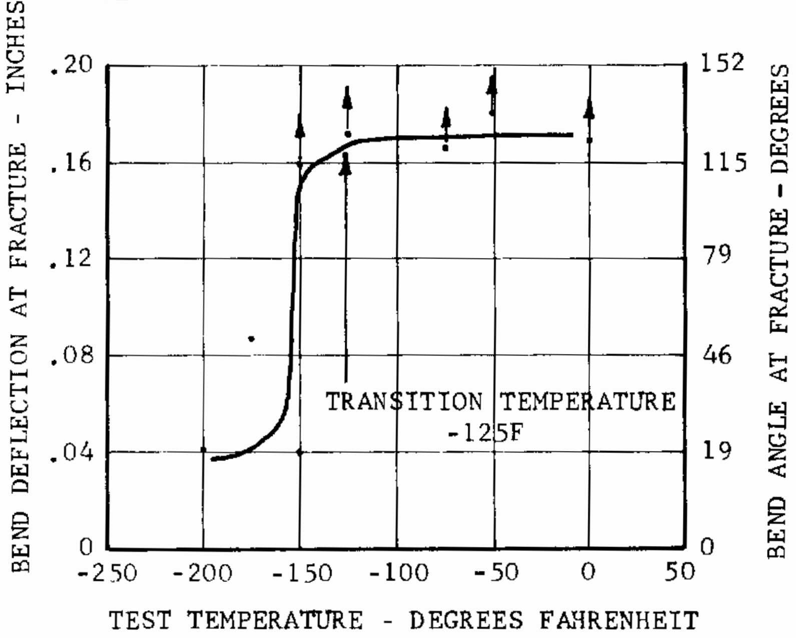
REMELT TEMPERATURE 2640F AT 1.2 psi
3180F AT .3 psi

MAG. 250X BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE 17 TZM TEE AND HONEYCOMB SPECIMENS BRAZED WITH Ti-25Cr-13Ni AND DIFFUSED

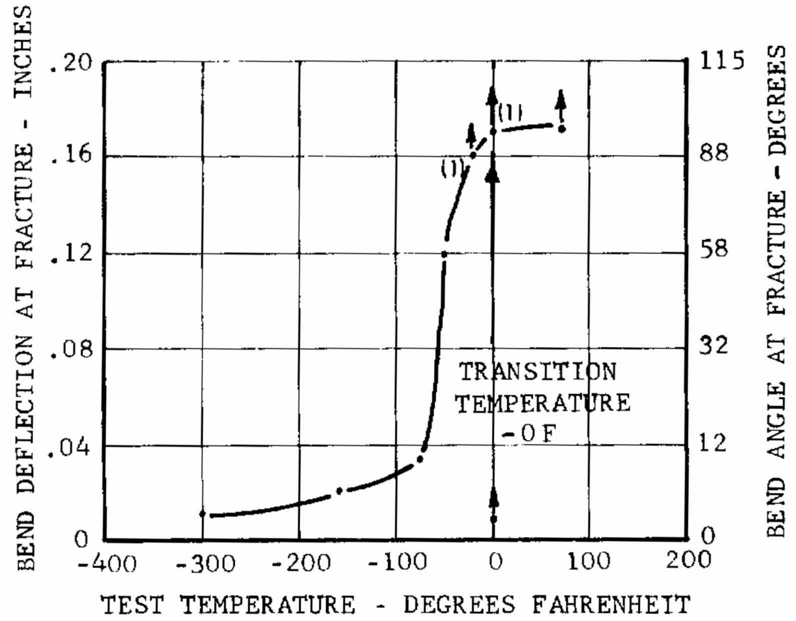


AS RECEIVED SHEET



SHEET

EXPOSED 1 MINUTE AT 2260F+ 16 HOURS AT 1900F + 8 HOURS AT 1950F + 40 HOURS AT 2000 F+ 56 HOURS AT 2050F



LAP JOINT

BRAZE ALLOY Ti-25Cr-13Ni
BRAZED 1 MINUTE AT 2260F
DIFFUSED 16 HOURS AT 1900F+ 8 HOURS AT 1950F + 40 HOURS AT 2000F + 56 HOURS AT 2050F

(1) BRAZE ALLOY CRACKING PERPENDICULAR TO FAYING PLANE - NO BASE METAL CRACKING

HEAD SPEED .05 INCH PER MINUTE

FIGURE 18 TRANSVERSE BEND TRANSITION TEMPERATURE OF 0.013 INCH TZM SHEET AND BRAZED TZM LAP JOINTS

The increase in bend transition temperature to 0F may be attributed to the presence of the braze alloy and/or specimen geometry. The braze alloy may have acted as a stress riser, initiating cracks in the base metal, thereby raising the transition temperature. In addition, these samples were approximately twice the thickness of base metal transition specimens. Therefore, the greater degree of biaxiality contributed to the increased transition temperature as well.

The bend test performed on brazed tee joints did not provide meaningful bend transition temperature data. However, this test did provide a measure of bend ductility at various temperatures. Two TZM tees, brazed with Ti-25Cr-13Ni and subjected to the standard diffusion treatment, required 45 degree bends at both 70 and 212F to produce fracture. In both cases failure occurred in the foil just above the fillet.

Transition temperatures of foil specimens were determined by notched tensile tests because the low stiffness of the foil did not permit use of the bend test. Transverse notched tensile transition temperatures of .002 inch foil are presented in Figure 19. All of these curves showed an initial increase in net section stress with decreasing temperature which is typical of body-centered cubic metals. A further decrease in temperature produced a precipitous reduction in net section stress due to the onset of brittle failure. This temperature was defined as the transition temperature.

The as-received foil exhibited a transition temperature of -210F. Following a simulated braze cycle and standard diffusion treatment, the transition temperature was raised to -120F. Modification of the standard diffusion treatment from 56 to 24 hours at 2050F produced no significant change in transition temperature. Thus, the standard diffusion treatment produced no greater foil embrittlement than the modified treatment.

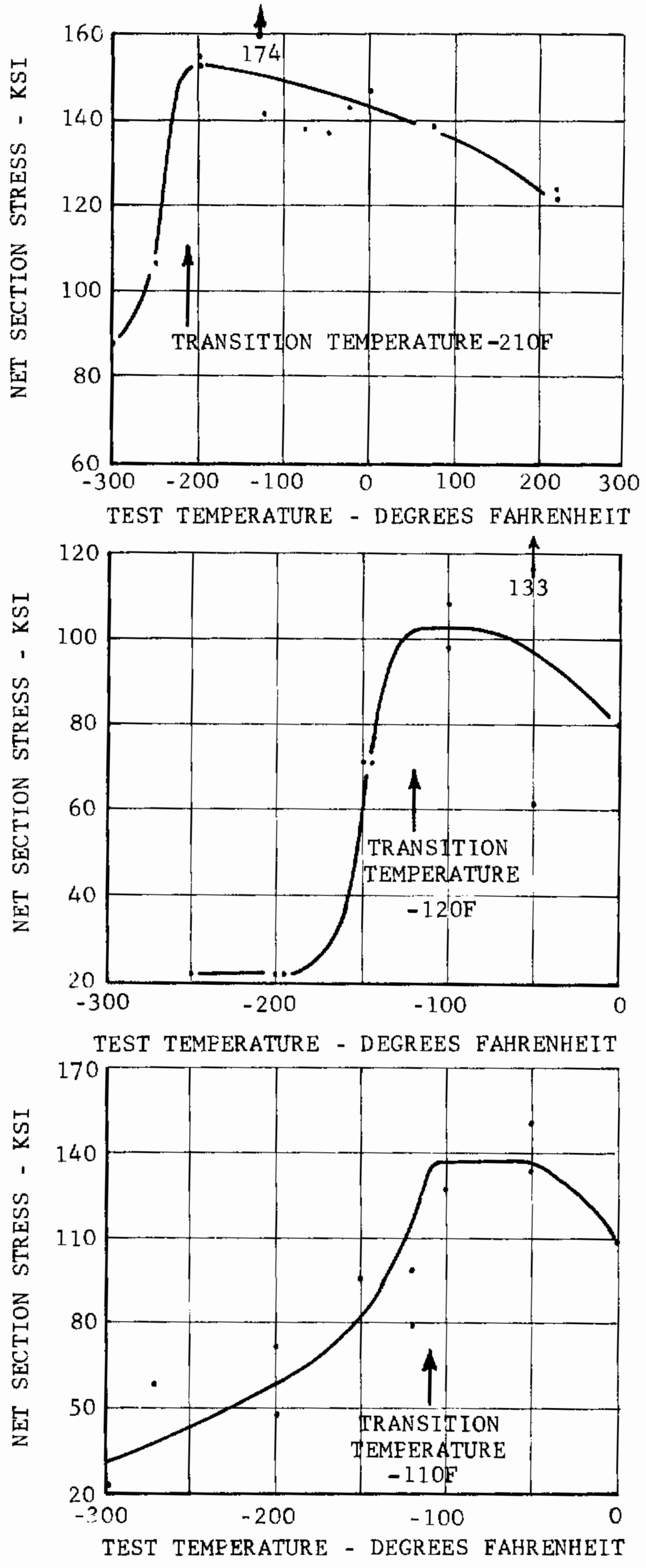
Recrystallization and Ductility

During this program .002, .013, and .040 inch thick TZM was subjected to a variety of single and multiple thermal exposures. None of these exposures produced any significant recrystallization of the .040 inch material. Recrystallization behavior of the .002 and .013 inch TZM is summarized in terms of the time-temperature parameter as shown in Figure 9.

The multiple thermal exposures produced varying amounts of recrystallization in the .002 inch foil. These multiple thermal exposures produced greater foil recrystallization than single exposures at the same parameter value. The parameter accurately predicted recrystallization behavior for single thermal exposures. Foil recrystallization produced by multiple exposures could only be approximated by this time-temperature parameter approach. Nevertheless, multiple thermal exposures of .002 inch TZM foil should be limited to a total parameter value of 82,000-83,500 based on a maximum of 80% recrystallization.

Figure 9 does not include a recrystallization curve for .013 inch sheet subjected to multiple exposures. No significant recrystallization was produced by the multiple exposures employed.

Qualitative correlations between foil recrystallization and embrittlement were observed. Substantial amounts of recrystallization reduced foil ductility somewhat. However, at 80-90% recrystallization, acceptable ductility was observed. Once complete recrystallization and grain growth occurred, severe embrittlement was noted.



AS RECEIVED
0% RECRYSTALLIZATION

EXPOSED 1 MINUTE AT 2260F
+ 16 HOURS AT 1900F + 8
HOURS AT 1950F + 40 HOURS
AT 2000F + 56 HOURS AT 2050F

50% RECRYSTALLIZATION

EXPOSED 1 MINUTE AT 2260F +
16 HOURS AT 1900F + 8 HOURS
AT 1950F + 40 HOURS AT
2000F + 24 HOURS AT 2050F

40% RECRYSTALLIZATION

HEAD SPEED - 0.1 INCH PER MINUTE

FIGURE 19 TRANSVERSE NOTCHED TENSILE TRANSITION TEMPERATURE OF .002 INCH TZM FOIL

Ta-10W BRAZING

Braze System Development

Table XIII summarizes the ductility and liquidus temperature data obtained on candidate tantalum braze systems. Braze system development followed the same basic procedures used on TZM. Simulated diffusion sink additions to the braze alloys were standardized at 10 percent base metal (Ta) - 15 percent diffusion sink powder.

Conventional Alloys

The first nine alloys listed in Table XIII were formulated for conventional brazing of tantalum. The as-melted Ta-36V exhibited a hardness of Rc 37 and good ductility. Aging 45 minutes at 2300F increased hardness to Rc 53 and produced severe embrittlement. The as-melted alloy solidified and cooled rapidly, thereby retaining the high temperature solid solution phase. Aging at 2300F permitted formation of the TaV_2 equilibrium phase which was very brittle. Since coating cycles are carried out at temperatures where TaV_2 can form and embrittle braze joints, no further effort was devoted to Ta-36V.

Melting of Cb-26Ti was difficult because of excessive titanium volatilization. Therefore, this alloy received no further attention. The Cb-10Ti-5Zr (D36) alloy was selected for tee joint evaluation because it is the lowest melting columbium base alloy readily available in foil form. The Cb-26V was also selected for tee joint evaluation because it exhibited the lowest liquidus temperature of the alloys considered for conventional brazing.

Melting temperature determinations on D36 and Cb-26V showed considerable variation depending upon melt sample geometry and furnace atmosphere. Liquidus temperature of .002 inch D36 foil was 4170F when determined in vacuum, and 4080F when determined in a 100 Torr argon atmosphere. Similarly, liquidus temperature of -100 mesh Cb-26V powder was above 4100F in vacuum and 3680F in 100 Torr argon. These differences were caused by volatilization of Ti, V, and Zr. All subsequent brazing with these alloys was conducted in a 100 Torr argon atmosphere to minimize volatilization effects.

The Ta-B and Cb-B alloys of Table XIII exhibited liquidus temperatures approximately 700-900F greater than indicated by published phase diagrams.[4] However, recent liquidus temperature data on Cb-B alloys[5] correlate well with the data reported here. The Ta-1.5B exhibited an acceptable liquidus temperature but the alloy was brittle. A reduction of the boron level to one percent resulted in a ductile alloy but the liquidus temperature was quite high. Therefore, this system was eliminated from further consideration. The Cb-2.8B was slightly ductile and exhibited an acceptable liquidus temperature. Both Cb-1.8B and Cb-1.3B exhibited better ductility than Cb-2.8B, although liquidus temperatures were higher. Both alloys were selected for tee joint evaluation.

Diffusion Sink Alloys

The above Ta-36V results showed that vanadium-base alloys were not promising for diffusion sink brazing of tantalum because diffusion and coating cycles would result in TaV_2 formation and thus joint embrittlement. Therefore, braze alloy development was concentrated primarily on titanium-base alloys.

TABLE XIII

TANTALUM BRAZE SYSTEMS

Alloy No.	Composition	Liquidus Temp. F	*Ductility	Increase in Liquidus Temp. F
Conventional Braze Systems				
51	Ta-36V (as melted)		D	
51	Ta-36V (aged 45 min. at 2300F)		VB	
84	Cb-26Ti		D	
165	Cb-26V	3680	D	
	Cb-10Ti-5Zr-(D36)	4080	D	
136	Ta-1.5B	4100	B	
151	Ta-1.0B	4260+	D	
137	Cb-2.8B	3830	SD	
152	Cb-1.8B	3870	D	
172	Cb-1.3B	4030	D	
Diffusion Sink Braze Systems				
73	Ti-37Zr	2880	D	
75	75(Ti-37Zr)-10Ta-15Mo	3010	D	130
76	75(Ti-37Zr)-25Ta	3100	D	220
77	75[75(Ti-37Zr)-10Ta-15Mo]-25Ta	3450	D	570
78	75[75(Ti-37Zr)-25Ta]-25Ta	3110	D	230
92	75[75(Ti-37Zr) -10Ta-15Mo]-10Ta-15Mo	3320	SD	440
41	Ti-29V-2Si	2820	SD	
53	75(Ti-29V-2Si)-25Ta	3020	D	200
64	75(Ti-29V-2Si)-10Ta-15Cb	3020	D	200
138	75(Ti-29V-2Si)-10Ta-15Mo	3150	D	330
71	75[75(Ti-29V-2Si)-25Ta]-25Ta	3240	D	240
72	75[75(Ti-29V-2Si)-25Ta]-10Ta-15Mo	**3400	D	400+
79	Ti-20V-13Fe	2640	B	
83	Ti-25V-10Fe	2630	D	
91	Ti-25V-10Fe-2Si	2560	B	
105	Ti-30V-13Fe-5Mn	2540	SD	
44	Ti-27V-7Fe	2700	D	
54	75(Ti-27V-7Fe)-25Ta	2960	D	260
63	75(Ti-27V-7Fe)-10Ta-15Cb	2980	D	280
67	75[75(Ti-27V-7Fe)-25Ta]-25Ta(as melted)	3240	D	280
67	(aged 30 minutes at 2000F)		D	
70	75[75(Ti-27V-7Fe)-25Ta]-10Ta-15Mo	3320	B	360
42	40Zr-30V-30Ti	2335	D	
52	75(40Zr-30V-30Ti)-25Ta (as melted)	2745	SD	410
52	(aged 30 min. at 2000F)		SD	
61	75(40Zr-30V-30Ti)-10Ta-15Cb	2790	SD	455
81	75[75(40Zr-30V-30Ti)-25Ta]-25Ta	3220	SD	465
82	75[75(40Zr-30V-30Ti)-25Mo]-10Ta-15Mo	3320	B	360

* D - Ductile B - Brittle

SD - Slightly Ductile VB - Very Brittle

** Solidus Temperature

A diffusion sink addition of Ta to the Ti-37Zr braze alloy produced a larger increase in liquidus temperature than a Mo addition. However, comparison of alloys #76 and #78 shows that the Ta addition to alloy #78 produced no further increase in the liquidus temperature. The 75(Ti-37Zr)-10Ta-15Mo, braze alloy #75, had the highest remelt temperature. This system was selected for evaluation on tee joints using a Ta diffusion sink.

Diffusion sink additions of Ta and Cb produced equivalent increases in the liquidus temperature of the Ti-29V-2Si alloy. Comparison of alloys #71 to #72 shows that Mo was a more potent diffusion sink than Ta. A braze alloy of alloy #53 composition exhibited the highest remelt temperature with a Mo diffusion sink. Therefore, this system was selected for evaluation on tee joints.

The Ti-29V-2Si braze alloy was also selected for tee joint evaluation because it exhibited an intermediate liquidus temperature. The two percent Si addition depressed the liquidus temperature of the Ti-V binary alloy by approximately 100F. A Mo diffusion sink was employed with this braze alloy.

A number of Ti-V-Fe alloys were prepared. The Ti-27V-7Fe was most promising based on liquidus temperature, ductility and amount of "incompatible" (Fe) additions. Liquidus temperature of this alloy was approximately 200F below the liquidus of the binary Ti-V alloy. Diffusion sink additions of Cb and Ta produced equivalent liquidus temperature increases. Mo additions led to somewhat higher remelt temperatures but produced embrittlement (alloy #70). Comparison of alloy #72 to #67 showed that the Ti-V-Si-Ta system has greater remelt potential than the Ti-V-Fe-Ta system.

Because of its intermediate liquidus temperature, the basic Ti-27V-7Fe braze alloy was selected for tee joint evaluation. A Ta diffusion sink appeared most promising. However, there was some question concerning the compatibility of Ta with the V in the braze alloy. Alloy #67 was aged 30 minutes at 2000F to determine if the system would be embrittled by TaV_2 formation. No change in hardness or ductility was produced by the aging treatment. This data also suggested that the Ti-V-Si system was compatible with Ta from the standpoint of TaV_2 formation.

The Zr-Ti-V system was discussed in detail with reference to TZM brazing. Several additional compositions in this system were also prepared as shown in Table XIII. Alloy #52 was aged 30 minutes at 2000F to determine compatibility of the Zr-Ti-V system with Ta. The aging treatment increased hardness from Rc 12 to Rc 29 but the alloy remained ductile. The 33Zr-34Ti-33V and 46Zr-34V-20Ti alloys evaluated on TZM appeared most promising for evaluation on tantalum.

A summary of the tantalum braze systems selected for further evaluation is given in Table XIV. Estimates of the amount of diffusion sink required for 3400 and 3800F remelt temperatures are also included. Pertinent braze alloy properties and powdering parameters are included in Table XV. The Ti and Ti-30V are included for reasons discussed in a subsequent section of this report.

Tee Joint Evaluation

Conventional Brazing

Microstructure and microhardness results on Ta-10W tee joints brazed with conventional braze alloys are shown in Figures D1-D4 of Appendix D. These .002-.010 inch joints were evaluated in the as-brazed condition and after a simulated service exposure of one hour at 3500F.

TABLE XIV

SELECTED TANTALUM BRAZE SYSTEMS

Braze Alloy	Liquidus Temp. F	Diffusion Sink Powder	Estimated % Diffusion Sink Req'd for Remelt Temp. of 3400 F	3800 F
Cb-10Ti-5Zr	4080	-		
Cb-1.3B	4030			
Cb-1.8B	3870			
Cb-26V	3680			
46Zr-34V-20Ti	2260	Ta	55	75
33Zr-34Ti-33V	2480	Ta	50	70
Ti-27V-7Fe	2700	Ta	55	70
Ti-29V-2Si	2820	Mo	60	75
Ti-28Zr-15Mo-10Ta	3000	Ta	25	45
Ti-21.5V-1.5Si-25Ta	3020	Mo	30	50

TABLE XV

TANTALUM BRAZE ALLOY PROPERTIES

Braze Alloy	Liquidus F & Ductility As Cast	Hardness As Cast (Rc)	Density gm/cm^3	Hydride Treatment	Liquidus F -100 Mesh Powder	Ductility of Melted Powder Patch
Cb-10Ti-5Zr (foil)	4080-D	-	6.98	-	-	-
Cb-1.3B	4030-D	24	8.44	575F-1-3/4 hr.	-	D
Cb-1.8B	3870-D	96 Rb	8.16	575F-1-1/2 hr.	3870	D
Cb-26V	3680-D	30	7.60	575F-1 hr.	-	D
46Zr-34V-20Ti	2260-D	33	5.88	1000F-1/2 hr.	2260	D
33Zr-34Ti-33V	2480-SD	33	5.58	1000F-3/4 hr.	2480	D
Ti-27V-7Fe	2700-D	33	5.11	700F-1/2 hr.	2730	SD
Ti-29V-2Si	2800-D	42	4.90	800F-1/2 hr.	2770	D
Ti-28Zr-15Mo-10Ta	3000-D	40	6.04	1000F-1 hr.	2980	D
Ti-21.5V-1.5Si-25Ta	3020-SD	42	5.94	750F-3/4 hr.	3030	D
Ti (foil)	3060-D	-	4.50	-	0	-
Ti-30V	2980-D	94 Rb	4.92	600F-1/2 hr.	2980	-

The Cb-26V, Cb-1.8B, and Cb-1.3B exhibited excellent filleting and flow; somewhat poorer but acceptable results were obtained with D36 (Cb-10Ti-5Zr). It was necessary to braze Cb-26V and D36 joints in a 100 Torr argon atmosphere to prevent excessive solute element evaporation encountered in vacuum brazing. The Cb-1.8B and Cb-1.3B joints could be successfully brazed in vacuum or argon.

A consideration of these data suggested that the Cb-1.3B offered the greatest overall potential for conventional brazing of Ta-10W. Therefore, several tee joints were tested to determine high temperature strength. Results were as follows:

Specimen No.	Foil Stress - psi	Failure Temp. F
T-16I	375	3880
T-16K	650	>3900
T-16N	650	>4000

These results show that the joints possessed good high temperature strength as well as some remelt temperature increase. The lower strength of specimen T-16I was probably caused by a larger gap between the foil leg and base sheet.

Diffusion Sink Brazing

With the exception of Ti-27V-7Fe, the diffusion sink braze alloys exhibited good filleting and flow. No significant differences in braze alloy behavior were noted when brazing in either a 10^{-4} Torr vacuum or a 300 Torr high purity argon atmosphere. The microstructures and hardness of these alloys are shown in Figures D5-D14 and discussed in detail in Appendix D.

An analysis of these data showed that diffusion sink powder additions produced effects similar to those observed on TZM tee joints. Sink powder additions alloyed completely or at least substantially with the braze alloys during the braze cycle. In addition, most of the braze systems showed less braze fillet-base metal diffusion when sink powder was present.

The primary reasons for Si, Fe, and Zr additions to these braze alloys were to reduce brazing temperatures and/or improve braze alloy filleting and flow. However, these elements exhibit limited solid solubility in tantalum and in the braze alloy matrices. The high fillet hardnesses observed, particularly after diffusion treating, were probably caused by these solute elements.

In view of the hardness increases observed after diffusion treating, the following additional compositions were evaluated:

Composition	Liquidus Temperature
1. Ti-10Ta	3130F
2. Ti-8Cb-1B	2950F
3. Ti-4Cb-1B	3100F
4. Ti-20V-0.5	2840F

Alloy #1 exhibited poor filleting and flow, as did alloys #2, #3, and #4 without boron additions. However, additions of 0.5-1.0 percent boron produced good filleting and flow. Braze alloy/Ta-10W diffusion couples were prepared with alloys #2, #3, and #4. Diffusion treating resulted in formation of a hard interface compound, presumably a boride. Therefore, these alloys did not offer good potential as diffusion sink braze alloys.

The above-mentioned studies showed that vacuum diffusion treatment of tee joints caused problems with respect to partial braze alloy volatilization. Encapsulation of these joints in a small evacuated retort reduced the problem but did not eliminate it. Therefore, further braze system evaluation was concentrated on lap and 2 x 2 inch honeycomb specimens because volatilization was minimized by these geometries.

All of the braze systems showed substantial microstructural changes after diffusion treatment. The microhardness increases were also indicative of joint embrittlement. Therefore, further effort was concentrated on pure titanium and Ti-30V as diffusion sink systems. These systems required higher braze temperatures and exhibited poorer filleting and flow. However, they offered the advantage of solid solution formation with tantalum. The 33Zr-34Ti-33V alloy was also selected for further evaluation primarily because of the relatively low braze temperature (2600F).

Lap Joint Evaluation

Lap joints (.010-.010 inch) were brazed with Ti and Ti-30V, given several diffusion treatments, and analyzed by electron probe analysis. These tests were conducted to establish an optimum diffusion treatment for attaining remelt temperatures of approximately 3800F. Results were as follows:

	Diffusion Treatment	*Composition at Center of Joint	
		Ti Braze	Ti-30V Braze
A.	24 hrs. at 2850F	58Ta-32Ti	59Ta-22Ti-7V
B.	24 hrs. at 2850F+ 16 hrs. at 2950F+ 8 hrs. at 3050F+ 16 hrs. at 3150F+	69Ta-20Ti	64Ta-21Ti-5V
C.	Same as B + 8 hrs. at 3250F	73Ta-16Ti	74Ta-13Ti-3V

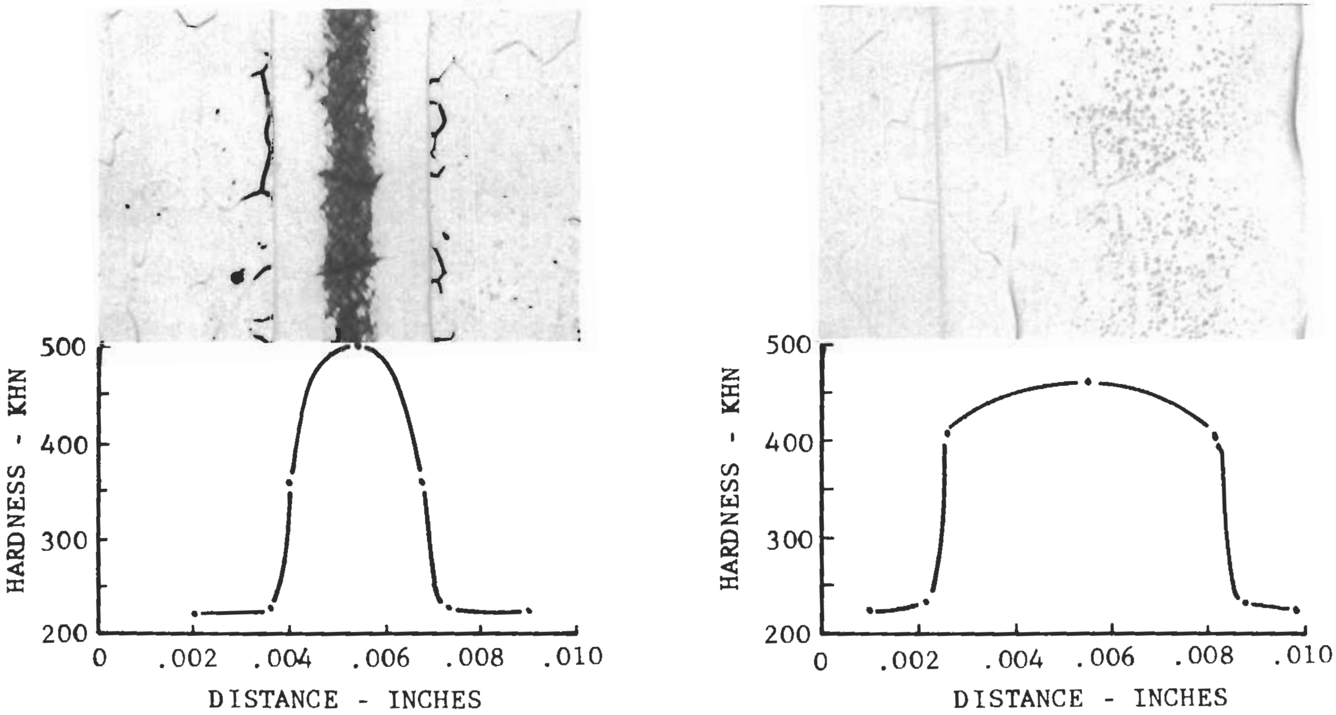
* Initial joint thickness was approximately .002 inch.

Joint compositions produced by diffusion treatment C were estimated to possess a solidus temperature of 3800F. However, later 2 x 2 inch honeycomb remelt tests showed that diffusion treatment "A" was more than adequate for a 3800F remelt temperature. Therefore, the lap joint diffusion treatment was standardized at 2850F for 24 hours. The differences between estimated versus measured remelt temperatures were probably caused by differences in joint thicknesses.

Microhardness traverses and microstructures of Ti and Ti-30V lap joints are shown in Figure 20. The as-brazed Ti joint contained an alpha prime structure at the center of the joint and a tantalum-stabilized beta structure near the base metal. Substantial grain boundary diffusion of titanium into the base metal was evident near the joint interface. After diffusion treatment, joint hardness decreased and alpha prime formation was suppressed by additional base metal diffusion. However, particles of a second, unidentified phase were noted. As-brazed and diffusion treated Ti-30V joints were essentially single phase. The diffusion treatment produced a mild increase in joint hardness.

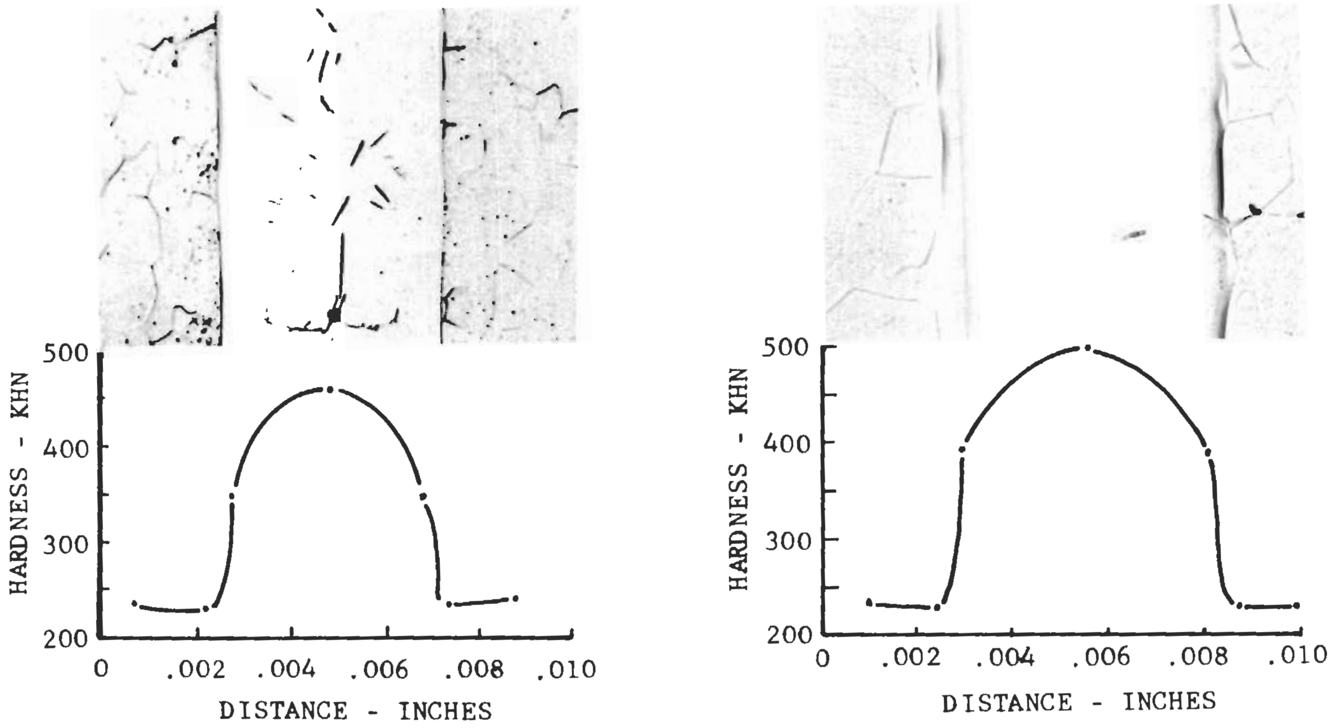
LBT-5D
Ti BRAZE - AS-BRAZED

LBT-5A
Ti BRAZE
DIFFUSED 24 HOURS AT 2850F



LBT-4D
Ti-30V BRAZE
AS-BRAZED

LBT-4A
Ti-30V BRAZE
DIFFUSED 24 HOURS AT 2850F



MAG. 250X BASE MATERIAL ETCHANT: 25 HF, 12.5 HNO_3, 12.5 H_2SO_4, 50 H_2O

FIGURE 20 MICROSTRUCTURES OF Ta-10W LAP JOINTS BRAZED WITH Ti AND Ti-30V

Microhardness traverses and microstructures of as-brazed and diffusion treated 33Zr-34Ti-33V lap joints are shown in Figure 21. Both structures contained three distinct phases in the joints. A marked increase in hardness was produced by diffusion treatment. The high hardness and multiphase structure was believed to have been caused by the zirconium contained in the braze alloy.

The microstructure of a lap joint brazed with Cb-1.3B is shown in Figure 22. The center of the joint contained a typical eutectic structure which was relatively soft (310KHN). Boron diffusion into the base metal produced a soft (148 KHN) boron depleted braze alloy zone near the base metal. Discontinuous grain boundary borides and a Widmanstatten boride precipitate within the base metal grains were observed.

Remelt temperatures of lap joints brazed with Ti, Ti-30V, and 33Zr-34Ti-33V are shown in Table XVI. Remelt temperatures exceeded 3800F in all cases.

Lap shear strength data are included in Table XVII. All of the joints exhibited high strength at 3500F. The Ti and Cb-1.3B joints exhibited almost equivalent strength. Thus, by diffusion sink brazing with Ti, maximum processing temperature was 1000F lower than the temperature required for conventional brazing with Cb-1.3B. The Ti-30V joints exhibited approximately 40% lower strength than the Ti and Cb-1.3B joints.

Honeycomb Evaluation

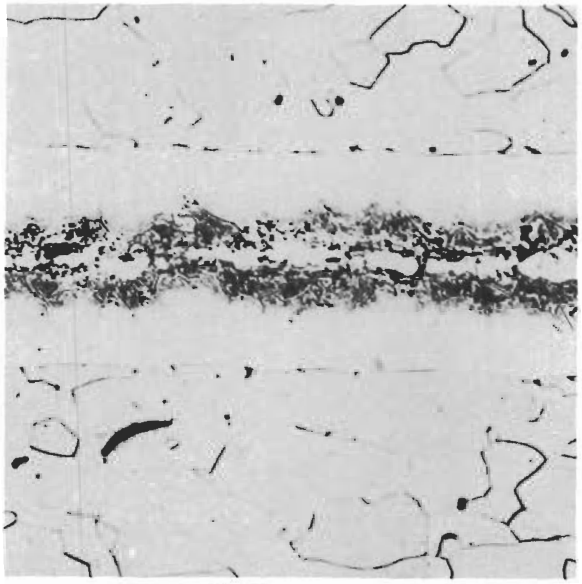
Remelt temperatures of 2 x 2 inch honeycomb specimens are recorded in Table XVIII. Specimens HT-6 and HT-8, brazed with Ti, showed that (1) the diffusion treatment was much greater than required for a 3800F remelt temperature, and (2) diffusion sink powder was not necessary for producing a high remelt temperature. Reducing the diffusion treatment to 24 hours at 2850F still produced remelt temperatures exceeding 3800F on specimens brazed with Ti and Ti-30V. Remelt temperatures of 33Zr-34Ti-33V specimens indicated that maximum service temperature for this system was approximately 3000F.

Strength tests on honeycomb specimens (2 x 2 inch) brazed with Cb-1.3B, Ti, and Ti-30V were performed using the conditions of one hour at 3500F under a 1.2 psi flatwise tensile stress. The Ti and Ti-30V specimens were diffusion treated for 24 hours at 2850F prior to testing. Duplicate tests showed that all these specimens withstood the exposure with no evidence of failure.

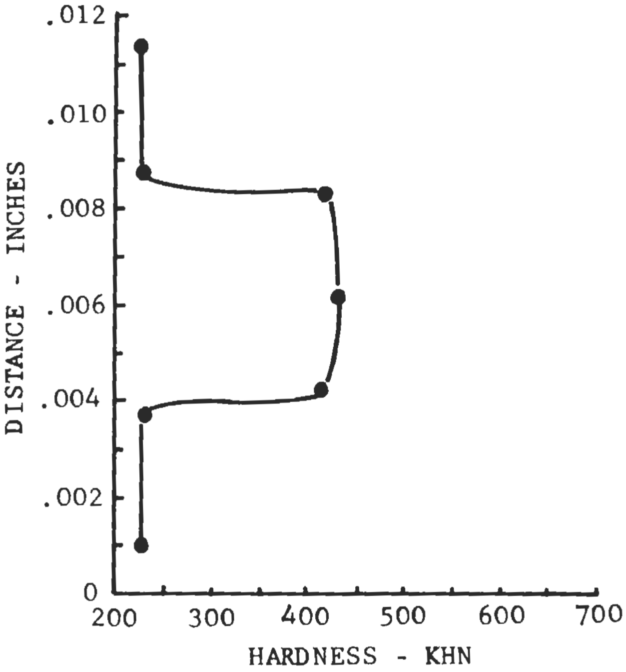
The specimens listed in Table XVIII showed substantial honeycomb foil embrittlement after diffusion treatment. Comparison between HT-8 and HT-12 showed that the reduced diffusion treatment produced a significant improvement in foil ductility. However, ductility still was not satisfactory.

Typical foil microstructures taken from diffusion treated honeycomb specimens are shown in Figure 23. These structures show that braze alloy volatilized within the sealed honeycomb cells, deposited on the foil, and diffused inward. This lowered the vapor pressure in the cells and permitted additional material to volatilize from the fillets. The extensive diffusion zones produced in this manner were relatively soft solid solutions. However, substantial grain boundary diffusion occurred particularly with Ti. It is probably this grain boundary diffusion which is responsible for the foil embrittlement observed on a macro scale. The same basic effect was observed on face sheets, but minor embrittlement was produced because (1) diffusion occurred from only one side of each face sheet and (2) the face sheet thickness minimized embrittling effects.

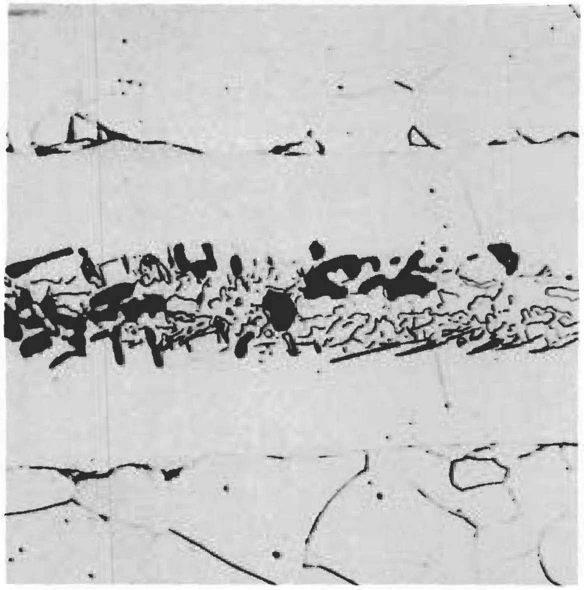
MT-9A



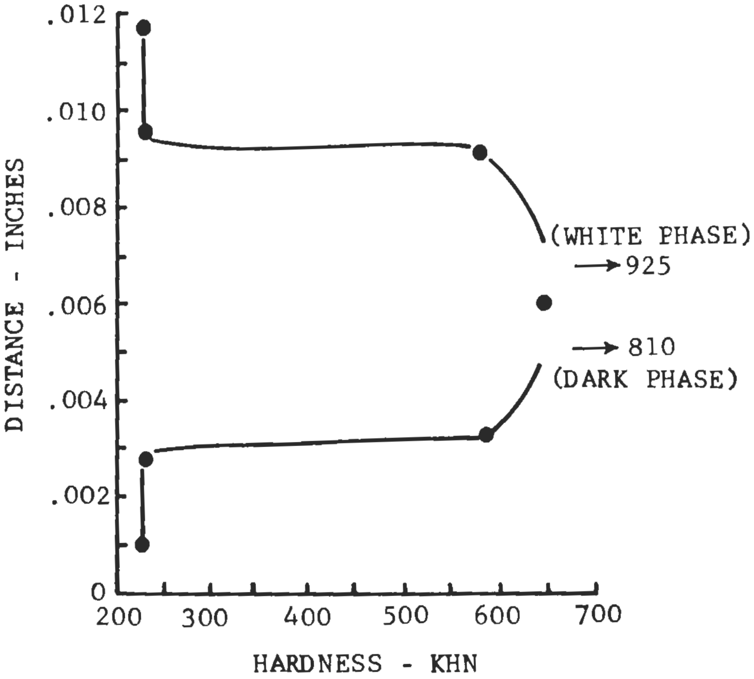
AS-BRAZED



MT-9B

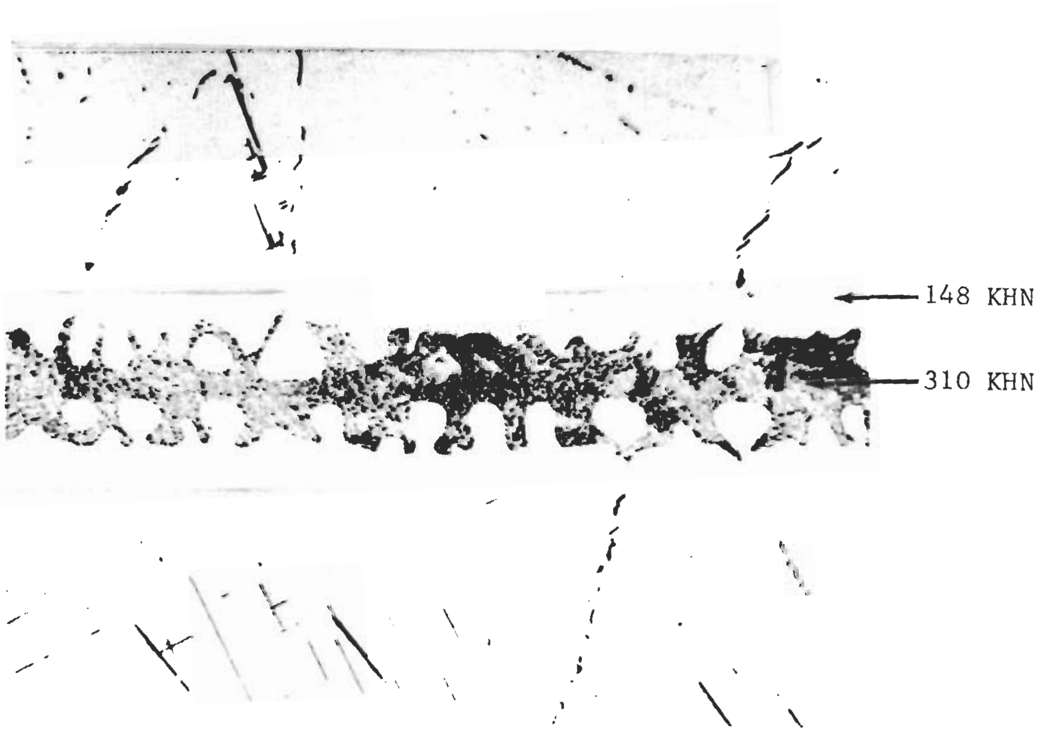


DIFFUSED 20 HOURS AT 2400F +44 HOURS AT 2500F + 24 HOURS AT 2600F



MAG. 250X	BASE MATERIAL ETCHANT:	25 HF, 12.5 H_2SO_4, 12.5 HNO_3, 50 H_2O
	BRAZE ALLOY ETCHANT:	1 HF, 2 HNO_3, 97 H_2O

FIGURE 21 MICROSTRUCTURES OF Ta-10W LAP JOINTS BRAZED WITH 33Zr-34Ti-33V



BRAZED 1 MIN AT 4150-4200F

MAG. 200X ETCHANT: 25HF, 12.5H_2SO_4, 12.5HNO_3, 50H_2O

FIGURE 22 Ta-10W LAP JOINT BRAZED WITH Cb-1.3B - AS-BRAZED

TABLE XVI

Ta-10W LAP JOINT REMELT TEMPERATURES

Sample No.	Braze Alloy	Diffusion Treatment	Remelt Temp F	Remelt Temp. Minus Braze Alloy Liquidus F
LT-10	Titanium	24 hrs. at 2850F	>4200	>1140
LT-11	Titanium	24 hrs. at 2850F	>4200	>1140
LT-16	Ti-30V	24 hrs. at 2850F	>4200	>1220
LT-17	Ti-30V	24 hrs. at 2850F	>4200	>1220
LT-7	33Zr-34Ti-33V	20 hrs. at 2400F+ 44 hrs. at 2500F+ 24 hrs. at 2600F	3830	1350
LT-8	33Zr-34Ti-33V		>3900	>1420

Notes: All specimens were .040 inch thick with a .120-.140 inch overlap. Thickness of braze joints was approximately .002 inch. Remelt tests conducted with 120 psi tension on base metal (40 psi shear stress on lap joint).

TABLE XVII

Ta-10W LAP JOINT SHEAR STRENGTHS AT 3500F

Sample No.	Braze Alloy	Diffusion Treatment	Shear Strength	Base Metal Stress
LT-2	Cb-1.3B	-	4330 psi	12,900 psi
LT-3	Cb-1.3B	-	3750	12,800
LT-4	Cb-1.3B	-	4200	12,600
LT-14	Titanium	24 hrs. at 2850F	3800	11,500
LT-15	Titanium	↓	4270	11,100
LT-18	Ti-30V	↓	2160	6,750
LT-19	Ti-30V	↓	2550	7,650
LT-20	Ti-30V	↓	3050	9,600

Notes: Specimens were .040 inch thick with a .120-.140 inch overlap. Thickness of braze joints was approximately .002 inch. Shear strength tests conducted at .05 inch/min. head speed. All specimens failed in braze joint.

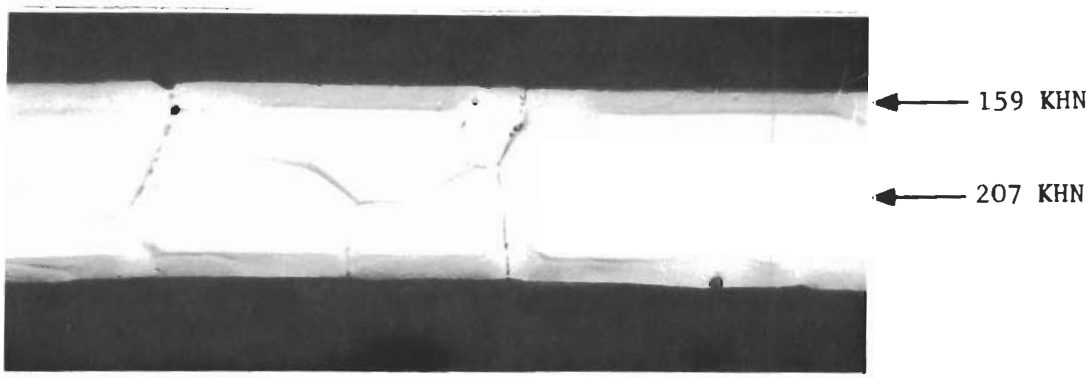
TABLE XVIII

Ta-10W HONEYCOMB REMELT TEMPERATURES

Sample No.	Braze Alloy	Diffusion Treatment	Remelt Temp. F	Remelt Temp. Minus Braze Alloy Liquidus F
HT-6	Ti+10 Wt.% Ta Sink	8 hrs. at 2850F+ 16 hrs. at 2950F+ 8 hrs. at 3050F+ 16 hrs. at 3150F+ 8 hrs. at 3250F	>3950	> 890
HT-8	Titanium		>3800	> 740
HT-12	Titanium	24 hrs. at 2850F	>3800	> 740
HT-13	Titanium	24 hrs. at 2850F	>3800	> 740
HT-10	Ti-30V	Same as HT-6, 8	>4000	>1020
HT-17	Ti-30V	24 hrs. at 2850F	>3800	>820
HT-18	Ti-30V	24 hrs. at 2850F	>3800	>820
HT-3	33Zr-34Ti-33V	20 hrs. at 2400F+ 44 hrs. at 2500F+ 25 hrs. at 2600F	3360	880
HT-4	33Zr-34Ti-33V		3200	720

All tests conducted at a heating rate of approximately 600F/minute and a flatwise tensile stress of 1.2 psi.

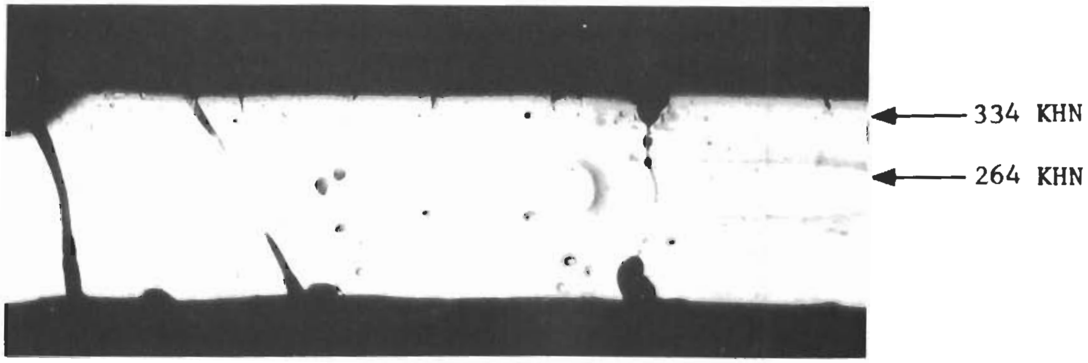
HT-4



a.

BRAZE ALLOY: 33Zr-34Ti-33V
DIFFUSION TREATMENT: 20 HOURS AT 2400F +
44 HOURS AT 2500F +
24 HOURS AT 2600F

HT-11



b.

BRAZE ALLOY: Ti
DIFFUSION TREATMENT: 24 HOURS AT 2850F

MAG. 500X

ETCHANT: 25 HF
12.5 HNO_3
12.5 H_2SO_4
50 H_2O

FIGURE 23 MICROSTRUCTURES OF Ta-10W HONEYCOMB FOIL AFTER DIFFUSION TREATING

Fillet microstructures from honeycomb specimens brazed with Ti are shown in Figure 24. The as-brazed fillet exhibited a stabilized beta region near the base metal and an alpha prime structure at the fillet extremities. A fine dispersion of what might be omega phase was centered between these structures. After diffusion treatment, the fillet contained a dark-etching phase and fillet hardness increased substantially. Similar results were observed in the honeycomb specimens brazed with Ti-30V as shown in Figure 25. These results were not consistent with data obtained on similar lap joints. Reasons for the high fillet hardnesses and second phase formation are not known at present. Additional effort is required to identify and solve this problem.

Transition Temperatures

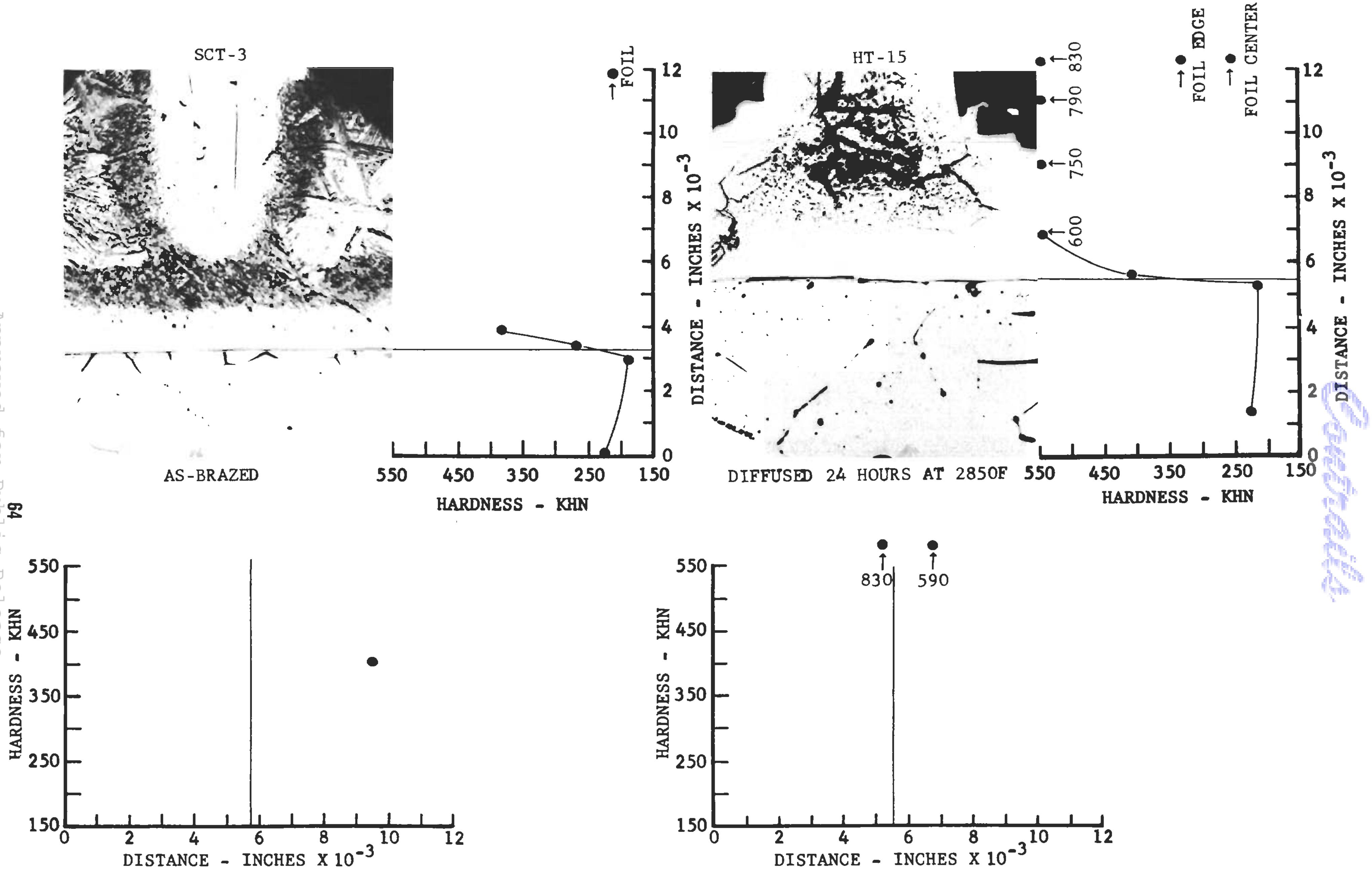
Transverse bend transition temperature was determined on .020 inch Ta-10W in the as-received condition and after two separate thermal exposures. These exposures simulated processing cycles for Ti diffusion sink brazing (one minute at 3200F plus 24 hours at 2850F) and Cb-1.3B conventional brazing (one minute at 4200F). These were the most severe exposures employed for diffusion sink and conventional brazing, respectively. Transverse bend transition temperatures were below -320F for all of these conditions.

Figure 26 shows the transverse bend transition temperature data obtained on .010-.010 inch lap bend samples brazed with Cb-1.3B, titanium, and Ti-30V. Lap bend samples brazed with Cb-1.3B exhibited a transition temperature of plus 140F, with a broad transition region extending from -20 to +140F. This increase in transition temperature was caused by the discontinuous boride phase formed in the base metal grain boundaries. These joints still exhibited ductility at room temperature as evidenced by the fact that they could be bent at least 25 degrees with no fracture.

Samples brazed with titanium and Ti-30V and diffusion treated, exhibited a transition temperature below -320F as shown in Figure 26. However, in all cases, metallographic analysis after testing showed braze alloy cracking perpendicular to the faying plane with no base metal cracking. Therefore, several samples were bent at -150F to determine the maximum bend angle which would produce no braze alloy cracking. The samples brazed with titanium showed no evidence of cracking after being subjected to bend angles of 10, 20 and 30 degrees. Samples brazed with Ti-30V showed cracking at 30 degrees but not at 10 or 20 degrees.

Several bend tests were performed on tee joints brazed with Cb-1.3B. In all cases, specimens tested at room temperature and -320F were bent greater than 80 degrees with no failure.

Transverse notched tensile transition temperatures of .002 inch foil are presented in Figure 27. As-received foil, as well as foil exposed to the diffusion sink processing cycles, exhibited a transition temperature below -300F. Foil subjected to the conventional brazing cycle exhibited a transition temperature of -200F. Net section stress was affected by thermal treatment as well. The room temperature net tensile stress for the material exposed to the diffusion sink process cycle was reduced to 75,000 psi. For the conventional brazing cycle a further reduction to about 40,000 psi was observed. These effects are due to recrystallization and grain growth. The grain growth achieved by the conventional brazing cycle resulted in single grains in the sheet thickness direction. Thus, the lower processing temperatures used for diffusion sink brazing resulted in better foil toughness as well as higher notched tensile strength.



AS-BRAZED

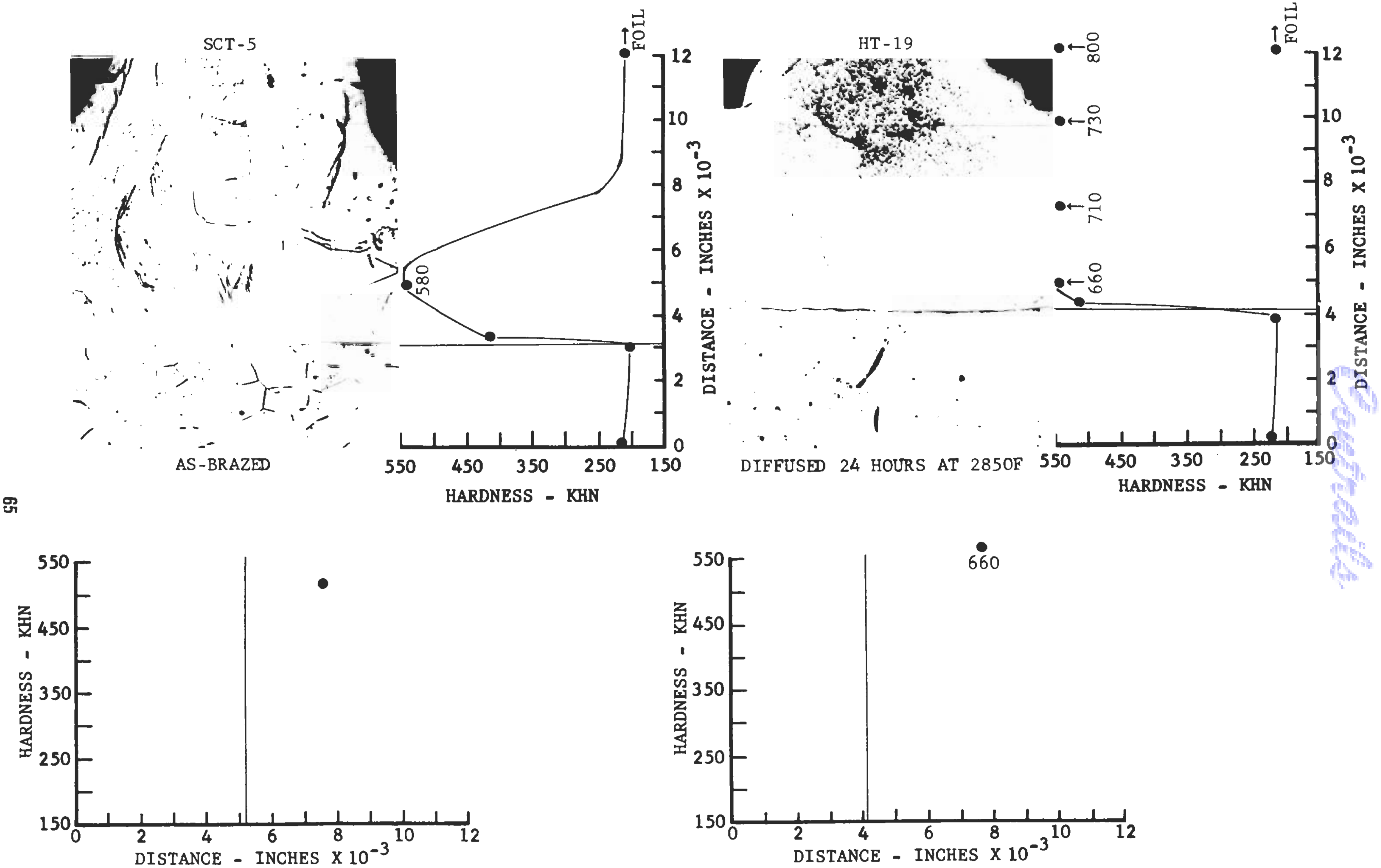
DIFFUSED 24 HOURS AT 2850F

BRAZE CYCLE:

BRAZE CYCLE:

MAG. 250X BASE MATERIAL ETCHANT:
BRAZE ALLOY ETCHANT: 25 HF, 12.5 H_2SO_4, 12.5 HNO_3, 50 H_2O

FIGURE 24 Ta-10W HONEYCOMB SPECIMENS BRAZED WITH PURE TITANIUM

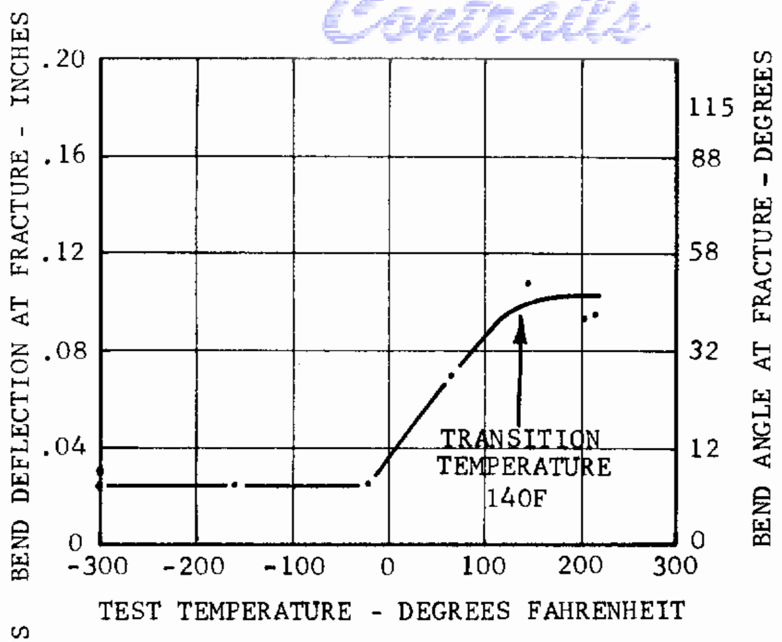


BRAZE CYCLE:

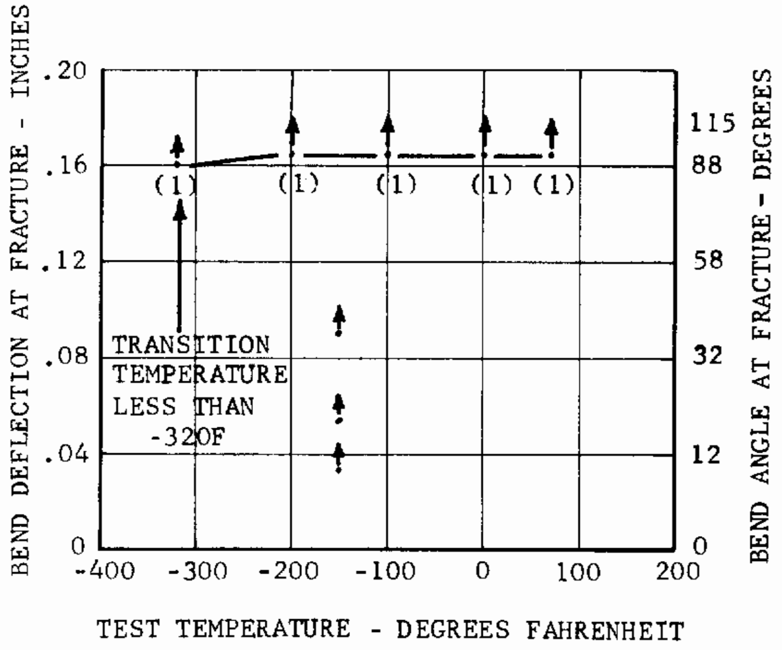
BRAZE CYCLE:

MAG. 250X BASE MATERIAL ETCHANT: 25 HF, 12.5 H_2SO_4, 12.5 H_2 HNO_3, 50 H_2O
BRAZE ALLOY ETCHANT:

FIGURE 25 Ta-10W HONEYCOMB SPECIMENS BRAZED WITH Ti-30V

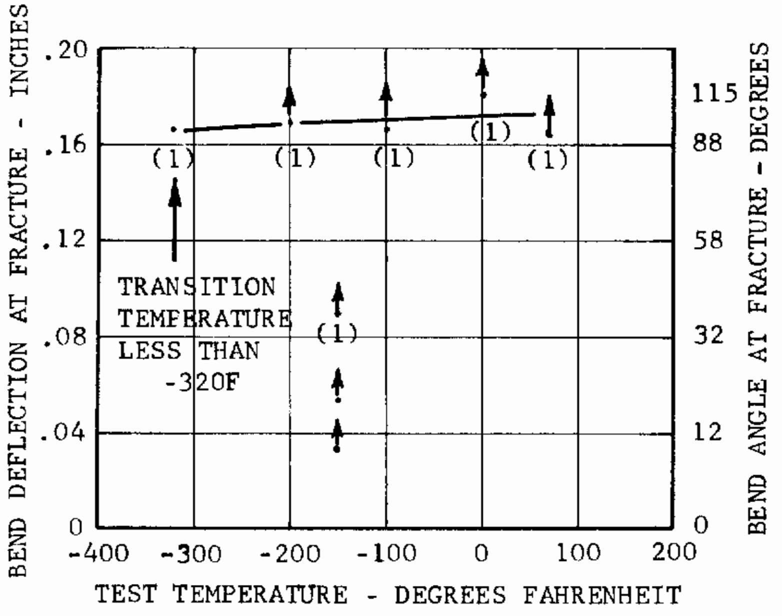


BRAZE ALLOY: Cb-1.3B
BRAZED 1 MINUTE AT 4200F



BRAZE ALLOY: TITANIUM
BRAZED 1 MINUTE AT 3200F
DIFFUSED 24 HOURS AT 2850F

(1) BRAZE ALLOY CRACKING PERPENDICULAR TO FAYING PLANE - NO BASE METAL CRACKING

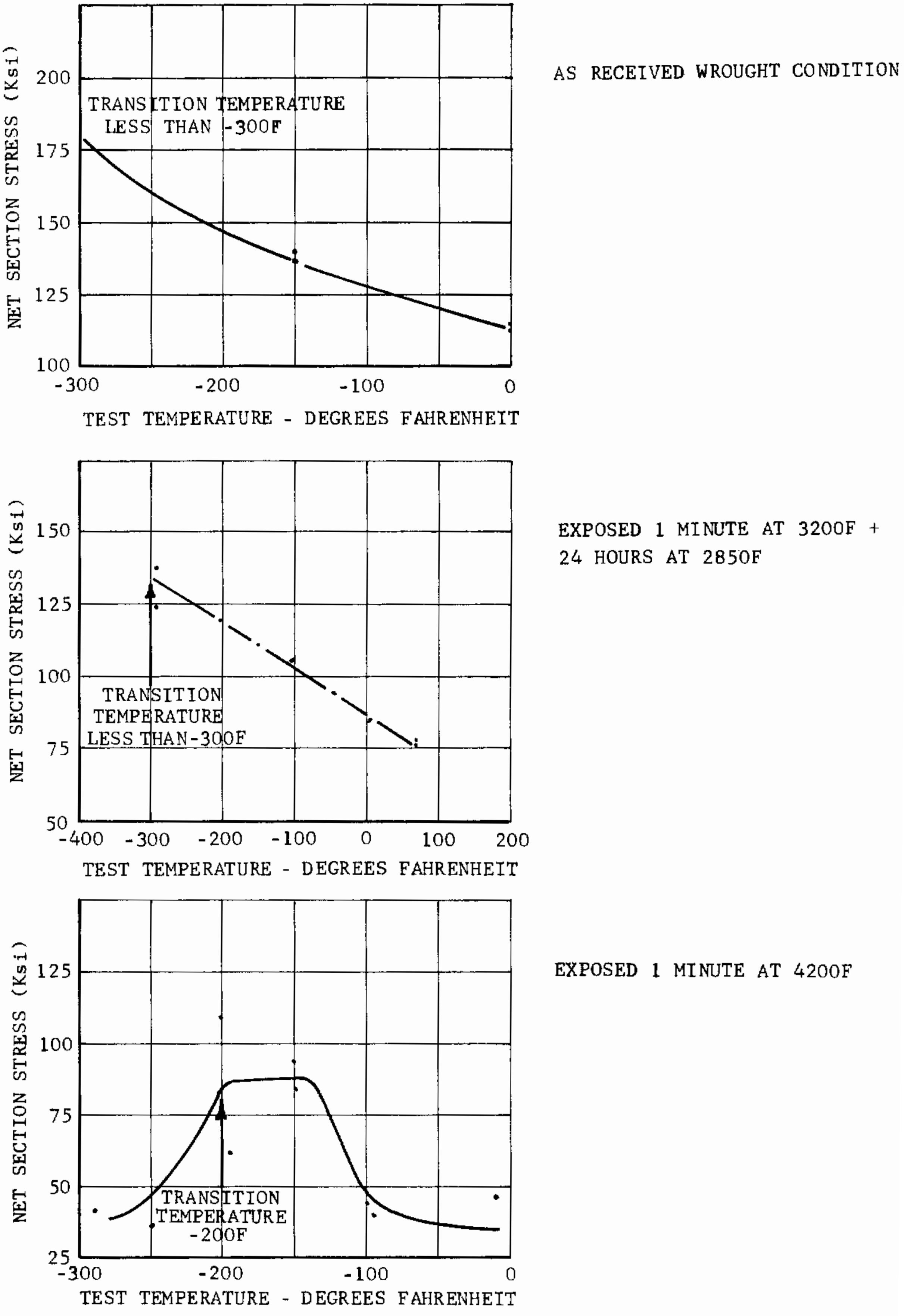


BRAZE ALLOY: Ti-30V
BRAZED 1 MINUTE AT 3100F
DIFFUSED 24 HOURS AT 2850F

(1) BRAZE ALLOY CRACKING PERPENDICULAR TO FAYING PLANE - NO BASE METAL CRACKING

HEAD SPEED .05 INCH PER MINUTE

FIGURE 26 TRANSVERSE BEND TRANSITION TEMPERATURES OF BRAZED Ta-10W LAP JOINTS



HEAD SPEED .10 INCH PER MINUTE

FIGURE 27 TRANSVERSE NOTCH TENSILE TRANSITION TEMPERATURE OF .002 INCH Ta-10W FOIL

BRAZE SYSTEM EVALUATION ON Ta-8W-2Hf AND Ta-30Cb-7.5V

The most promising braze systems evaluated on Ta-10W were selected for evaluation on Ta-8W-2Hf and Ta-30Cb-7.5V. Specific braze systems and parameters were as follows:

Base Metal	Braze Alloy	Diffusion Cycle	Intended Service Temperature
Ta-8W-2Hf	Cb-1.3B	-	3000-3500F
	Ti	24 hrs. at 2850F	
	Ti-30V	24 hrs. at 2850F	
Ta-30Cb-7.5V	Ti	6 hrs. at 2850F	2500-3000F
	Ti-30V	6 hrs. at 2850F	
	33Zr-34Ti-33V	20 hrs. at 2400F+ 44 hrs. at 2500F+ 24 hrs. at 2600F+	

The diffusion treatments for Ti and Ti-30V applied to Ta-30Cb-7.5V, were reduced from 24 to 6 hours at 2850F because of the lower service temperature requirements.

Tee Joint Evaluation

Tee joint strength test results on Ta-8W-2Hf and Ta-30Cb-7.5V are recorded in Tables XIX and XX, respectively. In all cases, the tees failed at temperatures well above the intended service temperatures.

Lap Joint Evaluation

Lap shear strength test results on Ta-8W-2Hf and Ta-30Cb-7.5V are recorded in Tables XXI and XXII respectively. All of these joints exhibited good high temperature strength. The Cb-1.3B provided somewhat higher joint strength on Ta-8W-2Hf than Ti or Ti-30V. In addition, joint strengths obtained with Cb-1.3B and Ti-30V were higher than obtained on similar Ta-10W specimens. For Ta-8W-2Hf, the Ti-30V produced higher joint strength than Ti, whereas the reverse trend was observed on Ta-10W. Detailed comparisons between the Ta-30Cb-7.5V joints were not possible because most of the specimens failed in the base metal. However, the Ti and Ti-30V joints were clearly stronger than 33Zr-34Ti-33V joints.

Transition Temperature

Transverse bend transition tests were conducted on .013 inch Ta-30Cb-7.5V and .010 inch Ta-8W-2Hf base metal samples. These alloys were tested in the as-received condition and after the severest thermal exposures encountered in brazing. These exposures consisted of one minute at 3200F plus 6 hours at 2850F for Ta-30Cb-7.5V, and one minute at 4200F for Ta-8W-2Hf. In all cases, transverse bend transition temperatures based on the same criteria employed for the Ta-10W alloy were below -320F.

The Ta-30Cb-7.5V lap bend samples brazed with titanium at 3200F for one minute and diffusion treated at 2850F for 6 hours exhibited a transverse bend transition temperature below -320F. Metallographic analysis, after testing, showed no braze alloy or base metal cracking.

The Ta-8W-2Hf lap bend samples brazed with Cb-1.3B at 4200F for one minute exhibited a transverse bend transition temperature of 0F. This transition temperature increase was substantially lower than the increase produced by Cb-1.3b on Ta-10W, shown in Figure 26.

TABLE XIX

Ta-8W-2Hf TEE JOINT STRENGTH TESTS

Sample No.	Braze Alloy	Diffusion Treatment	Failure Temp. F
TH-3A	Cb-1.3B	-	3750
TH-3B	Cb-1.3B	-	>3850
TH-1A	Titanium	24 hrs. at 2850F	>3850
TH-1B	Titanium	24 hrs. at 2850	>3860
TH-2A	Ti-30V	24 hrs. at 2850F	3840
TH-2B	Ti-30V	24 hrs. at 2850F	>3880

Notes: All tests conducted at a heating rate of approximately 600F/min. and a tensile stress of 650 psi on the tee.

TABLE XX

Ta-30Cb-7.5V TEE JOINT STRENGTH TESTS

Sample No.	Braze Alloy	Diffusion Treatment	Failure Temp. F
TC-1A	33Zr-34Ti-33V	20 hrs. at 2400F+ 44 hrs. at 2500F+ 24 hrs. at 2600F	3720
TC-1B	33Zr-34Ti-33V		3750
TC-2A	Titanium	6 hrs. at 2850F	3550
TC-2B	Titanium	6 hrs. at 2850F	3700
TC-3B	Ti-30V	6 hrs. at 2850F	3850
TC-3C	Ti-30V	6 hrs. at 2850F	>3880

Note: All tests conducted at a heating rate of approximately 600F/min. and a tensile stress of 650 psi on the tee.

TABLE XXI

Ta-8W-2Hf LAP SHEAR STRENGTHS

Sample No.	Braze Alloy	Diffusion Treatment	Test Temp F	Shear Strength	Base Metal Stress
THL-6	Cb-1.3B	-	3000	7810	22,650
THL-5	Cb-1.3B	-	3500	4910	14,350
THL-2	Titanium	24 hrs. at 2850F	3000	6760	20,450
THL-1	Titanium	24 hrs. at 2850F	3500	3430	10,900
THL-7	Ti-30V	24 hrs. at 2850F	3000	7150*	24,500
THL-4	Ti-30V	24 hrs. at 2850F	3500	3980	11,250

Notes: Specimens were .040 inch thick with a .120-.140 inch overlap. Thickness of braze joints was approximately .002 inch. Shear strength tests conducted at .05 inch/min. head speed.

*Base metal failure - remaining samples failed in braze joint.

TABLE XXII

Ta-30Cb-7.5V LAP SHEAR STRENGTHS

Sample No.	Braze Alloy	Diffusion Treatment	Test Temp. F	Shear Strength	Base Metal Stress
TCL-1	33Zr-34Ti-33V	20 hrs. at 2400F+ 44 hrs. at 2500F+ 24 hrs. at 2600F	2500	3890 psi	22,670 psi
TCL-2	33Zr-34Ti-33V		3000	3225	20,170
TCL-3	Titanium	6 hrs. at 2850F	2500	8690*	50,670
TCL-4	Titanium	6 hrs. at 2850F	3000	4965*	23,580
TCL-5	Ti-30V	6 hrs. at 2850F	2500	8925*	48,330
TCL-6	Ti-30V	6 hrs. at 2850F	3000	4550*	25,580

Notes: Specimens were .030 inch thick with a .120-.140 inch overlap. Thickness of braze joints was approximately .002 inch. Shear strength tests conducted at .05 inch/min. head speed.

*Base metal failure - remaining samples failed in braze joint.

MANUFACTURING APPLICABILITY

The final test of a braze alloy system must be based upon practical considerations encountered in real manufacturing operations. Some of these important considerations include braze alloy/oxidation coating compatibility, adaptability to existing brazing facilities and inspection techniques on the final brazement. In this section the activities carried out in this program aimed at the practical utilization of the developed braze alloy systems are discussed.

Braze Alloy-Coating Compatibility

The lap joint specimen used for braze alloy-coating compatibility evaluation was selected for the following reasons:

1. The specimen simulated an edgemember to face sheet joint with braze alloy exposed at the faying plane. This is the basic geometry found in a typical honeycomb panel.

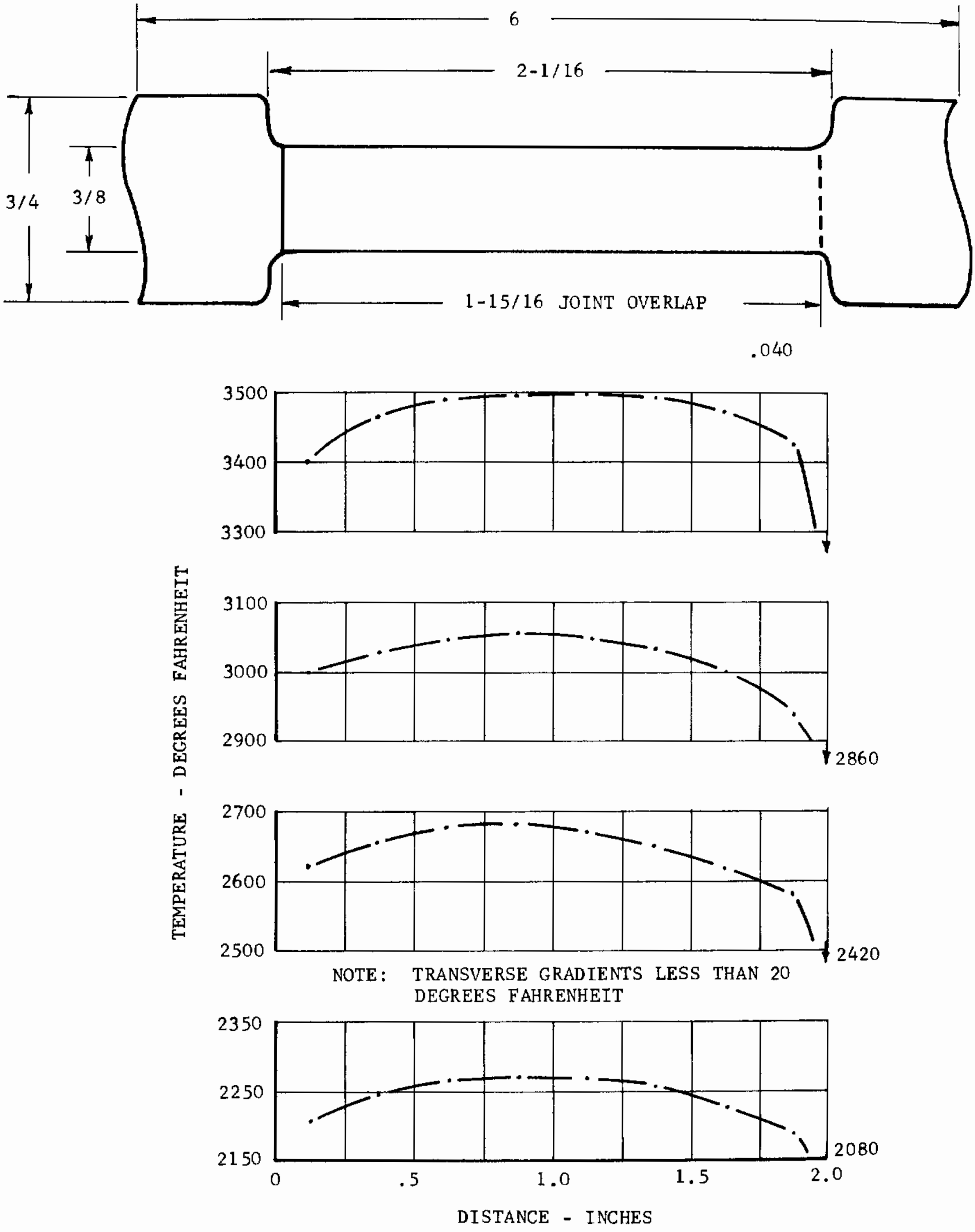
2. The specimen geometry provided a cross section of constant resistivity which was amenable to direct resistance heating with minimum temperature gradients as shown in Figure 28.

Specific base metal-braze alloy-coating combinations investigated are included in Table XXIII. In all cases temperatures are reported as brightness temperatures because the emissivity behavior of the coatings was unknown under the reduced pressure conditions employed. For all the coatings employed, the emissivities are estimated to be from 0.60-0.80. Based on these values, the true temperatures would be approximately 50-200F greater than the reported brightness temperatures. In addition, several Ta-10W specimens brazed with Ti were coated with the unmodified silicide. Each of these specimens separated across the faying plane after coating. Therefore, high temperature tests could not be performed. The cause of specimen failure is not known. All TZM specimens coated with PFR-6 exhibited coating cracks at edge areas. These cracks were caused by a combination of the coating thickness and edge radii employed. However, the specimens were still protected and coating evaluation was not affected.

Specimen failure occurred at braze alloy-coating areas and/or base metal-coating areas. Table XXIII lists the testing conditions and types of failure based on visual observation, and metallographic analysis and microhardness measurements on selected specimens.

Figure 29 shows the microstructure of a typical as-coated TZM specimen coated with PFR 6. The braze joint was severely attacked by the coating along the braze alloy-base metal interface. Thus, high temperature test results were not meaningful in terms of coating-braze alloy behavior. However, these results did show that the base metal was protected to a maximum temperature between 2625 and 2920F based on test conditions employed.

Figure 30 shows the microstructure of a Ta-10W joint, brazed with Cb-1.3B, coated with Sn-25Al, and tested at 2870F. The coating reacted with the braze alloy during testing and formed an alloy which melted and partially flowed away from the joint. Reaction products remaining on the base metal were protective based on microhardness data. However, severe joint recession occurred.



NOTE: TRANSVERSE GRADIENTS LESS THAN 20 DEGREES FAHRENHEIT

FIGURE 28 THERMAL GRADIENTS IN RESISTANCE HEATED COATING COMPATIBILITY SPECIMEN

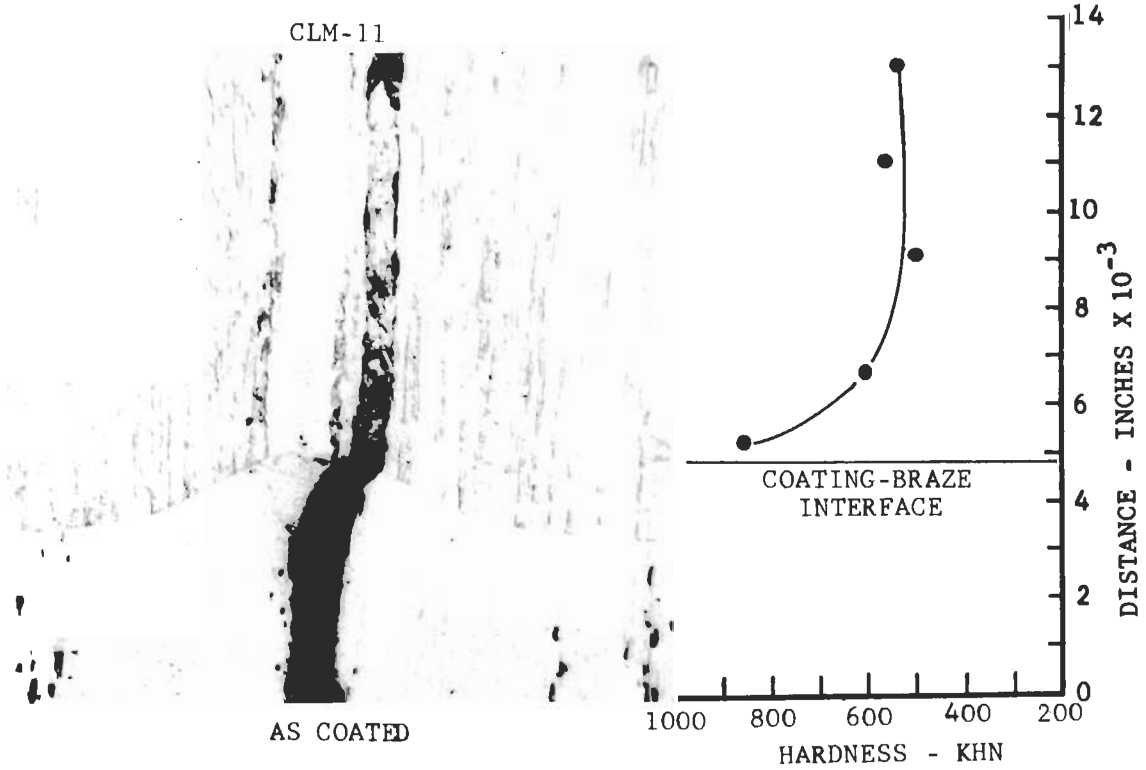
TABLE XXIII

COATING-BRAZE ALLOY COMPATIBILITY

Sample No.	Braze Alloy	Test Cycle	Type of Failure Coating-Base Metal	Coating-Braze Alloy
PFR-6 on TZM				
CLM-4	Ti-25Cr-13Ni	2920F for 3 min.	√	√
CLM-12	Ti-25Cr-13Ni	2625F for 47 min.		√
CLM-3	Ti-25Cr-13Ni	2540F for 60 min.		√
CLM-8	Ti-25Cr-13Ni	2430F for 51 min.		√
Sn-25Al on Ta-10W				
CLT-3	CB-1.3B	3330F for 3 min.	√	√
CLT-2	Cb-1.3B	3250F for 6 min.	√	√
CLT-6	Cb-1.3B	2870F for 25 min.		Heavy interaction but protection maintained
CLT-11	Ti	3330F for 11 min.	√	√
CLT-12	Ti	2870F for 60 min.		√
CLT-13	Ti	2640F for 60 min.		Heavy interaction but protection maintained
CLT-17	Ti-30V	2870F for 23 min.	√	√
CLT-19	Ti-30V	2780F for 25 min.		√
CLT-18	Ti-30V	2410F for 60 min.		Mild interaction but protection maintained
Unmodified Silicide on Ta-10W				
CLT-7	Cb-1.3B	2900F for 43 min.	√	√
CLT-5	Cb-1.3B	2840F for 56 min.	√	√
CLT-1	Cb-1.3B	2700F for 60 min.		
CLT-16	Ti-30V	3000F for 13 min.	√	√
CLT-15	Ti-30V	2900F for 5 min.	√	√
CLT-14	Ti-30V	2800F for 60 min.		√

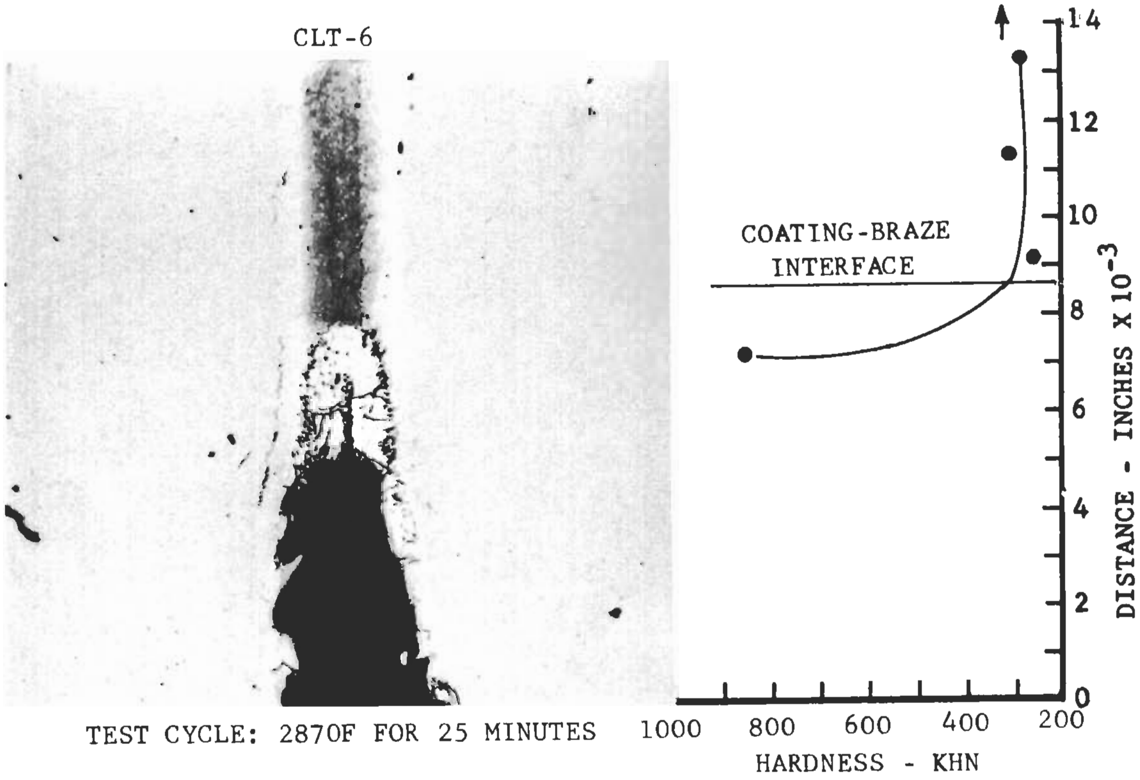
Coating Thicknesses: PFR-6 - .0029 to .0032 inch
Sn-25Al .0007 to .001 inch
Unmodified Silicide .0018 to .0021 inch

Test Conditions: 1.2 psi air atmosphere
Air Flow Rate - 5 cubic feet per hour



MAG. 200X ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O

FIGURE 29 COMPATIBILITY OF PFR-6 COATING WITH Ti-25Cr-13Ni ON TZM



TEST CYCLE: 2870F FOR 25 MINUTES

MAG. 200X ETCHANT 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE 30 COMPATIBILITY OF SN-25A1 COATING WITH Cb-1.3B ON Ta-10W

The Ta-10W specimens brazed with Ti and Ti-30V also showed substantial interaction between the joints and the Sn-25Al coating after testing at lower temperatures. However, the reaction products remained in the joint and substantially less melting and recession occurred. Microhardness data confirmed that joint and base metal protection was maintained. Overall test results obtained with Sn-25Al show that the base metal was protected to a maximum temperature of approximately 2870F under the test conditions employed.

Figure 31 shows the microstructure of a Ta-10W joint brazed with Cb-1.3B, coated with an unmodified silicide, and tested at 2700F. In this sample, braze alloy did not flow to the edge of the joint. Nevertheless, the excellent throwing power of the coating provided protection of the recess area as evidenced by microhardness data. This base metal-braze alloy-coating system exhibited excellent compatibility. In addition, the coating provided excellent base metal and braze joint protection up to 2700-2840F.

The Ta-10W joints, brazed with Ti-30V and silicide coated, exhibited poor braze alloy coating compatibility as shown in Figure 32. During coating, silicon diffused into the braze joint and reduced the joint melting temperature. During testing, melting occurred at the braze alloy-coating interface resulting in a loss of oxidation protection. Overall test results obtained with this coating indicate the base metal was protected to a maximum brightness temperature of 2800F.

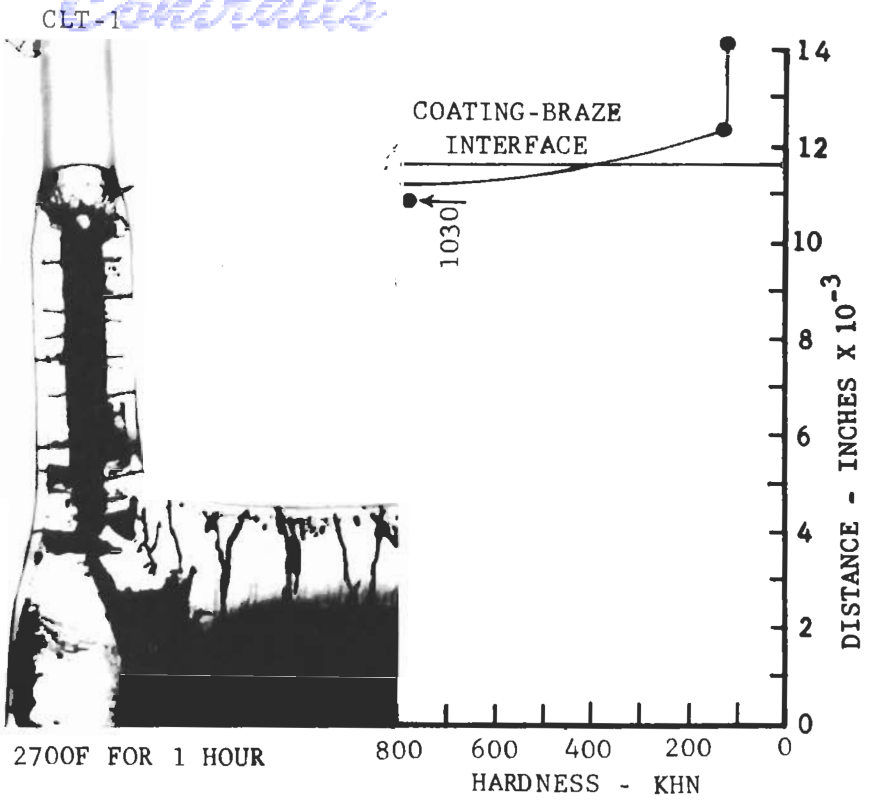
In general, overall results show that braze alloy-coating compatibility is poor. In some cases the braze alloys are compatible with coatings but only at temperatures well below the maximum capability of the coating-base metal system. The major factor causing this compatibility problem is the rapid interdiffusion between braze alloys and coatings which results in the formation of low melting and/or non-protective phases. Therefore, further effort in this area should concentrate on methods for coating exposed braze joints with base metal. This would eliminate the braze alloy-coating compatibility problem and provide greater latitude in braze alloy development. Thus, a coating developed for a base metal would be directly applicable to brazed structures.

Quartz Lamp Brazing of TZM

During this investigation, several closed cell TZM honeycomb panels were brazed by Northrop Norair personnel as part of Contract AF 33(657)-8910. Early in the program, a 6 x 6 x ½ inch honeycomb panel was brazed with edge closures. Braze alloy powder (46Zr-34V-20Ti) was placed on face sheets and faying planes. A fifteen percent addition of Ta sink powder was placed at honeycomb fillet and node areas.

The panel was brazed one minute at 2400F, using the Nortobraze quartz lamp brazing process. The brazing envelope contained a 500 torr argon atmosphere. This experiment showed that (1) braze alloy and diffusion sink powder placement techniques were applicable to manufacturing operations, and (2) lacquer binder could be removed effectively from a closed cell structure by vacuum purging at 600-1200F. The marginal flowability of the braze alloy also was confirmed.

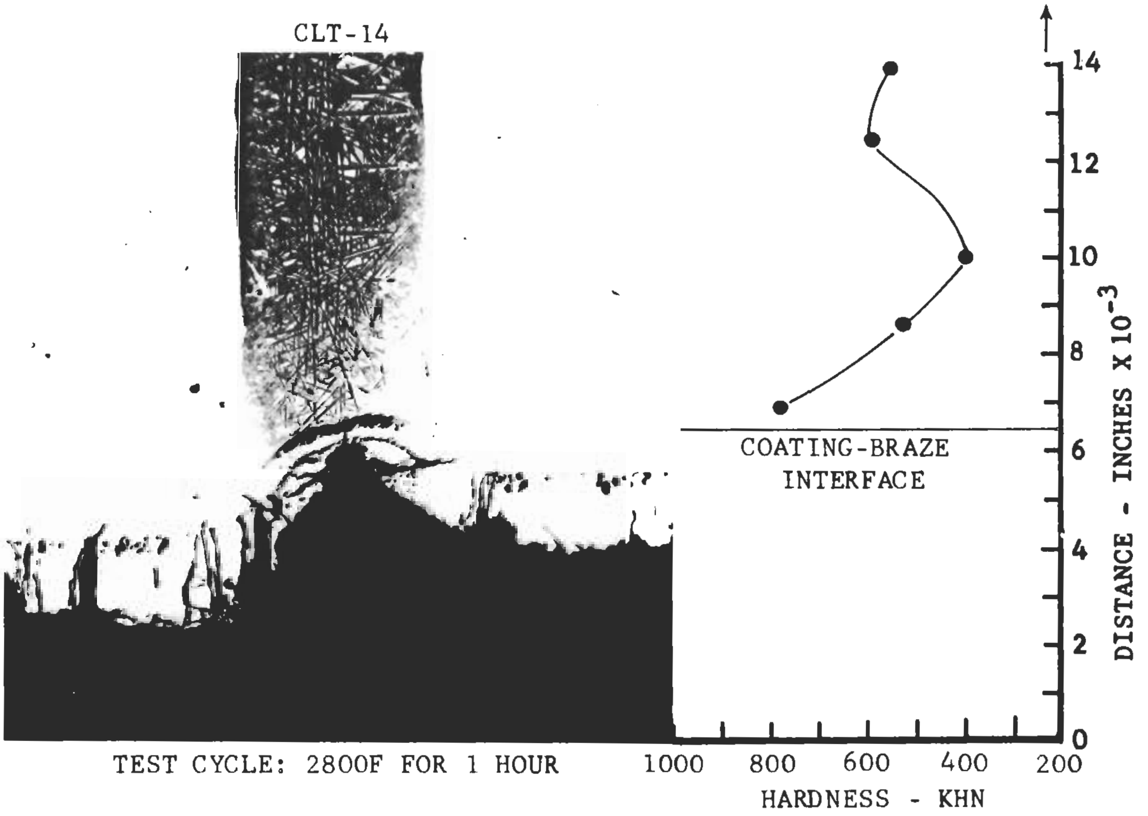
Later, a 6 x 6 x ½ inch TZM honeycomb panel with no edge closures was quartz lamp brazed with Ti-25Cr-13Ni (.22 gm/in^2/face sheet). The panel was brazed one minute at 2250-2300F in a 200 torr argon atmosphere. After the standard diffusion treatment discussed previously, a 2 x 2 inch sample was cut from the center of the panel. This sample exhibited a remelt temperature of 3000F under a 0.3 psi flatwise tensile stress. The remelt temperature was reasonably consistent with previous data obtained on 2 x 2 inch specimens brazed by the quartz lamp method (see Table XII).



TEST CYCLE: 2700F FOR 1 HOUR

MAG. 200X ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE 31 COMPATIBILITY OF UNMODIFIED SILICIDE COATING WITH Cb-1.3B ON Ta-10W



TEST CYCLE: 2800F FOR 1 HOUR

MAG. 200X ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE 32 COMPATIBILITY OF UNMODIFIED SILICIDE COATING WITH Ti-30V ON Ta-10W

As part of Northrop Norair's commitment on this program, a 5 x 5 x ½ inch honeycomb panel shown in Figure 33 was prepared using the Nortobraze quartz lamp process. A corner clip arrangement was employed to provide corner sealing and reinforcement using lap joints amenable to brazing. The purpose of this panel was to evaluate final Ti-25Cr-13Ni brazing parameters and techniques.

In order to maintain thin braze joints (.001 inch max.), it was necessary to feed the corner clips from outside the faying plane. This was accomplished by drilling a total of eight 1/8 inch diameter holes in each clip. These holes were filled with braze alloy which fed the joint by capillary attraction. It would also have been desirable to place braze alloys outside the face sheet to edge-member joints. However, this was not possible because of tooling requirements. Therefore, braze alloy was evenly placed on the faying planes using a .054 gm/in^2 loading. This was equivalent to a 0.006 inch braze alloy thickness. The panel was quartz lamp brazed in vacuum using a braze cycle of one minute at 2300F.

Results obtained on this panel indicate that it is difficult to achieve fit-up tolerances of .001 inch maximum which are required for good remelt temperatures. Thus, some voids were noted in many areas representing lap joint configurations. Additional effort is required to modify the braze alloy and brazing parameters to permit development of high remelt temperature in thicker joints.

Non-Destructive Testing

Several 2 x 2 inch TZM honeycomb specimens brazed with Ti-25Cr-13Ni, and Ta-10W specimens brazed with Ti were X-rayed in the as-brazed condition. Fillets and nodes were not detectable because of the large differences between base metal and braze alloy absorption properties. Similar X-ray results were observed after diffusion treating even though the fillets and nodes contained 30-60 percent base metal. These results indicated that conventional X-ray techniques are not applicable to these braze alloy-base metal combinations.

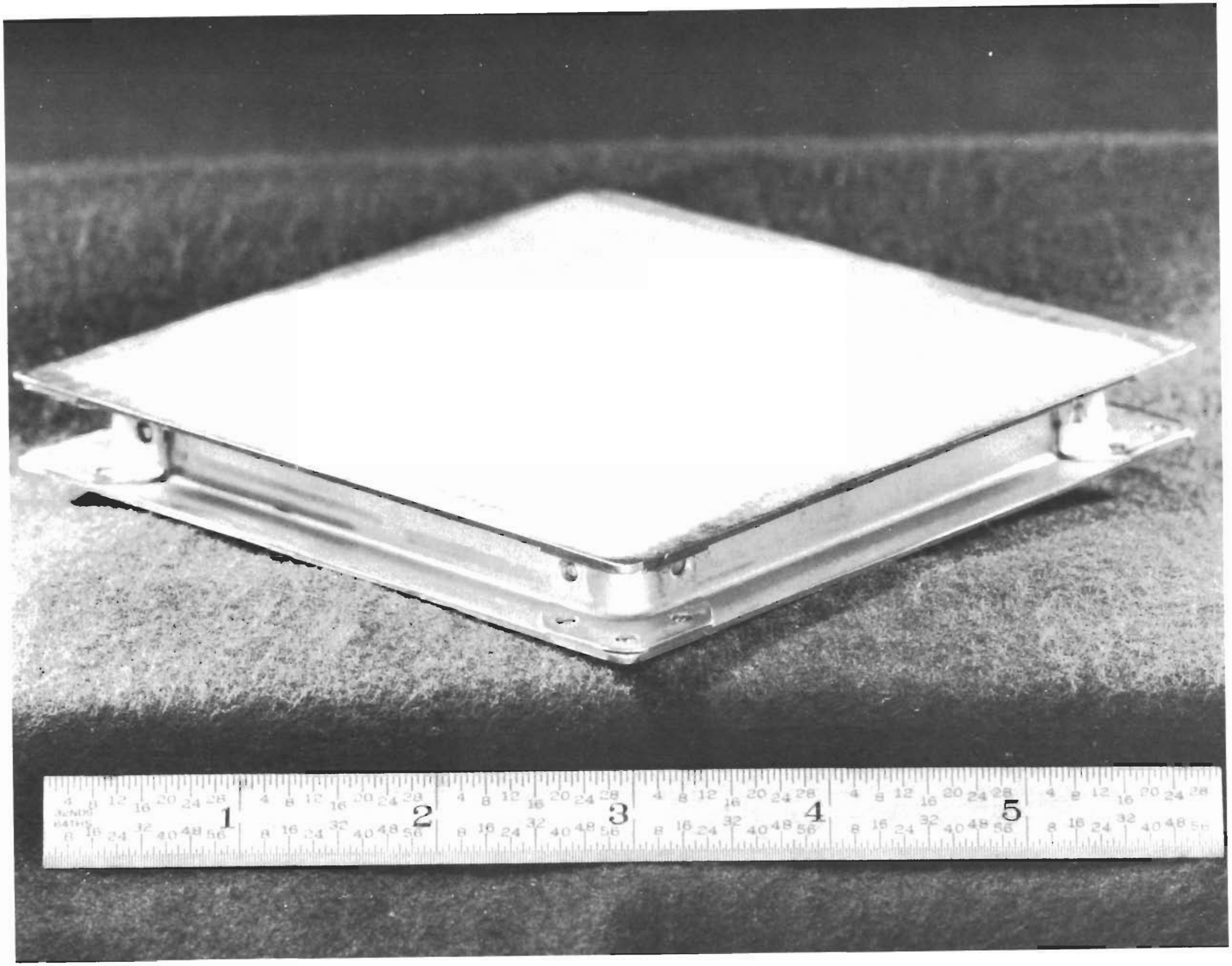


FIGURE 33 TZM HONEYCOMB PANEL BRAZED WITH Ti-25Cr-13Ni

V INTERPRETATION OF RESULTS

There are several approaches for producing high braze joint remelt temperatures in refractory alloys. Diffusion sink brazing was the most promising approach for the specific requirements of this program. Diffusion sink brazing is based on brazing at relatively low temperatures followed by reacting the braze alloy with a diffusion sink powder placed at fillet areas and/or the base metal itself during a subsequent low temperature diffusion treatment. Thus, a new alloy is formed with a high remelt temperature. One of the major advantages of this approach is that systems may be selected so that braze alloy-sink powder-base metal interactions result in solid solution formation, thereby assuring joint ductility.

Although techniques were developed for placing sink powders at fillet and node areas on honeycomb core, the maximum quantities of sink powders attainable by this means were relatively small in terms of the amounts needed to produce desired remelt temperatures. Thus, it was necessary for the base metal to provide a major portion of the total diffusion sink requirement.

Braze system evaluation on Ta-10W and TZM showed that high remelt temperatures were achieved using the base metal alone as the diffusion sink. Any benefits of sink powder additions were largely offset by reduced braze fillet-base metal diffusion rates. This was particularly undesirable in TZM joints since rapid diffusion rates were essential for developing high remelt temperatures within the limited diffusion cycles dictated by recrystallization behavior.

The reduced fillet-base metal diffusion observed in joints containing sink powder is explainable, since the driving force for diffusion is partly dependent upon concentration differences between the fillet and base metal. For example, the Mo concentration difference initially was 100 percent in a TZM joint containing no sink powder. For a similar TZM joint containing 10 percent Mo powder, the initial difference between Mo concentration in the fillet and base metal was only 90 percent. Thus, the rate of fillet-base metal diffusion was reduced in this case.

The fact that sink powders are not required is an advantage from a standpoint of simplified manufacturing procedures. However, the results showed that sink powder additions offer an excellent approach for minimizing erosion effects sometimes encountered in conventional brazing.

TZM MOLYBDENUM

Thermal processing cycles associated with brazing, diffusion treating, and coating are limited by recrystallization and embrittlement behavior of TZM core (foil). These processing exposures must be limited to a total thermal exposure parameter value of approximately 81,500-83,000 based on the parameter $K = T(29 + \log t)$ where T = Rankine temperature and t = time in minutes. Multiple thermal exposures produce more recrystallization than a single thermal exposure at the same parameter value.

Diffusion treatment temperatures should be below the braze alloy solidus to prevent fillet melting and run-off. If the solidus is too low, long impractical diffusion times are required. In such cases the length of time may be reduced somewhat by using a "stepped" diffusion treatment whereby temperature is gradually increased as diffusion progresses. If the braze alloy solidus is too high, then high braze temperatures are required which produce recrystallization or insufficient remaining thermal exposure for diffusion treatment. Consideration of these factors indicates that the braze alloy solidus should be above 2050F with a braze temperature within the 2200-2300F range. The thermal exposure parameter shows that optimum post-braze diffusion treatments may be based on long times at low temperatures rather than short times at higher temperatures. The former type of treatment offers the advantage of less base metal recrystallization for a given amount of braze alloy-base metal diffusion.

Alloys in the Zr-V-Ti, Ti-Ni-Si, and Ti-Cr-Ni systems were evaluated for diffusion sink brazing of TZM. Of these the Ti-25Cr-13Ni diffusion sink braze system was clearly the most promising. An optimum diffusion treatment compatible with foil recrystallization behavior was developed.

The evaluation of braze alloys for TZM included the utilization of tee joints, lap joints, 1 x 1 inch honeycomb and 2 x 2 inch honeycomb samples. The remelt and strength results obtained from these various specimens did not agree, indicating that the results were specimen geometry sensitive. This sensitivity came about from two main factors; namely, one, volatilization of braze alloy constituents and two, joint thickness. Both of these factors had an influence on the amount and distribution of a deleterious secondary phase, Ti_2Ni, formed during brazing and diffusion. High strengths and remelts were achieved in tee joints where volatilization of the braze alloy had occurred from the fillet regions. High strengths and remelts were achieved in lap joints when joint thicknesses were 1 mil or less. The strength and remelt temperatures achieved in honeycomb configurations were governed by fit-up mainly, since little evaporation of the braze alloy could occur in the closed cell honeycomb at these temperatures. The excellent fit-up achieved in the Nortobraze quartz lamp brazing manufacturing process was responsible for the superior honeycomb panels produced by this means compared to laboratory made specimens.

Brazing procedures and techniques were verified by fabrication of a completely ductile, typical, 5 x 5 x 1/2 inch honeycomb panel configuration complete with edge closures. This panel brazed at 2250-2300F will exhibit a remelt temperature in excess of 3000F. Procedures developed in the laboratory were found applicable to manufacturing operations with one exception. The .001 inch maximum braze joint thickness was difficult to maintain on lap joints such as face sheet to edgemember joints.

Thus, diffusion sink brazing has been found highly applicable to TZM. However, additional optimization effort is required in the following areas:

(1) Develop greater joint thickness tolerances.
(2) Develop greater high temperature strength.

TANTALUM ALLOYS

Since the tantalum alloys considered in this program do not exhibit embrittlement upon recrystallization, conventional as well as diffusion sink brazing approaches were utilized. The conventional brazing approach led to the development of a high melting point braze alloy (Cb-1.3B) that resulted in honeycomb panels of good ductility and high strength.

Diffusion sink brazing was successfully demonstrated. Using this technique maximum brazing temperatures were at least 1000F lower than required for conventional brazing. The braze alloys employed were (1) Ti, (2) Ti-30V, and (3) 33Zr-34Ti-33V. High strength (2160-4270 psi) and remelt temperatures(3300-4200F) were achieved. However, an improvement in the ductility of the core is desirable.

All honeycomb specimens produced by diffusion sink brazing exhibited significant embrittlement of the core in the as-diffusion treated condition. During diffusion treatment, braze alloy volatilized within the cells and deposited on the foil. This deposit preferentially diffused along the grain boundaries of the foil. Embrittlement occurred in spite of the fact that a relatively soft solid solution zone was formed. Limited data also showed that reduced diffusion temperatures markedly reduce foil embrittlement caused by this mechanism. Additional effort is required to alleviate this problem by optimization of the diffusion treatment and/or reducing braze alloy vapor pressure by alloying.

The diffusion treated Ti and Ti-30V joints were essentially single phase, ductile solid solutions. However, honeycomb fillets exhibited high hardnesses and a two-phase structure. Additional effort is required to determine the reasons for this anomaly and to correct the problem.

COATING COMPATIBILITY

Overall results on TZM and Ta-10W show that braze alloy-coating compatibility is poor. In some cases the braze alloys are compatible with coatings, but only at temperatures well below maximum capability of the coating-base metal systems. The only exception to this observation is the Cb-1.3B braze alloy coated with an unmodified silicide.

The major factors causing this incompatibility problem are (1) rapid interdiffusion between braze alloys and coatings and (2) the coating-braze alloy interaction generally results in low melting, non-protective reaction products.

VI CONCLUSIONS

MOLYBDENUM-TZM

1. Diffusion sink brazing with a Ti-25Cr-13Ni braze alloy (braze temperature 2250-2300F) permitted brazing below the recrystallization temperature of TZM. Remelt temperatures exceeding 3100F were attained on tee and lap joints.

2. Brazing techniques and the Ti-25Cr-13Ni braze alloy were applicable to brazing of closed cell honeycomb. Remelt temperatures as high as 3180F were achieved.

3. The Ti-25Cr-13Ni braze alloy exhibited poor compatibility with a modified silicide coating both in the as-coated condition and following oxidation tests.

4. Manufacturing applicability of the Ti-25Cr-13Ni braze alloy and brazing techniques was demonstrated using the Nortobraze quartz lamp brazing process. Optimum results were attained by maintaining joint thickness at .001 inch or less.

TANTALUM ALLOYS - Ta-10W, Ta-8W-2Hf, Ta-30Cb-7.5V

1. Diffusion sink brazing with Ti and Ti-30V (braze temperature 3050-3200F) produced remelt temperatures exceeding 3800F on tee and lap joints. Diffusion sink brazing with 33Zr-34Ti-33V (braze temperature 2600F) produced remelt temperatures exceeding 3200F.

2. Braze alloys and techniques developed were applicable to brazing closed cell honeycomb panels which withstood a one-hour exposure at 3500F under a flatwise tensile stress of 1.2 psi.

3. A Cb-1.3B braze alloy showed excellent potential for conventional brazing of closed cell honeycomb panels in vacuum or argon. Brazed honeycomb specimens loaded to a 1.2 psi flatwise tensile stress withstood a one-hour exposure at 3500F with no failure.

4. The Cb—1.3B braze alloy exhibited good coating compatibility with an unmodified silicide coating. Other braze alloy coating combinations exhibited relatively poor compatibility.

VII REFERENCES

1. Hugill, D. B., et al, Quartz Lamp Radiant Heat Brazing of Large Refractory Metal Honeycomb Sandwich Panels, ASD IR-7-937a (IV), 10 April 1963 - 10 July 1963, AF 33(657)-8910, (Northrop Corp., Norair Division, Hawthorne, California)

2. McCown, J. W., et al, Manufacturing Methods and Design Procedures for Brazed Refractory Metal Honeycomb Sandwich Panels, ASD TDR 62-937 (I, II, III), November 1961 - September 1962, AF 33(657)-7276, (Martin Marietta Corp., Baltimore, Maryland)

3. Stone, L. H., Freedman, A. H., Mikus, E. B., Brazing of Thin Gage Rene' 41 Honeycomb, Welding Journal, September 1963, pp. 397-s to 403-s

4. English, J. J., Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten, DMIC Report 152, 28 April 1961, (Battelle Memorial Institute, Columbus, Ohio)

5. Young, W. R., Alloy Systems for Brazing of Columbium and Tungsten, ASD TR 61-592, January 1962, AF 33(616)-7484, (General Electric Co., Evandale, Cincinnati, Ohio)

APPENDIX A

LITERATURE SURVEY

APPENDIX A
LITERATURE SURVEY

Literature surveys were conducted through the Defense Metals Information Center and the Defense Documentation Center. The subjects searched included brazing approaches and techniques, refractory alloy brazing, oxidation protective coatings for molybdenum and tantalum, and phase diagrams of potential braze systems.

Brazing of refractory alloys for high temperature service, and protective coating of tantalum were found to be in relatively early stages of development; only limited information was available. The following discussion is a summary and analysis of the available information as it applied to this program at its inception.

MOLYBDENUM BRAZING

Thermal Fmbrittlement

It is well known that molybdenum alloys can be seriously embrittled by thermal exposures which produce recrystallization.[1] Therefore, a brazing study on molybdenum must consider the effects of brazing thermal exposures on recrystallization and embrittlement behavior.

Recent studies have shown that the recrystallization temperature ranges for .011 inch and .002 inch Mo-.5Ti-.08Zr (TZM) are approximately 2400F-2700F and 2100F - 2500F, respectively, for a six minute exposure at temperature.[2,3] The lower recrystallization resistance of the .002 inch foil could be the controlling factor in establishing a maximum brazing temperature for TZM honeycomb structures.

The same investigations also showed that recrystallization per se did not cause severe embrittlement of .011 inch TZM and .010 inch Mo-.5Ti. Small amounts of recrystallization (5-15 percent) produced a slight degree of embrittlement based on bend transition temperature data. Increasing amounts of recrystallization up to at least 80 percent produced no additional embrittlement. However, once recrystallization was essentially completed and substantial grain growth occurred, severe embrittlement was observed. Bend test data indicated that recrystallized .002 inch TZM foil possessed substantially better bend ductility than .011 inch TZM sheet in the same condition. This may have resulted from the higher degree of biaxiality for the sheet versus foil.

These observations suggested several practical implications. First, brazing cycles which produce recrystallization, but no appreciable grain growth, may be tolerable with respect to ductility. Secondly, it may be possible to base brazing cycles on the higher recrystallization behavior of the TZM sheet rather than the foil and still maintain adequate ductility. Both of these factors permitted brazing temperatures as high as 2400F rather than 2100F based on a criterion of 0 percent maximum recrystallization of the foil.

It was shown that a Larson-Miller type time-temperature parameter can accurately predict recrystallization behavior of TZM sheet exposed to a wide range of single thermal exposures.[3] In addition, the parameter can be used to predict recrystallization behavior for multiple exposures at a single temperature. However, double thermal exposures using two different times and temperatures produce a greater amount of recrystallization than predicted by the parameter. A correction factor applied to the parameter was found to provide an approximate correlation between recrystallization behavior and such multiple thermal exposures.

The above approach was used to establish maximum allowable brazing temperatures, since the time-temperature parameter can be used to establish the maximum allowable thermal exposure for all thermal cycles required in the brazing fabrication process. The post braze thermal cycles could include a diffusion heat treatment and an oxidation protective coating cycle.

Taking into account probable post braze thermal cycles, it appeared that a one-minute braze cycle at temperatures to 2400F could be employed for brazing TZM honeycomb panels. This braze cycle, together with post braze thermal cycle, should be compatible with a satisfactory level of panel ductility.

Conventional Brazing

A number of investigations[2,4,5,6,7,8,9] have studied the use of precious metals, iron, nickel, and cobalt alloys for brazing molybdenum. These fillers have been considered for conventional brazing as well as for approaches aimed at increased joint remelt temperatures. Conventional brazing is defined as brazing with a filler possessing a solidus temperature at least 200F above the intended service temperature.

The reported applicability of these systems varied from good to poor. Phase diagram relationships indicated that most of these systems formed brittle intermetallic compounds and/or low melting phases with molybdenum at the filler-base metal interfaces. Thus, one would expect these systems to exhibit poor compatibility with molybdenum. However, in some cases the as-brazed joints were reported to be ductile. This may have resulted from rapid braze cycles which minimized base metal-braze alloy interaction. Regardless of this, actual applications of these joints would require a protective coating cycle followed by a service cycle. During these thermal exposures base metal-filler diffusion could occur to form the brittle or low melting phases predicted from phase diagrams.

Feinstein[7] studied the effects of elevated temperature diffusion treatments on molybdenum joints brazed with Au-17.5Ni. It was found that the diffusion treatments produced a Au-Ni-Mo intermetallic compound which reduced room temperature strength, presumably by joint embrittlement. McCown et al[9] reported that TZM joints brazed with a cobalt base alloy (Haynes 25) were embrittled by subsequent thermal exposures.

Young and Jones[10] studied solid state diffusion bonded joints between Mo-.5Ti and iron, nickel, and cobalt base alloys. Diffusion treatments resulted in intermetallic compound formation at the joint interfaces. The brittleness of the intermetallic zone was clearly indicated by the high interface microhardness data reported. Thus, the studies confirmed that iron, nickel, and cobalt-base alloys were not promising braze fillers for molybdenum.

Conventional brazing of molybdenum alloys has been investigated using higher temperature fillers which brazed in the 2900F - 3200F range.[2,9,10] The fillers were basically titanium alloys which were compatible with molybdenum based on phase diagram relationships. These alloys formed ductile joints but the high brazing temperatures recrystallized and embrittled the base material. Thus, use of titanium alloys eliminated the braze alloy-base metal compatibility problem but substituted a recrystallization and embrittlement problem.

It appears that conventional brazing temperatures could be increased by using very short braze cycles. However, it is impractical to consider braze cycles of less than one minute at temperature. When the time-temperature parameter is used to determine the temperature that would produce 100 percent recrystallization of TZM during a one-minute braze cycle, a temperature of 2700F for .011 inch TZM sheet and 2550F for .002 inch TZM foil was calculated. Thus, rapid cycle conventional brazing offered no promise for producing ductile TZM honeycomb panels for 3000F service.

High Remelt Temperature Brazing

Effective utilization of molybdenum brazements to 3000F requires the development of braze alloys which braze below the recrystallization temperature, but develop high remelt temperatures. This approach would retain base metal ductility in the as-fabricated condition and still permit high service temperatures.

"Diffusion sink" brazing is an approach for increasing braze joint remelt temperatures which has received some study. This concept involves the reaction of a braze alloy with the base material and/or refractory metal powder additions after proper filleting and flow have occurred. The reaction takes place during the braze cycle or during a post braze diffusion treatment at a lower temperature. The diffusion reaction results in a new alloy in the joint with a higher melting temperature.

McCown, et al[9] investigated an 80(Ti-8.5Si) -20 molybdenum powder diffusion sink braze system for TZM. This system required a braze temperature of 2550F followed by a three hour diffusion treatment at 2200F. Joint remelt temperatures from 2950 to 3150F were reported on .010 inch gage tee joints lightly loaded to 2-6 psi tension on the legs of the tees. The data also showed the remelt temperature to decrease with increased joint loading. The braze joints were reported to be ductile, but the 2550F braze temperature was observed to be somewhat high from the standpoint of base metal recrystallization. In another investigation of the Ti-8.5Si alloy[11] it was concluded that the 2550F braze temperature of this alloy resulted in recrystallization of the TZM. This study raised some questions regarding the ductility of the alloy as well.

Hugill, et al[12] investigated a Ti-13.5Cr-8.5Si alloy, which was reported to possess excellent potential for brazing TZM.[9] Tee joints were brazed with the braze alloy alone and with a columbium powder diffusion sink addition. The braze alloy melted at approximately 2380F and exhibited good filleting and flow at 2450F. The columbium diffusion sink and a diffusion treatment of one hour at 2200F produced relatively mild increase in remelt temperature. This may have resulted from limited diffusion reactions produced by the diffusion treatment employed.

The most important conclusions of this work were that the braze alloy exhibited marginal ductility and the columbium powder additions did not improve ductility. In addition, the diffusion treatment produced a significant increase in the microhardness of the braze alloy and presumably a decrease in ductility.

A "reactive brazing" concept has been considered for producing high remelt temperatures on refractory alloy brazements[13]. Reactive brazing is based on using a braze alloy containing a strong melting temperature depressant. The depressant is selected to react with the base material or powder additions to form a high melting intermetallic compound during a post-braze diffusion treatment. By removing the depressant in this manner, the joint remelt temperature is increased. As an example of this approach, an alloy designated RGN-15 (Zr-21Cb-4Be) was used to braze .006 inch TZM tee joints at 2150F.[11] A subsequent five hour diffusion treatment at 2200F produced a remelt temperature of 2980F with a 1000 psi stress on the base material. The joints were reported to be ductile at room temperature based on bending the .006 inch leg of the tee at some distance from the fillet. This test produced substantial deformation of the base material but little deformation of the joint.

A reactive Pt-B braze system for brazing tungsten was reported to produce lap joint remelt temperatures approaching 4000F under a 21.5 psi shear stress.[14] This system appeared to offer promise for brazing molybdenum; however, McCown, et al[9] evaluated the alloy on TZM tee joints and found it extremely brittle in the as-brazed condition.

The concept of reactive brazing offers potential for increasing joint remelt temperatures. Successful application of this concept appears highly dependent upon controlling the intermetallic compound reaction to form discrete particles. If continuous intermetallic compound films are present in the grain boundaries or along the base metal-fillet interfaces, joint ductility would be seriously impaired.

TANTALUM BRAZING

Thermal Embrittlement

Available information[15,16,17] indicated that tantalum alloys are not severely embrittled by recrystallization and grain growth. This behavior is in sharp contrast to that reported for molybdenum alloys. Thus, there appears to be no metallurgical reason why tantalum alloys could not be brazed at temperatures approaching 4000F to obtain service to 3500F. However, brazing temperatures in excess of 3200F would present severe manufacturing and equipment problems. Therefore, brazing to obtain high remelt temperatures, as well as conventional brazing, was considered highly desirable.

Conventional Brazing

Very little information was reported on brazing tantalum alloys for high temperature service. Young and Jones[10,18], concentrated primarily on development of conventional braze alloys for columbium and tungsten. Some of these systems appeared applicable to tantalum brazing. The V-35Cb and Ti-30V braze alloys developed for columbium were used to braze Ta-30Cb-5V joints. Excellent filleting and flow were reported and it was concluded that these alloys offered potential for tantalum brazing.

In the same investigations several columbium-base alloys were identified for conventional brazing of tungsten for service to 3500F. Of these, a Cb-2.2B alloy appeared to offer excellent potential for conventional brazing of tantalum alloys for 3500F service.

The filleting and flow properties of several potential braze alloys were determined on pure tantalum tee joints.[19] No significant differences in braze alloy behavior were noted between vacuum or argon brazing atmospheres. Pure titanium and Ti-30V exhibited poor filleting and flow. A Ti-13V-11Cr-3Al alloy exhibited fair filleting and flow while excellent results were observed with Ti-30Cr and V-20Ti.

High Remelt Temperature Brazing

No references were found on brazing of tantalum to develop high remelt temperatures. However, the diffusion sink and reactive brazing concepts discussed for molybdenum are applicable to tantalum alloys as well.

OTHER BRAZING APPROACHES

Investigations were conducted on systems that develop high remelt temperatures by evaporation of a volatile melting temperature depressant from the braze alloy.[20,21] This work was conducted using nickel-base braze alloys but the concept is applicable to brazing in general. The approach offers excellent potential but is subject to joint geometry limitations. Since closed cell honeycomb structures were used in this program, the volatile element concept was not pursued.

An exothermic brazing approach is under investigation for brazing refractory alloys at temperatures up to 3100F.[22] This concept is actually a conventional brazing approach using an exothermic reaction as the heat source rather than conventional heating equipment. The process offers distinct advantages from the equipment standpoint. However, it also poses a serious problem with regard to temperature control. This problem complicated the development of braze systems on this program and therefore exothermic brazing was not utilized.

OXIDATION PROTECTIVE COATINGS

Oxidation protective coatings for brazed molybdenum and tantalum joints should be compatible with the braze joints as well as the base materials. A recent summary of coating research effort[23] indicates that little attention has been directed to this area. This gap in fundamental information has made it difficult to consider coating compatibility as one parameter of braze alloy development. Estimates of braze alloy-coating compatibility should be possible from phase diagram and thermodynamic data.

Molybdenum Coating

Numerous studies have been devoted to development of coatings for molybdenum. Most of the coatings interacted with the base material. Therefore, substrate thickness below .020 - .030 inch becomes an important variable where thin gage TZM honeycomb structures are involved.

An investigation is presently in progress to determine applicability of available coatings to .006 inch TZM foils.[24] A number of coatings are being screened and the following coatings have been found to offer promise for advanced evaluation.

1. Chance Vought - 2 cycle Si-(Cr+B), pack cementation
2. General Telephone and Electronics - 70Sn-25Al-5Mo, spray and sinter coating
3. Pfaudler - PRF-6, pack cementation
4. Chromalloy - W-3, pack cementation

The results of this evaluation provided a good basis for TZM coating selection.

Hugill, et al[12] found that several titanium-base braze alloys for TZM were not compatible with the Pfaudler PRF-6 coating. The braze alloys were attacked during the coating cycle. Subsequent oxidation tests in air showed the coating to provide little protection to the braze alloys. This limited data suggested that titanium-base braze alloys, in general, may not be compatible with silicide coatings.

Tantalum Coating

At present only two coatings have received concentrated attention for tantalum protection. These are the Sn-Al type[25,26] and the silicide type[27]. The Sn-Al type coating appears to be useful to approximately 3400F in air. Maximum useful temperature decreases in rarified air atmospheres due to coating evaporation. Columbium and vanadium-containing tantalum alloys were found to be compatible with the coating. Alloying elements which form oxides thermodynamically more stable than Al_2O_3 are detrimental to oxidation resistance in amounts greater than 5-10 percent.

Zirconium and hafnium are prime examples.

The silicide type coating appears to be useful to approximately 3000F in air. Composition of the substrate significantly affects coating performance. Tungsten, molybdenum, and vanadium improve the oxidation protection at high temperatures. Vanadium is particularly effective in enhancing low and high temperature oxidation protection. Hafnium appears to be somewhat detrimental to coating behavior.

No information was available on braze alloy-coating compatibility. Nevertheless, the data on effects of base metal alloying elements on coating performance provided a basis for estimating possible braze alloy-coating interactions.

PHASE DIAGRAM DATA

Molybdenum braze Systems

Four compilations were found to contain most of the available phase diagrams of interest[28,29,30,31]. These data showed that W, Ta, Cb, Cr, V and Ti are compatible with molybdenum based on a criterion of complete solid solubility. However, the melting temperatures of W, Ta, and Cb are too high to consider them as braze alloy matrices. The brittle behavior of chromium precluded its consideration as a braze alloy matrix. Titanium and vanadium are the most promising braze alloy matrices with titanium offering the greatest potential for the following reasons:

1. Titanium exhibits a lower melting temperature than vanadium.
2. More phase diagram data is available for titanium systems than vanadium systems.
3. The melting temperature of titanium can be more easily depressed to the desired 2000F - 2300F range.

Since titanium melts at 3050F, it was necessary to reduce the melting temperature by alloying. The most potent melting temperature depressants for titanium are Fe, Ni, Co, Cu, Mn, Si, Cr, Zr, and Be. Very limited data were available on the Ti - Be system. With the exception of Cr, these solute elements exhibit limited solid solubility in molybdenum. No elements were found which are both compatible with molybdenum and able to depress the melting temperature of titanium to the desired range. Consequently, the formulation of titanium-base braze alloys requires a consideration and balance between the following factors:

1. The quantity of depressant required to obtain the desired melting temperature.
2. The influence of the depressant on braze alloy ductility.
3. Phase relationships in the Ti - depressant (s) - Mo system with respect to intermetallic compound and low melting phase formation.
4. The influence of diffusion sinks on phase relationships, ductility and melting temperature of the braze alloy-base metal - diffusion sink system.

From phase diagram data[28] it appeared that binary alloys of titanium containing Fe, Ni, Co, Cu, Mn, and possibly Be could be formulated to melt within the desired range. However, relatively large solute additions were required. These additions could seriously reduce ductility.

An investigation of Ti - Fe alloys indicated that iron levels well below those required to reach the desired melting range produced serious embrittlement.[32]

Several alloys from the Ti-Fe-Mn system were also evaluated. Alloy selection was based on the liquidus data of Murakami, et al.[33] It was found that alloys which melted within the desired temperature range were very brittle. The embrittling effects of Mn and Fe were quite similar. Therefore, the Ti-Fe and Ti-Fe-Mn systems offer limited potential as braze alloys.

The influence of Co, Ni, and Cu on ductility of titanium is not known at the levels of interest. Of these elements, Cu appears least promising because it is not as strong a melting temperature depressant as Co and Ni. Therefore, the Ti-Co-Cr and Ti-Ni-Cr systems offer potential because a portion of the Co and Ni could be replaced with Cr which is compatible with molybdenum. Liquidus isotherms in the Ti-Cr-Ni system have been developed as shown in Figure A1. It seems reasonable to assume that the form of the liquidus isotherms for the Ti-Cr-Co system are quite similar.

The Ti-Cr-Fe system appeared to offer potential as a braze alloy if the Fe content can be held at low levels to minimize embrittlement. Some available data on solidus temperatures in the Ti-Cr-Fe system[34] offered a basis for alloy formation.

Data have been reported on liquidus isotherms for the Ti-Cr-Mo system.[35] The data indicate that a Ti-Cr braze alloy offers excellent remelt potential using the diffusion sink brazing approach with molybdenum as the sink. However, the minimum melting temperature of alloys in the Ti-Cr system is approximately 2550F.

A Ti-13.5Cr-8.5Si alloy has been suggested for brazing TZM.[9] The liquidus temperature of the alloy is approximately 2400F. An estimate of the liquidus temperatures in the Ti-Cr-Si system indicates that approximately 2400F is the minimum melting temperature of potential alloys. Substitution of Ni for Cr in this system offers potential for lower melting alloys. The estimated liquidus temperatures for the Ti-rich corner of the Ti-Ni-Si system are shown in Figure A2.

Binary phase diagrams indicated that nickel is a potent melting temperature depressant for both titanium and zirconium. In addition, titanium and zirconium are compatible. Therefore, the Ti-Zr-Ni system appeared attractive from the standpoint of melting temperature and ductility.

A Ti-48Zr-4Be alloy was evaluated as a braze alloy for TZM.[9] This system was noted to be extremely brittle. Since the alloying behavior of Be with Zr and Ti is similar, it appears that the lack of ductility would extend to Ti-Be alloys. It is estimated that a minimum of 2 percent Be is required to depress the melting temperature of titanium to the desired range. Alloy ductility at this beryllium level is highly questionable.

Solid state phase relationships in the Ti-Zr-V system were investigated.[36] Further studies determined the ductility and melting temperatures of a number of alloys in this system.[10] These data were employed to estimate the liquidus isotherms shown in Figure A3. This system appeared very attractive in that a wide range of melting temperatures was possible.

Zirconium exhibits limited solubility in molybdenum and a $ZrMo_2$ intermetallic compound. Limited data on the Mo-Ti-Zr phase diagram[31] show that Ti suppresses formation of $ZrMo_2$. Therefore consideration of a Ti-Zr-V braze alloy for TZM appeared justified. However, the alloy must be formulated with the lowest Zr content and highest Ti content consistent with melting temperature requirements.

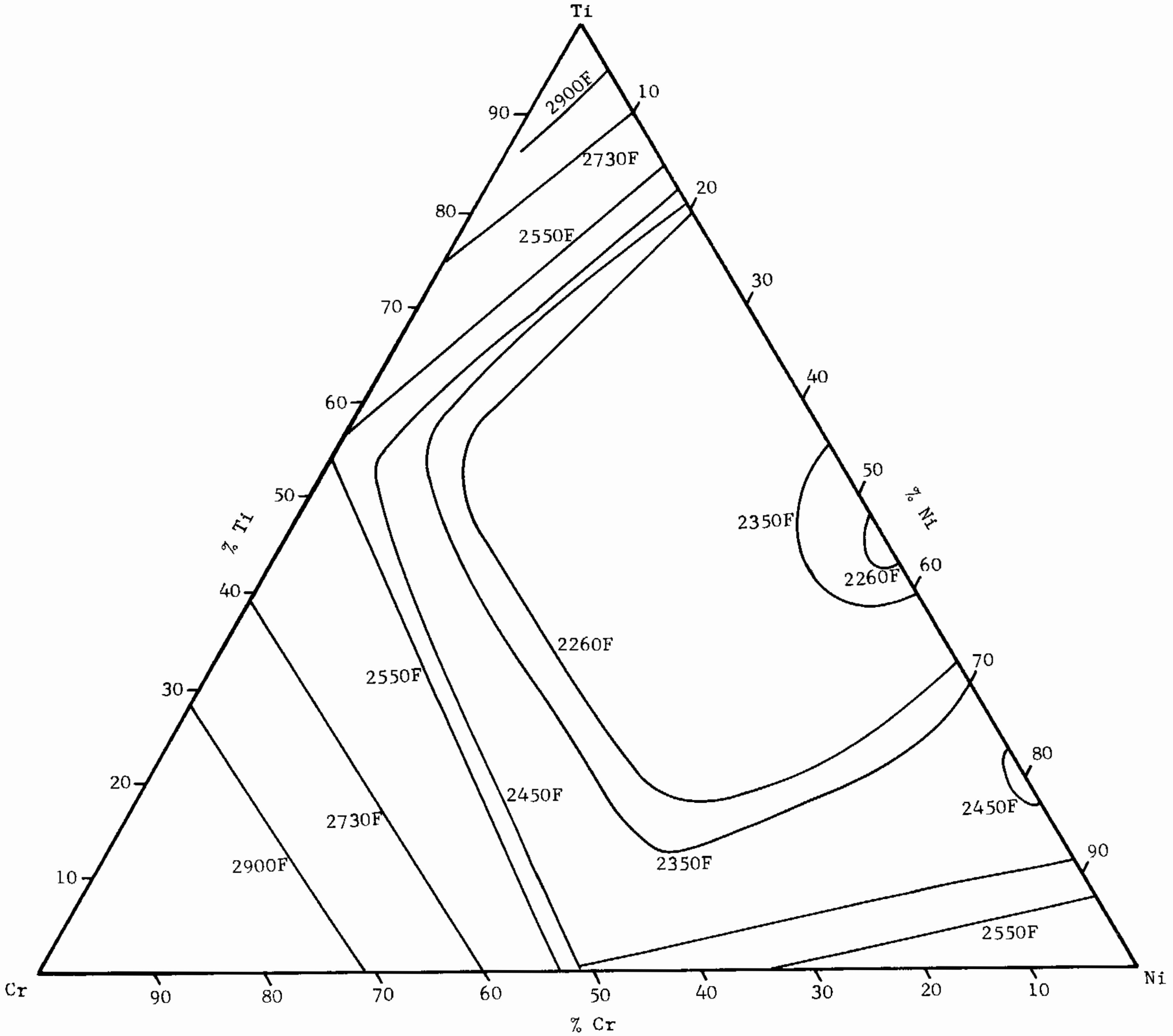


FIGURE A1 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-Cr-Ni SYSTEM

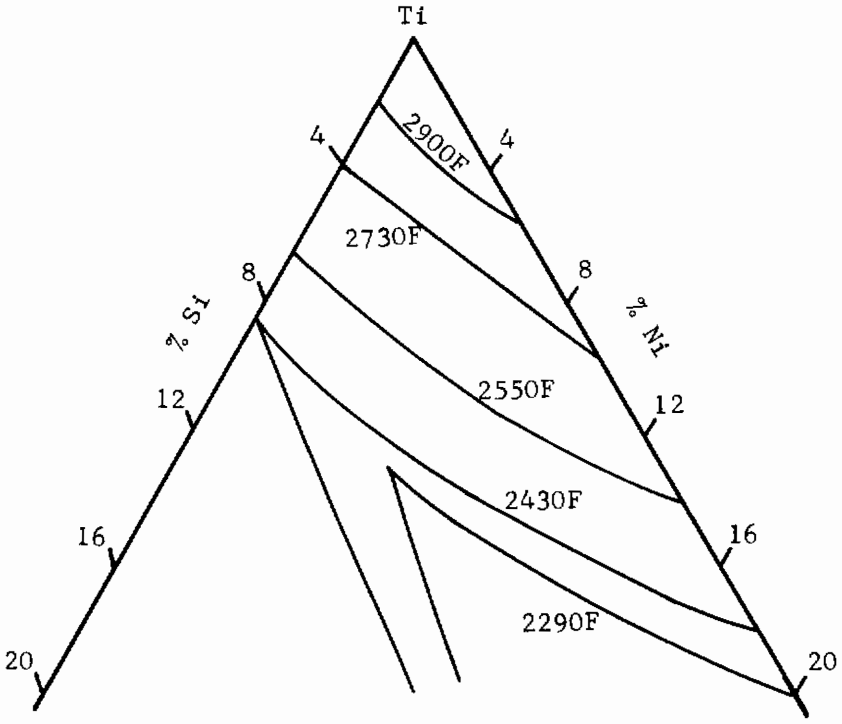


FIGURE A2 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-RICH CORNER OF THE Ti-Ni-Si SYSTEM

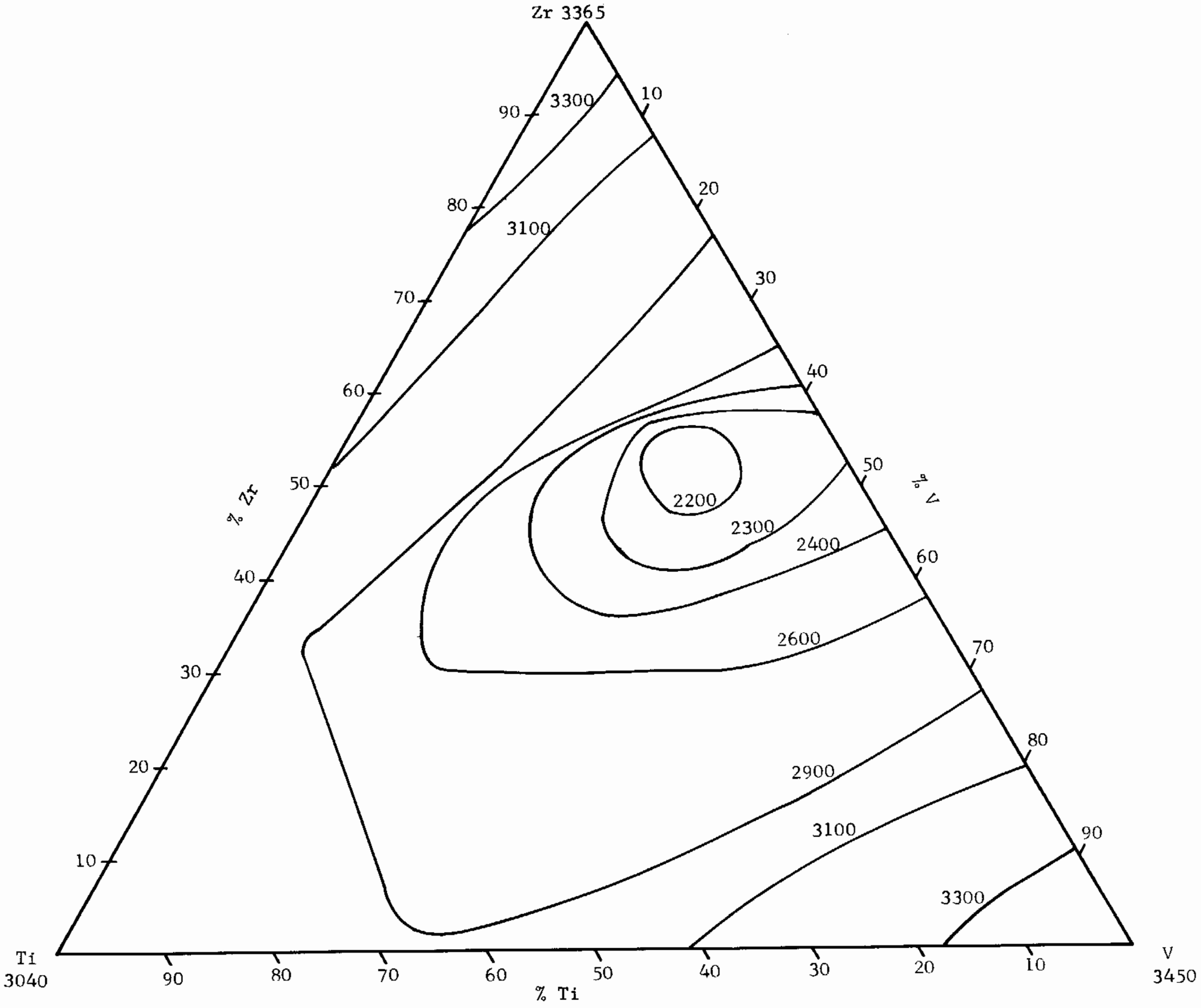


FIGURE A3 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr SYSTEM

The Ti-V-Zr system offered possibilities for reactive brazing. The phase diagram of Figure A3 shows that if Zr and/or V can be preferentially removed from the alloy, the liquidus temperature will be increased. These elements all show a high negative free energy of formation for high melting carbides and borides. If there are distinct differences in reaction rates, it may be possible to selectively form Zr and V compounds in preference to Ti compounds.

Incorporating the boron and/or carbon powders in the diffusion sink powder offered an attractive approach for adding these elements. This should result in formation of discrete boride and/or carbide particles rather than continuous films.

Limited data on melting temperatures and ductility of Zr-V-Cb alloys was reported.[10] This alloy system offered some promise for developing TZM braze alloys.

Selection of optimum diffusion sinks for the above mentioned braze alloy systems required consideration of the following points.

1. Metallurgical compatibility of the diffusion sink with the base material and braze alloy.
2. Potential remelt temperature increase.
3. The quantity of diffusion sink powder that could be placed at fillet areas without inhibiting braze alloy filleting and flow.

The most logical diffusion sinks for the above systems are the refractory metals W, Ta, Cb, and Mo. All of these elements are compatible with Mo. However, W can be eliminated because of its brittle behavior and lack of compatibility with titanium. Tantalum is promising because it exhibits a high melting temperature, good ductility and high density. High density is advantageous in permitting larger sink additions to the fillets on a weight percentage basis.

The Ta, Mo, and Cb binary phase diagrams with titanium indicate that Ta and Mo offered the greatest potential for increasing the remelt temperature of pure Ti. However, it is difficult to predict remelt potential and phase relationships in the multi-component systems represented by the braze alloy-diffusion sink systems. A major unknown was the quantity of diffusion sink powder that can be placed at fillets without impeding braze alloy flow. In view of these complex considerations it appeared that selection of optimum diffusion sinks required detailed experimental effort.

Tantalum Braze Systems

Phase diagram data[28,29,30,31] show that W, Mo, and Cb are compatible with Ta based on a criterion of complete solid solubility. The elements Ti, V, Zr, and Hf are compatible with Ta at high temperatures but the systems show solid state transformations over broad composition ranges at lower temperatures. The transformation in the Ti-Ta system is the allotropic titanium transformation which is not expected to cause embrittlement. However, the transformations in the V, Zr, and Hf binaries with Ta could cause embrittlement. It has been reported[18] that a Zr-34 Ta alloy is brittle in the as-cast condition.

The elements W, Ta, Mo, Cb, and Hf appear applicable as conventional braze alloy matrices for 3500F service. However, W and Mo was eliminated because of their limited ductility. Hafnium was eliminated because it is not compatible with tantalum coatings. Thus Cb and Ta offered the greatest potential as braze alloy matrices.

A review of phase diagram data indicated that Ti and V are the most promising melting temperature depressants for Cb and Ta. It was reported that Ta-base alloys with Ti and V are somewhat difficult to arc-melt due to excessive volatilization of the solute elements.[10] Since Cb melts at a much lower temperature than Ta, Cb-base alloys with Ti and V appeared more promising. In addition, some data was available on ductility and melting temperatures of these alloy systems.[10]

The Ta-B and Cb-B systems also appeared promising for conventional brazing. The published phase diagram for the Cb-B system[30] shows a eutectic at approximately 2950F and 2.2 percent B. Data by Young and Jones[10] indicate that the eutectic temperature is approximately 3800F - 4000F. It was also noted that Cb-B alloys containing up to 2.2 percent B are ductile. If this data is correct, the Cb-B system offers promise for conventional brazing.

The published Ta-B phase diagram[30] shows a eutectic at approximately 3300F and 1.3 percent B. One would expect the Ta-B eutectic to melt at a higher temperature than the Cb-B eutectic. Therefore, if the data on the Cb-B system by Young and Jones are correct, the accuracy of the Ta-B phase diagram may be questionable. It appeared that some experimental evaluation of these systems was necessary to establish melting temperatures. If the melting temperature is above 3700F, the systems offered excellent potential for conventional brazing. If the temperatures reported in the published phase diagrams are correct, these systems may offer promise for diffusion sink brazing at lower temperatures.

Titanium, V, and Zr were found to offer the most promise as braze alloy matrices for diffusion sink brazing below 3200F. A revised diagram of the Ta-Zr system[37] showed that Ta exhibits a very mild effect on the melting temperature of Zr. Therefore, Zr was eliminated as a braze alloy matrix. The applicability of V as a matrix was questionable due to possible embrittlement by formation of TaV_2. Thus, Ti was judged to be the most promising matrix for diffusion sink braze alloys.

The most promising melting point depressants for Ti are V, Zr, Cr, Fe, Si and Mn. Only V and Zr are completely compatible with Ti. Manganese was eliminated because it was similar in behavior to Fe but not as potent a depressant.

The binaries Ti-30V and Ti-40Zr represent the minimum melting temperatures in these systems and exhibit good potential as basic braze alloys. However, ternary alloy additions to Ti-30V are considered necessary to improve filleting and flow. These additions will reduce the melting temperature further.

The Ti-V-Si system appeared promising particularly from the standpoint of improved filleting and flow. The estimated liquidus temperatures for the Ti-V-Si system are shown in a portion of Figure A4. These data show that Si will depress the melting temperature of the Ti-V system.

Binary phase diagram data show that Fe is a good melting temperature depressant for Ti and a fair depressant for V. In addition, V exhibits reasonably high solid solubility for Fe. Thus, the Ti-V-Fe system was attractive for lowering the melting temperature of the Ti-V system. The influence of Fe in filleting and flow of the Ti-V system was unknown. However, it is possible that Fe could improve alloy behavior.

The Zr-V-Ti system discussed previously for brazing molybdenum also offered potential for brazing tantalum. This system had possibilities for reactive as well as diffusion sink brazing using the principles discussed earlier. Information obtained on the binary phase diagrams of Cb and Ta with iridium, rhodium, platinum and

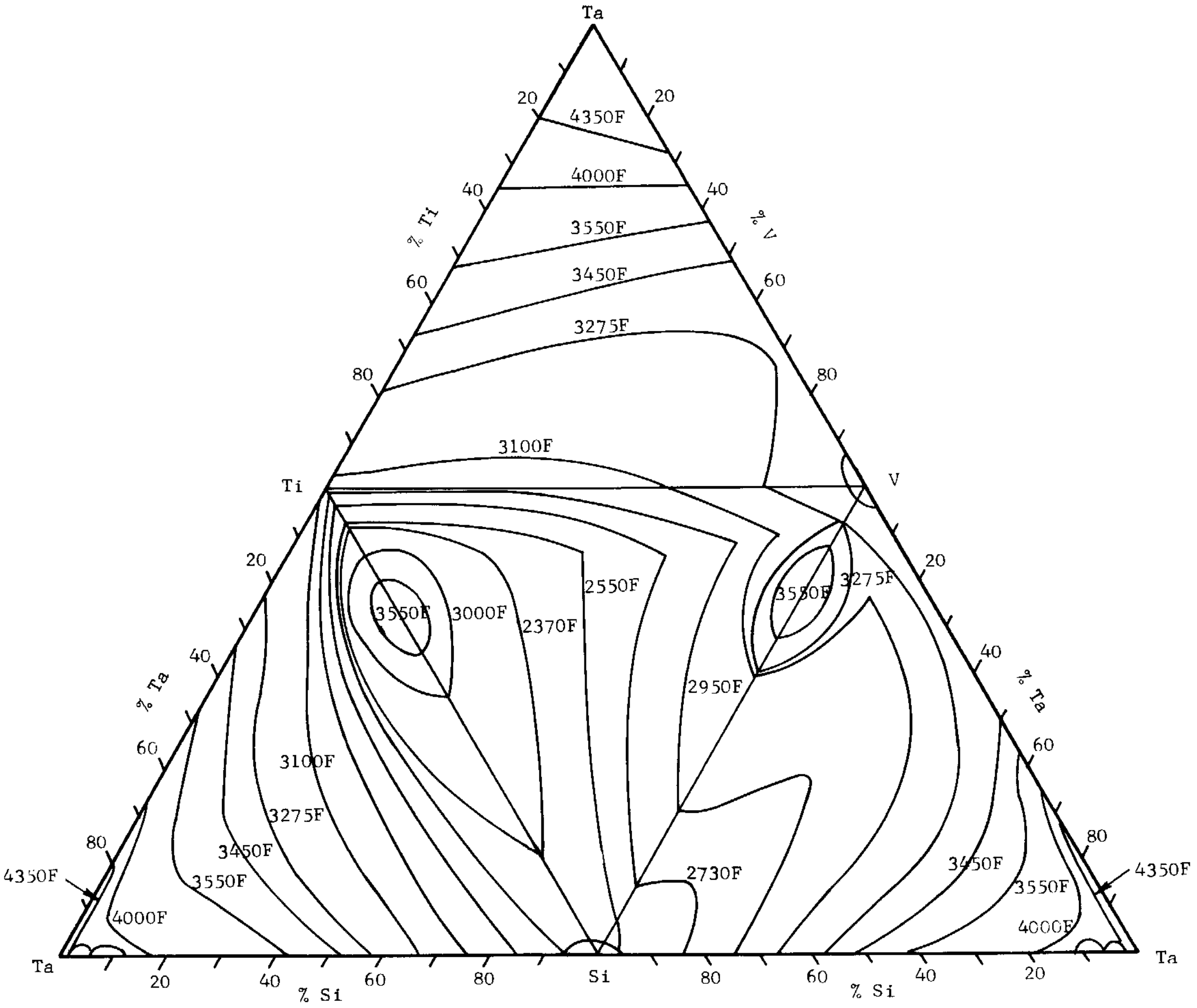


FIGURE A4 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Si-Ta SYSTEM palladium[38] show potential alloys with melting temperatures of approximately 3300F or lower. However, the diagrams show that Cb or Ta diffusion sink additions within relatively broad ranges result in sigma phase formation and embrittlement. Therefore, these systems offered limited potential as braze alloys.

The Ta-B and Cb-B systems discussed in relation to conventional braze alloys offered possibilities for diffusion sink brazing. Determination of melting temperatures in these systems was necessary to confirm their applicability.

The selection of optimum diffusion sinks for tantalum is subject to the same considerations mentioned previously for molybdenum. The diffusion sink remelt potential of the Ti-Zr-V system was estimated for Cb and Ta sink additions. The estimated ternary liquidus surfaces of the Ti-Zr-V-Cb and Ti-Zr-V-Ta quaternary tetrahedrons were estimated and projected on a plane. The results are shown in Figures A5 and A6.

From these figures it can be seen that small diffusion sink additions of Ta or Cb to the Ti-Zr-V ternary produce relatively mild increases in remelt temperature. However, larger additions could produce proportionally greater increases.

Portions of Figures A5 and A6 show similar trends for Cb and Ta additions to the Ti-Zr and Ti-V systems. The estimated liquidus temperatures for the Ti-V-Si-Ta system shown in Figure A4 also exhibit this trend.

RESUME 'OF SURVEY

On the basis of the extensive literature survey, experience and limited experimental data the following highlights were noted with regard to refractory alloy brazing prior to the initiation of this program.

1. Brazing temperatures for TZM honeycomb panels should be limited to 2400F (1 minute exposure) to retain optimum base metal ductility.

2. Brazing temperatures as high as 2600F (1 minute exposure) for TZM honeycomb panels may result in acceptable base metal ductility.

3. Conventional brazing of TZM does not produce ductile honeycomb panels for service to 3000F.

4. Tantalum alloys are not seriously embrittled by high temperature exposures. Therefore, conventional brazing for service to 3500F is metallurgically acceptable.

5. Brazing fillers for molybdenum and tantalum alloys should be based on alloys exhibiting solid solubility in the base metal to assure joint ductility and metallurgical compatibility.

6. Diffusion sink and reactive brazing are the most promising methods for brazing molybdenum and tantalum alloys to develop high remelt temperatures and thus high service temperatures.

7. No reasonably suitable braze fillers for molybdenum and tantalum alloys have been developed to date for the service temperatures considered in this program.

8. In general Ti-base alloys offer the greatest potential for brazing TZM.

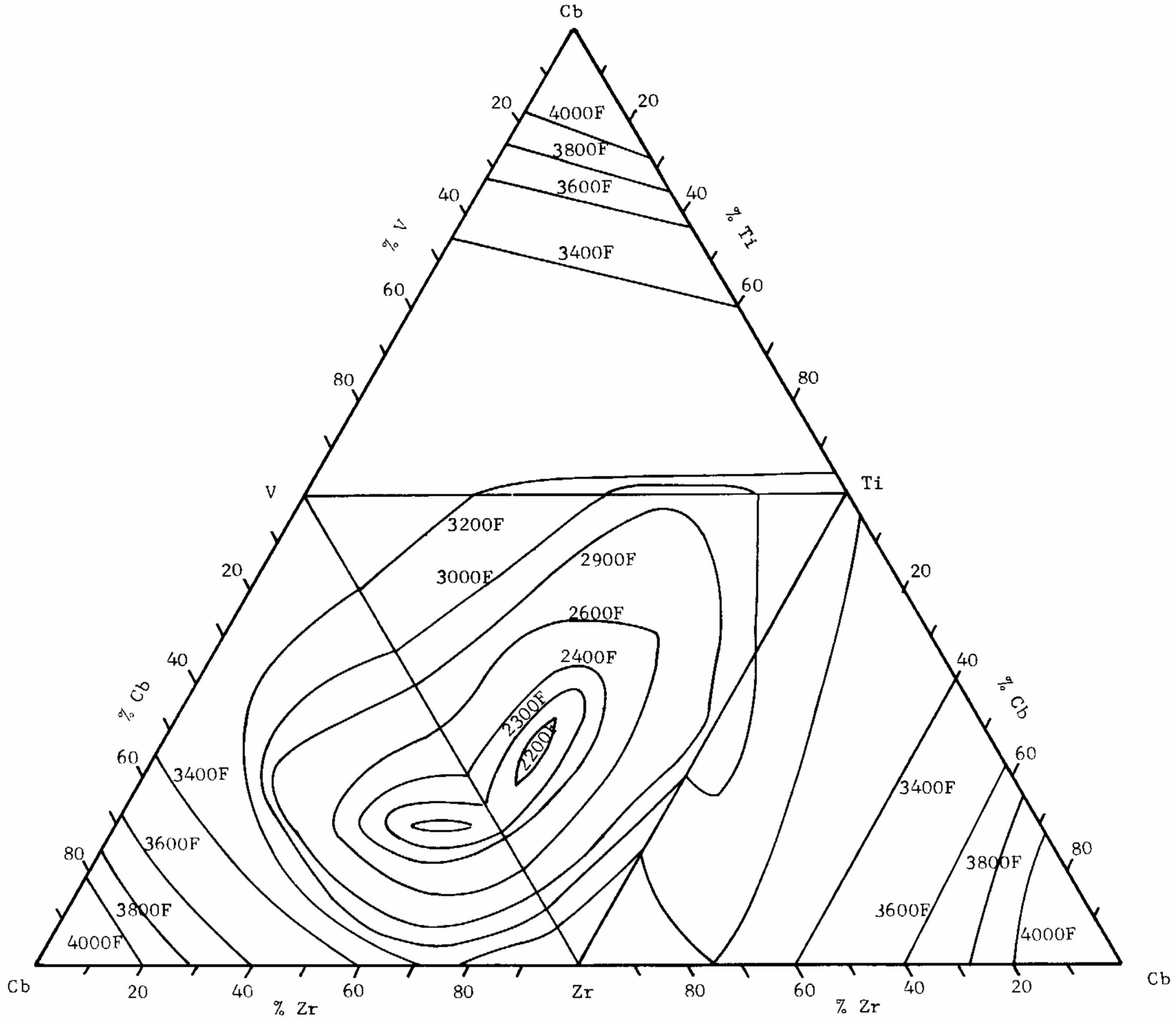


FIGURE A5 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr-Cb SYSTEM

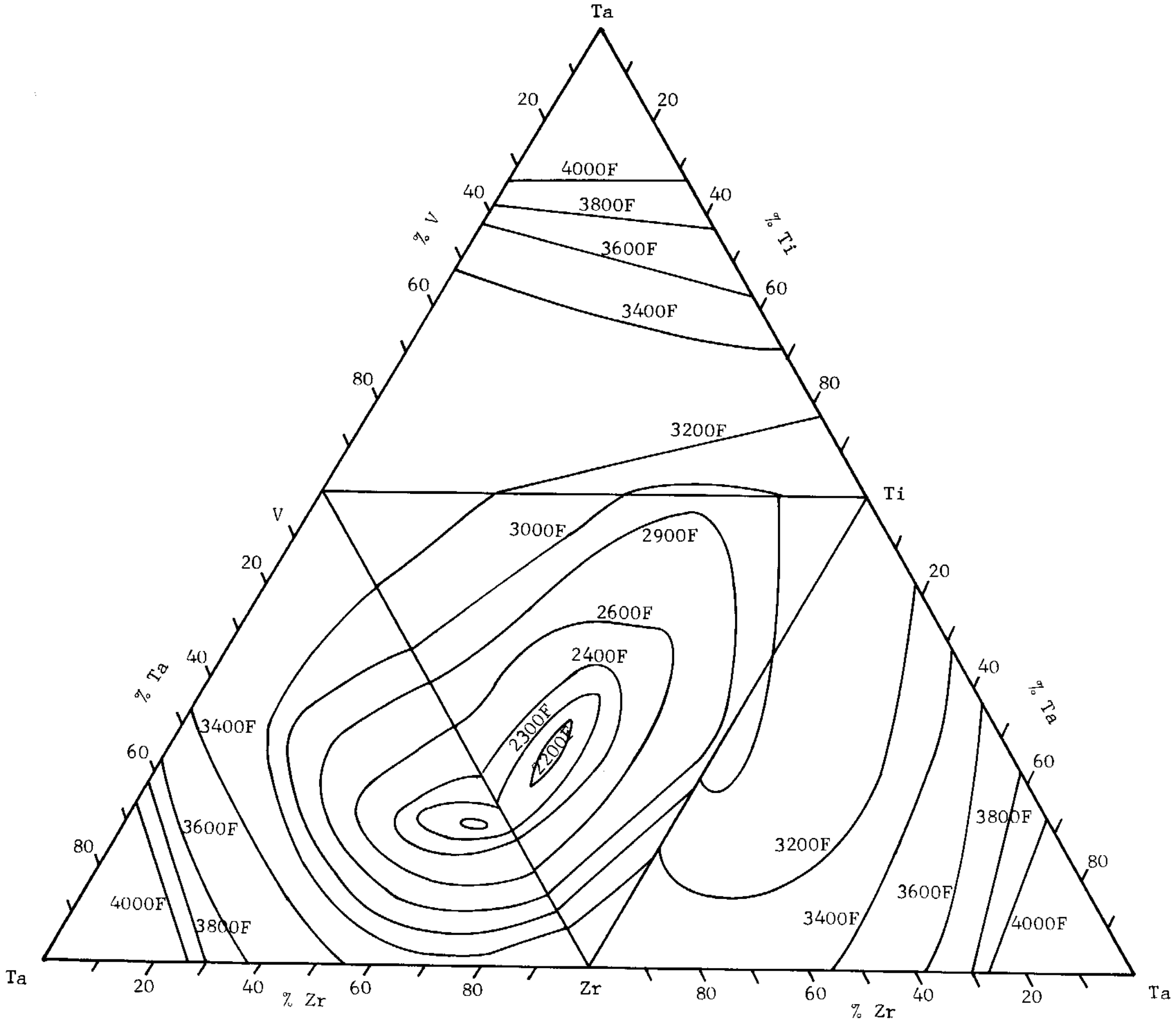


FIGURE A6 ESTIMATED LIQUIDUS ISOTHERMS IN THE Ti-V-Zr-Ta SYSTEM

9. The following alloy systems appear most promising for molybdenum braze alloy development:

   Ti-Co
   Ti-Ni
   Ti-Co-Cr
   Ti-Ni-Cr
   Ti-Fe-Cr
   Ti-Cr
   Ti-Ni-Si
   Ti-Zr-V
   Zr-V-Cb

10. The most promising diffusion sink elements are Ta, Cb, and Mo.

11. The following alloy systems offer the greatest potential for conventional brazing of tantalum:

    Cb-V
    Cb-Ti
    Ta-B
    Cb-B

12. The following alloy systems offer the greatest potential for high remelt temperature brazing of tantalum.

    Ti-Zr
    Ti-V-Si
    Ti-V-Fe
    Zr-V-Ti
    Ta-B
    Cb-B
    Ti-V-Fe-(Cb,Ta, or Mo)
    Ti-V-Si-(Cb,Ta, or Mo)
    Ti-Zr- (Cb,Ta, or Mo)

13. Several promising high temperature coatings are available for base metal protection of TZM and Ta-10W alloys.

14. Coating/braze alloy compatibility problems may exist for titanium base braze alloys on TZM using pack cementation type coatings.

15. No data on coating/braze alloy compatibility on Ta base alloys was found.

APPENDIX A REFERENCES

1. Semchysen, M., Barr, R. Q., Mechanical Properties of Molybdenum and Molybdenum - Base Alloy Sheet, ASTM, STP No. 272, 1959
2. Freedman, A. H., Recrystallization Behavior and Brazing of Molybdenum and Columbium Alloys, Report No. NOR 62-195, November 1962, (Northrop Corp., Norair Division, Hawthorne, California)
3. Freedman, A. H., Unpublished Data, (Northrop Corp., Norair Div., Hawthorne, Calif.)
4. Kaarlela, W.T., Development of Construction Methods for Sandwich-Brazed Titanium Molybdenum, MR 57-9, January 30, 1962, AF33(657)-7248, (General Dynamics Corp., Convair, Fort Worth, Texas)
5. Dukes, W. H., Gosden, C. E., Kappelt, G. F., Mirti, A. E., Manufacturing Methods for Insulated and Cooled Double-Wall Structures, ASD TR 61-7-799, Section I, Vol. II, May, 1961, AF33(600)-40100, (Bell Aerosystems Co., Buffalo, New York)
6. Jacobson, M. I., Martin, D. C., Voldrich, C. B., Production of Sound Ductile Joints in Molybdenum, WADC TR 53-401, January 1954, (Battelle Memorial Institute, Columbus, Ohio)
7. Feinstein, L., Investigation of Electron Device Materials Technology Studies of Brazing and Metal Joining Problems, July 1961, Final Report for USAF, AF 19(604)-7323, AD 264459, (Stanford Research Institute, Menlo Park, Calif.)
8. Unpublished Information, (Northrop Corp., Norair Div., Hawthorne, California)
9. McCown, J.W., et al, Manufacturing Methods and Design Procedures for Brazed Refractory Metal Honeycomb Sandwich Panels, ASD TDR 62-937 (I, II, III), November 1961 - September 1962, AF33(657)-7276, (Martin Marietta Corp., Baltimore, Md.)
10. Young, W.R., Jones, E.S., Joining of Refractory Metals by Brazing and Diffusion Bonding, ASD TDR 63-88, January 1963, AF33(616)-7484, (General Electric Co. - Evandale, Cincinnatti, Ohio)
11. Metcalfe, A.G., Joining of Refractory Metal Foils, Report RDR-1324-2, January 1963, AF33(657)-9442, (Solar, San Diego, California)
12. Hugill, D.B., et al, Quartz Lamp Radiant Heat Brazing of Large Refractory Metal Honeycomb Sandwich Panels, ASD IR-7-937a (IV), 10 April 1963 - 10 July 1963, AF33(657)-8910, (Northrop Corp., Norair Div., Hawthorne, California)
13. Metcalfe, A.G., Reactive Brazing - A New Joining Method, Metal Progress, May 1963 pp. 83-86
14. Haynes, C.W., Development of Low Temperature Brazing of Tungsten for High Temperature Service, Report RDR 1249-6, March 26, 1962, NOw 61-0414-c, (Solar, San Diego, California)
15. Imgram, A.G., Mallett, M.W., Koehl, B.G., Bartlett, E.S., Ogden, H.R., Notch Sensitivity of Refractory Metals, ASD TR 61-474, January 1962, AF33(616)-7604, (Battelle Memorial Institute, Columbus, Ohio)

APPENDIX A REFERENCES (Cont.)

16. Ogden, H.R., et al, Scale-Up Development of Tantalum-Base Alloys, ASD TR 61-684, March 1962, AF33(616)-7452, (Battelle Memorial Institute, Columbus, Ohio)

17. Schmidt, F.F., Imgram, A.G., Klopp, W.D., Bartlett, E.S., Ogden, H.R., Investigation of Tantalum and its Alloys, ASD TDR 62-594, October 1962, AF33(616)-7688, (Battelle Memorial Institute, Columbus, Ohio)

18. Young, W.R., Alloy Systems for Brazing of Columbium and Tungsten, ASD TR 61-592, January 1962, AF33(616)-7484, (General Electric Co.-Evandale, Cincinnati, Ohio)

19. Freedman, A.H., Unpublished Data, (Northrop Corp., Norair Div., Hawthorne, Calif.)

20. Lehrer, W.M., Schwartzbart, H., Development of Partially Volatile Brazing Filler Alloys for High-Temperature Application and Resistance to Oxidation, WADC TR 59-404, December 1959, AF33(616)-6882, (Armour Research Foundation, Chicago, Illinois)

21. Bredzs, N., Rudy, J.F., Schwartzbart, H., Development of Partially Volatile Brazing Filler Alloys for High-Temperature Application and Resistance to Oxidation, WADD TR 59-404, Part II, June 1961, AF33(616)-6882, (Armour Research Foundation, Chicago, Illinois)

22. Banning, R.O., Armstrong, J.R., Long, R.A., The Investigation of Exothermic Brazing of Refractory Alloys, Quarterly Report No. 1, 28 February 1963, N600 (19) 59237, (Narmco Research and Development Div., San Diego, California)

23. Gibeaut, W.A., Ogden, H.R., Summary of the Seventh Meeting of the Refractory Composites Working Group, DMIC Report No. 184, May 30, 1963, (Battelle Memorial Institute, Columbus, Ohio)

24. Moore, V.S., Stetson, A.R., Evaluation of Coated Refractory Metal Foils, Report RDR 1325-2, 21 January 1963, and Report RDR 1325-3, 12 April 1963, (Solar, San Diego, California)

25. Lawthers, D.D., Sama, L., High Temperature Oxidation Resistant Coatings for Tantalum Base Alloys, ASD TR 61-233, October 1961, AF33(616)-7462, (Sylcor Div., Sylvania Electric Products, Inc., Bayside, N. Y.)

26. Sama, L., High Temperature Oxidation Resistant Coatings for Tantalum Base Alloys, ASD TDR 63-160, February 1963, AF33(657)-7339, (General Telephone and Electronics Labs., Inc., Bayside, N. Y.)

27. Hallowell, J.B., Maykuth, D.J., Ogden, H.R., Coatings for Tantalum-Base Alloys, ASD TDR 63-232, April 1963, AF33(657)-7909, (Battelle Memorial Institute, Columbus, Ohio)

28. Hansen, M., Constitution of Binary Alloys, (McGraw-Hill Book Co., Inc., New York City, N. Y.), 1958

29. Maykuth, D.J., Ogden, H.R., Jaffee, R.I., The Effects of Alloying Elements in Titanium, Volume A, Constitution, DMIC Report 136A, 15 September 1960, (Battelle Memorial Institute, Columbus, Ohio)

30. English, J.J., Binary and Ternary Phase Diagrams of Columbium, Molybdenum, Tantalum, and Tungsten, DMIC Report 152, 28 April 1961, (Battelle Memorial Institute, Columbus, Ohio)

31. English, J.J., Binary and Ternary Phase Diagrams of Columbium, Molydenum, Tantalum, and Tungsten, DMIC Report 183, 7 February 1963, (Battelle Memorial Institute, Columbus, Ohio)

32. Freedman, A.H., Unpublished Data, (Northrop Corp., Norair Div., Hawthorne, California)

33. Murakami, Y., Yukawa, Y., Enjyo, T., On the Liquidus Surface of the Ti-Fe-Mn System, Nippon Kinzoku Gakkai, Vol. 22, 1958

34. Kessler, H.D., Rostoker, W., Van Thyne, R.J., Titanium Phase Diagrams, WADC TR 52-335, November 1953, (Armour Research Foundation, Chicago, Illinois)

35. Elliott, R.P., Levinger, B.W., Rostoker, W., System Titanium-Chromium-Molybdenum, Trans. AIME, Vol. 197, 1953, pp. 1544-1548

36. Nowikow, A., Baer, H.G., The Ternary System Ti-V-Zr, Zeitschrift fur Metallkunde, Vol. 49, 1958, pp. 195-199

37. Pease, L.F., Brophy, J.H., A Revised Diagram for the Tantalum-Zirconium System, (Massachusetts Institute of Technology, Cambridge, Mass.)

38. Private communication with Prof. N.J. Grant of Massachusetts Institute of Technology, Cambridge, Mass.

APPENDIX B

TZM DIFFUSION
TREATMENT CALCULATIONS

APPENDIX B

TZM DIFFUSION TREATMENT CALCULATIONS

CALCULATION OF THERMAL EXPOSURES FOR 2050F DIFFUSION TEMPERATURE

Assume:

(1) A maximum total exposure, K , of 85,000.

(2) A prior braze cycle of one minute at 2400F.

K = Maximum total exposure parameter

K_B = Exposure parameter for braze cycle

T_B = Brazing temperature in °R

T_D = Diffusion temperature in °R

t_B = Brazing time in minutes

Determination of K_B:

$$K_B = T_B(29 + \log t_B)$$

$$K_B = 2860\ (29 + \log 1)$$

$$K_B = \underline{82{,}900}$$

Equivalence of Braze Cycle to Time at 2050F:

$$K_B = T_D(29 + \log t)$$

$$82{,}900 = 2510\ (29 + \log t)$$

$$\log t = 4.0279$$

$$t = 10{,}560 \text{ minutes} = \underline{176 \text{ hours}}$$

therefore; one minute at 2400F = 176 hours at 2050F

Equivalence of Total Exposure to time at 2050F

$$K = T_D(29 + \log t)$$

$$85{,}000 = 2510\ (29 + \log t)$$

$$\log t = 4.865$$

$$t = 73{,}380 \text{ minutes} = \underline{1220 \text{ hours}}$$

Therefore, after a braze cycle of one minute at 2400F, a diffusion treatment of as long as 1,044 hours at 2050F may be employed.

CALCULATION OF BRAZE ALLOY-BASE METAL DIFFUSION FOR A FIXED DIFFUSION TREATMENT

Determine the point at which a 50 percent Mo-50 percent Ti alloy will form through a planar interface between pure Mo and pure Ti after a specific diffusion cycle.

1. Assume a maximum total thermal exposure (braze cycle plus diffusion treatment) of 85,000 for the TZM.
2. Assume a diffusion temperature of 2165F.
3. From Figure 2, the allowable diffusion time at 2165F is 35 hours.

Let: Co = initial Mo concentration in Ti = 0 percent

Cs = concentration of Mo at Ti surface = $\frac{100\% + 50\%}{2} = 75\%$

C = concentration of Mo in Ti at position (x) at time (t) = 50%

x = distance in centimeters

D = diffusivity constant, $\frac{\text{cm}^2}{\text{sec.}}$

t = time, seconds

$$\frac{C-Cs}{Co-Cs} = \frac{2}{\sqrt{\pi}} \int_0^{\lambda} e^{-\lambda^2} d\lambda \quad *$$

Where $\lambda = \frac{x}{2\sqrt{Dt}}$

$$\frac{C-Cs}{Co-Cs} = \frac{50\% - 75\%}{0\% - 75\%} = .333$$

Substituting .333 into the preceding integral and solving yields $\lambda = .3$

$$x = 2\lambda\sqrt{Dt}$$

According to the data of D. Goold**, at 2165F

$D = 2.1 \times 10^{-9} \frac{\text{cm}^2}{\text{sec}}$, $t = 35 \text{ hrs.} = 126 \times 10^3 \text{ sec.}$

$$x = 2 \times .3 \sqrt{2.1 \times 10^{-9} \; .126 \times 10^3}$$

$x = \underline{9.78 \times 10^{-3} \text{ cm.}}$

Therefore, after a 35-hour diffusion treatment at 2165F, the depth of diffusion to a 50Mo-50Ti composition is 9.78×10^{-3} cm.

* Reference 1

** Reference 2

APPENDIX B REFERENCES

1. L. S. Darken, R. W. Gurry, Physical Chemistry of Metals, McGraw-Hill Book Company, Inc., New York, N. Y., 1953, P. 443.

2. D. Goold, Diffusion of Aluminum, Tin, Vanadium, Molybdenum, and Manganese in Titanium, Journal of the Institute of Metals, June, 1960, page 444.

APPENDIX C

EVALUATION OF TZM TEE JOINTS

An analysis of the braze alloys evaluated on TZM tee joints is present in this Appendix along with hardness and photomicrographs. The two microhardness curves for each tee represent (1) a traverse along the foil center line from above the fillet extending into the face sheet and (2) a traverse approximately 0.003 inch above and parallel to the fact sheet fillet interface.

Figures C1 and C2 show results obtained on the 46Zr-34V-20Ti diffusion sink braze alloy with and without Ta sink powder additions. These results may be summarized as follows:

1. Only partial braze alloy-sink powder reaction was noted in the as-brazed condition. More complete reaction occurred during diffusion.

2. Ta sink powder additions produced a substantial increase in fillet hardness during the diffusion treatment.

3. Diffusion treated joints with and without sink powder showed relatively little braze fillet-base metal diffusion.

A reactive brazing approach was also investigated using 46Zr-34V-20Ti with carbon powder additions. This approach involved reaction of carbon with the braze alloy to form discrete high melting carbide particles. Powder additions of Mo plus C were also investigated as a combination of reactive and diffusion sink brazing. The results, shown in Figures C3 and C4, are summarized as follows:

1. A maximum of 1.67 weight percent carbon or 9.5 percent Mo plus .5 percent carbon could be placed in the joints. Higher additions seriously impeded braze alloy filleting and flow.

2. These carbon additions were theoretically too low to produce necessary amounts of carbides to realize desired remelt temperatures.

3. Erratic braze alloy filleting was produced by these sink powder additions. The fillets were also weak and easily fractured during metallographic mounting in bakelite.

4. The as-brazed joint containing 1.67 percent carbon showed initiation of discrete carbide particle formation.

5. Substantial segregation was observed in as-brazed and diffused joints containing the Mo plus C sink mixture.

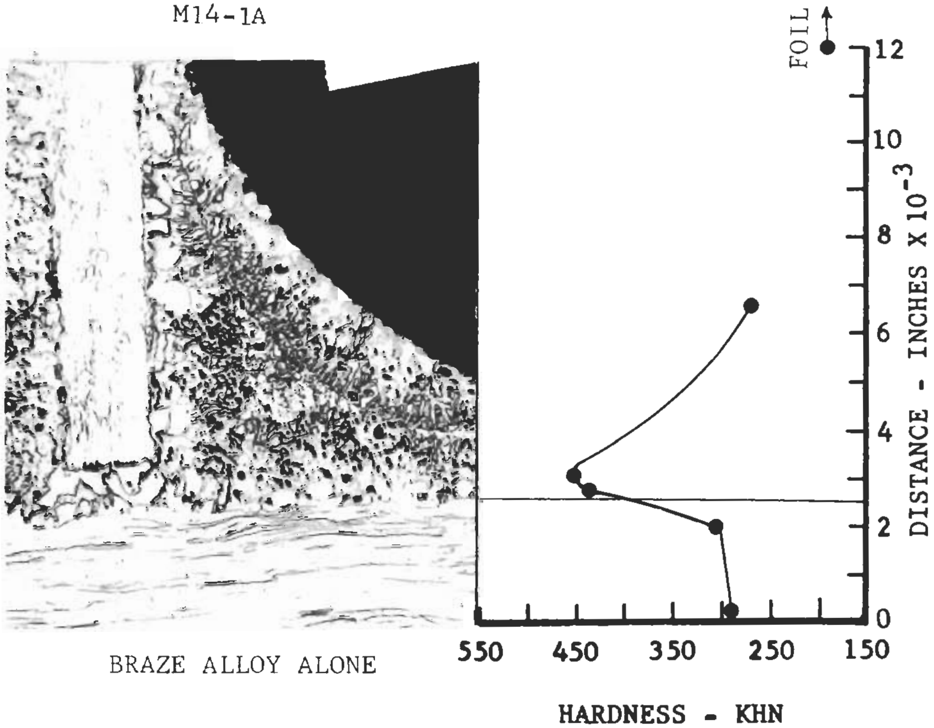
6. Diffusion treatment produced little change in fillet microstructures and minimal fillet-base metal diffusion.

Results obtained with Ti-8Ni-7Si are shown in Figures C5 and C6 and summarized as follows:

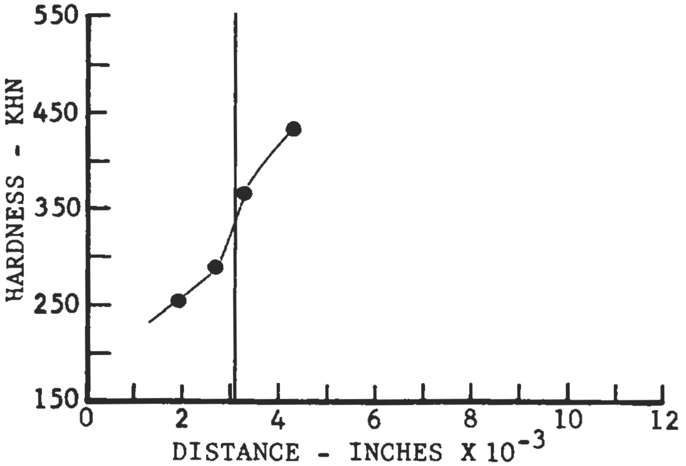
1. The diffusion temperature was above the solidus temperature of the fillet without sink powder causing partial fillet melting and run-off.

2. No fillet melting was observed in the joint containing Mo sink powder. Thus, sink powder raised the fillet solidus above the diffusion temperature.

M14-1A

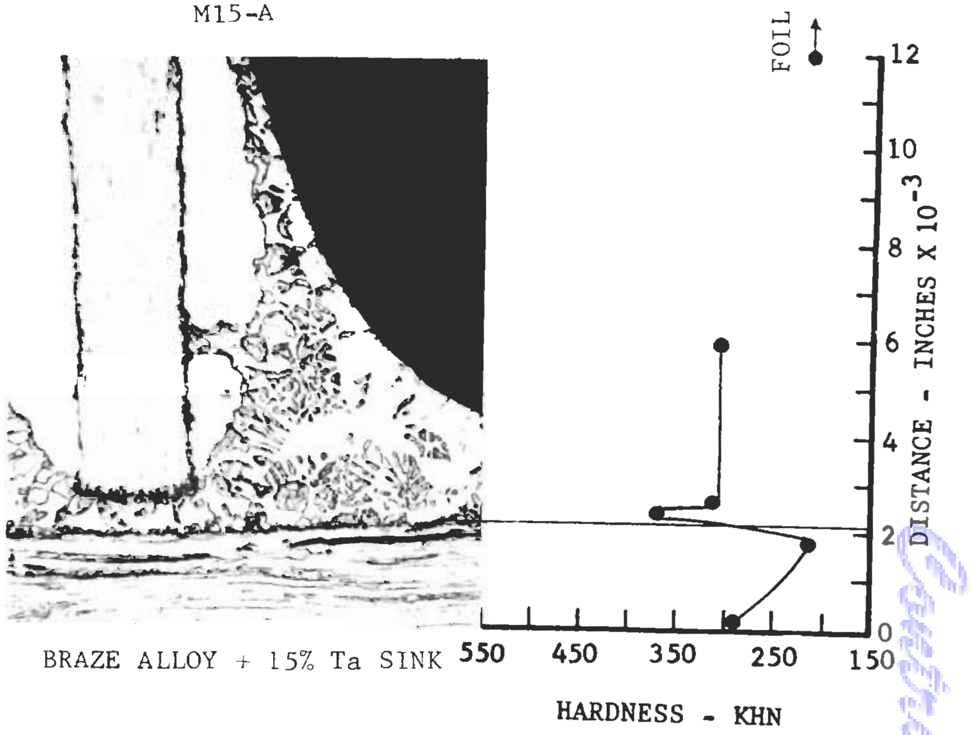


BRAZE ALLOY ALONE

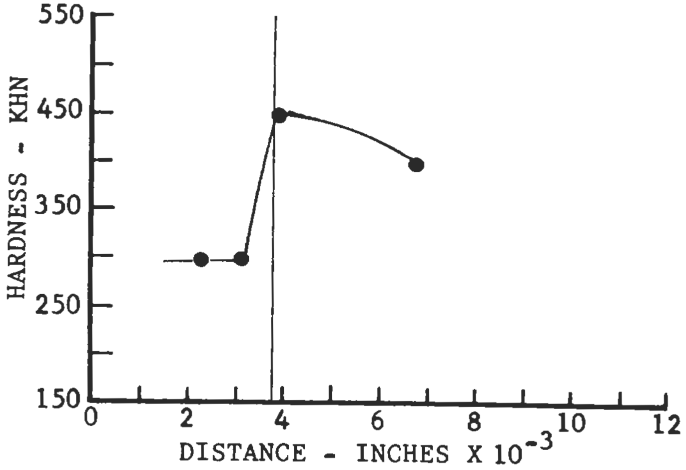


BRAZE CYCLE: 2400F - 1 MIN.

M15-A



BRAZE ALLOY + 15% Ta SINK

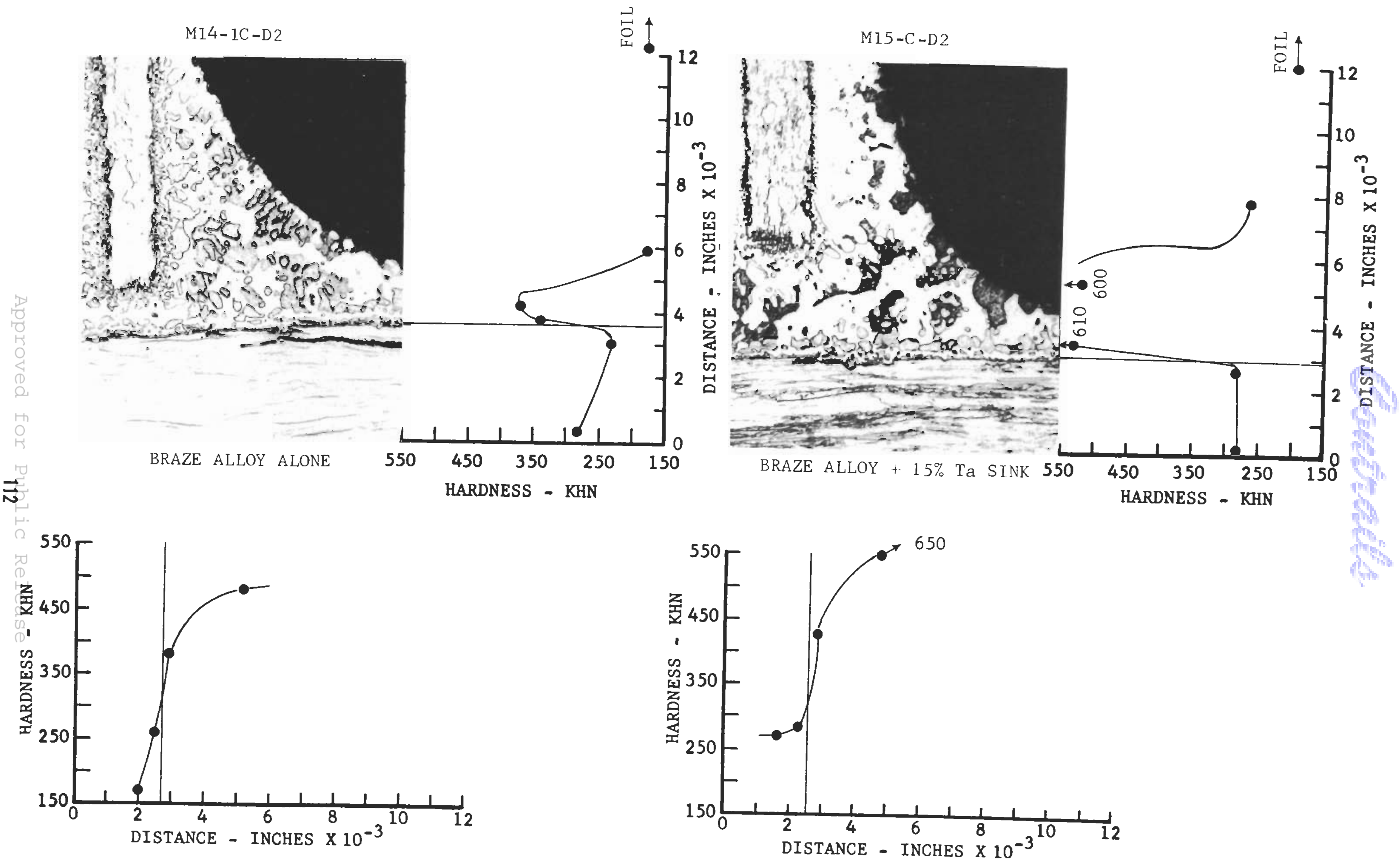


BRAZE CYCLE: 2400F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: } 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT:

FIGURE C1 TZM TEE JOINTS BRAZED WITH 46Zr-34V-20Ti - AS BRAZED



BRAZE ALLOY ALONE

BRAZE ALLOY + 15% Ta SINK

BRAZE CYCLE: 2400F - 1 MIN.

BRAZE CYCLE: 2400F - 1 MIN.

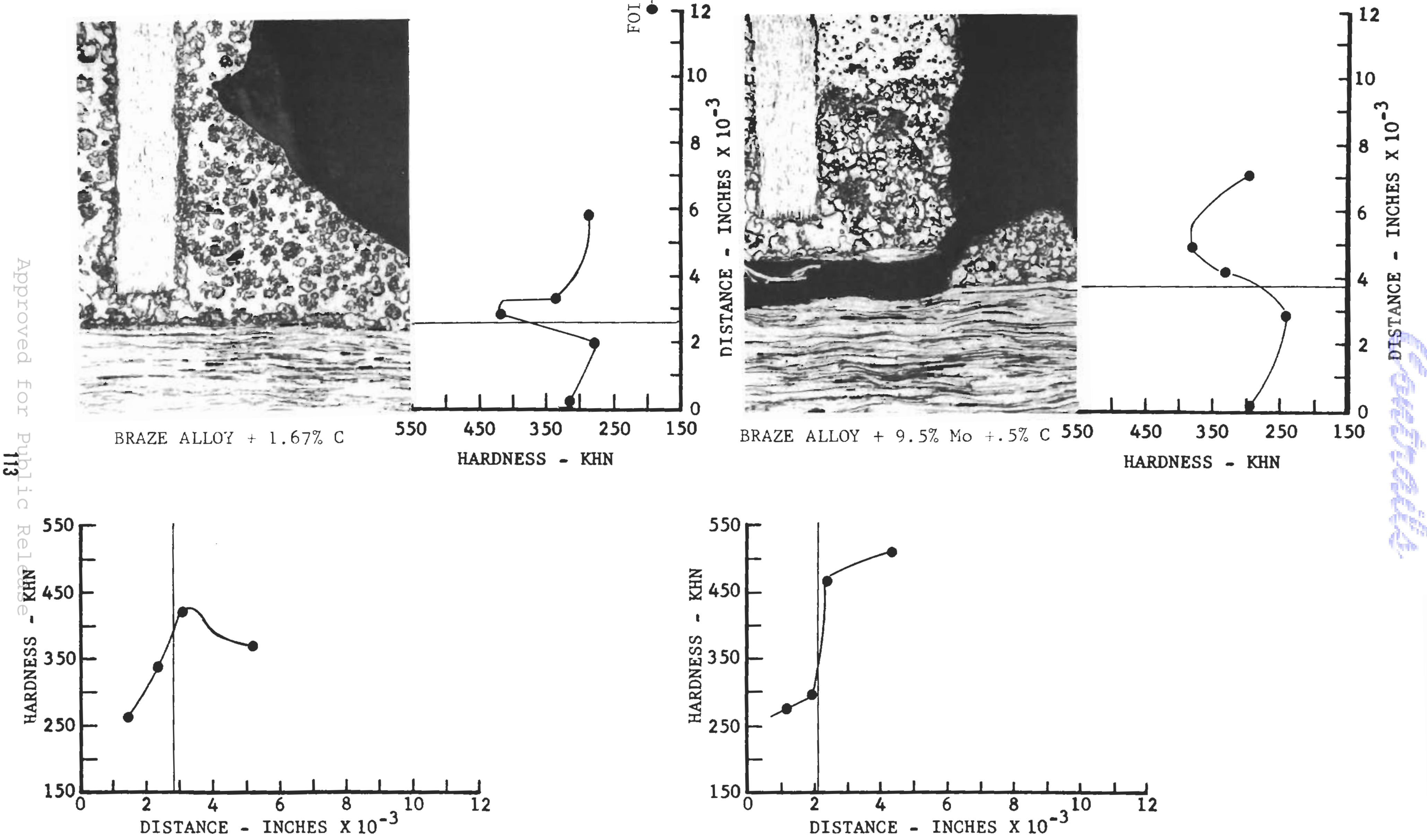
MAG. 250x

BASE MATERIAL ETCHANT: 10 gm. NaOH, 30 gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE C2 TZM TEE JOINTS BRAZED WITH 46Zr-34V-20Ti - DIFFUSED 20 HRS AT 2040F

M16-1A

M19-A



BRAZE ALLOY + 1.67% C

BRAZE ALLOY + 9.5% Mo +.5% C

BRAZE CYCLE: 2400F - 1 MIN.

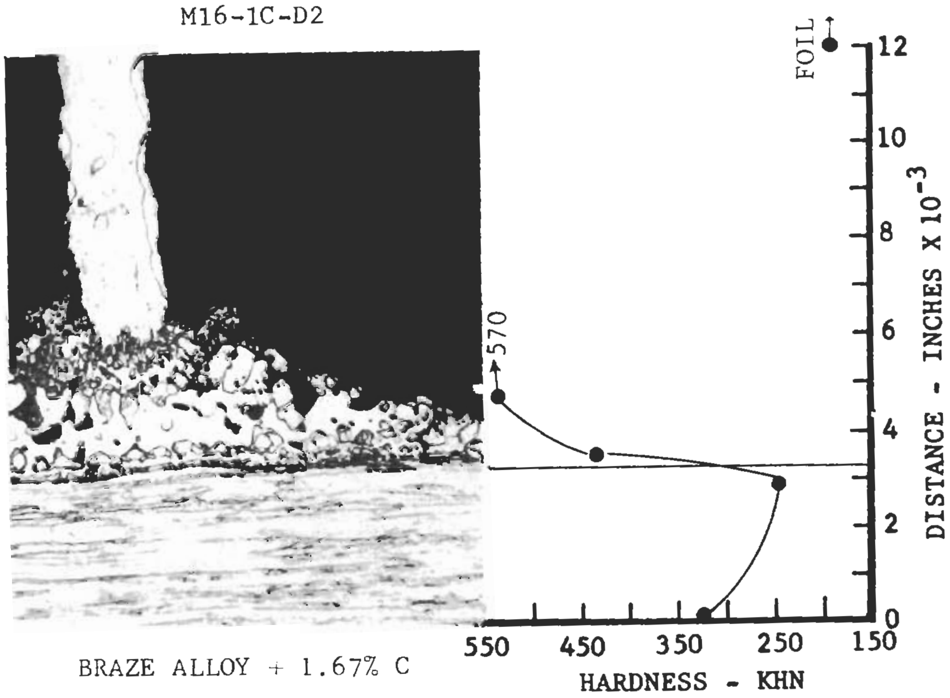
BRAZE CYCLE: 2400F - 1 MIN.

MAG. 250 x

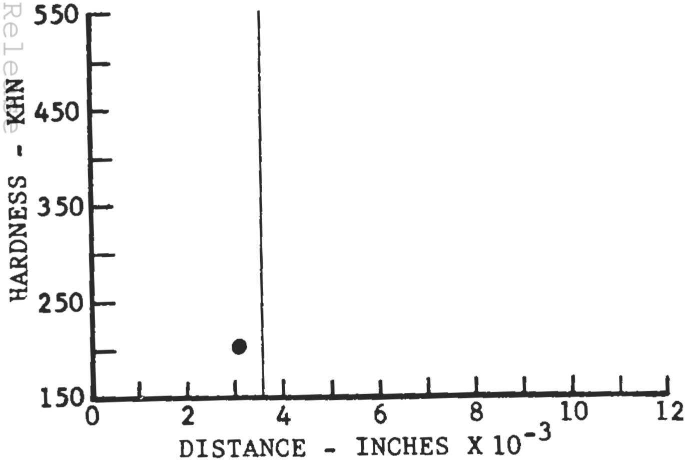
BASE MATERIAL ETCHANT } 10 gm. NaOH, 30 gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT }

FIGURE C3 TZM TEE JOINTS BRAZED WITH 46Zr-34V-20Ti - AS BRAZED

M16-1C-D2

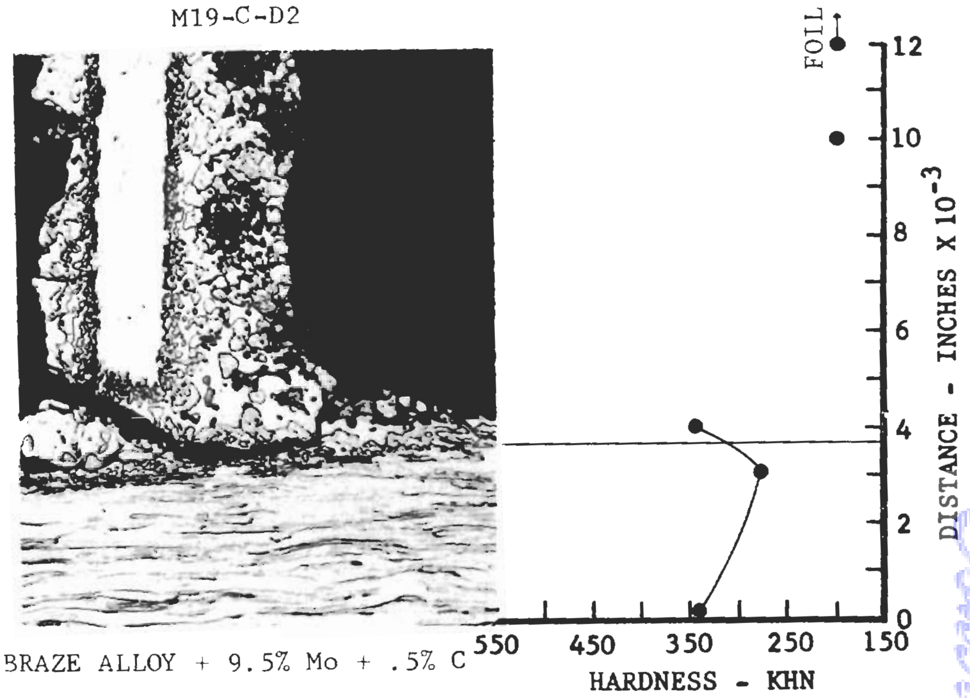


BRAZE ALLOY + 1.67% C

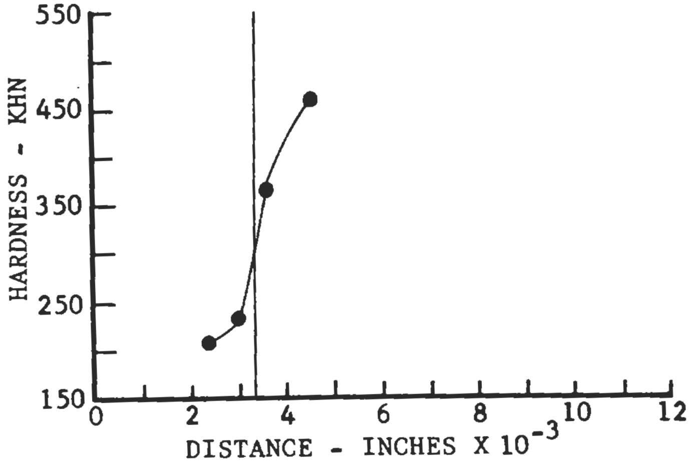


BRAZE CYCLE: 2400F - 1 MIN.

M19-C-D2



BRAZE ALLOY + 9.5% Mo + .5% C



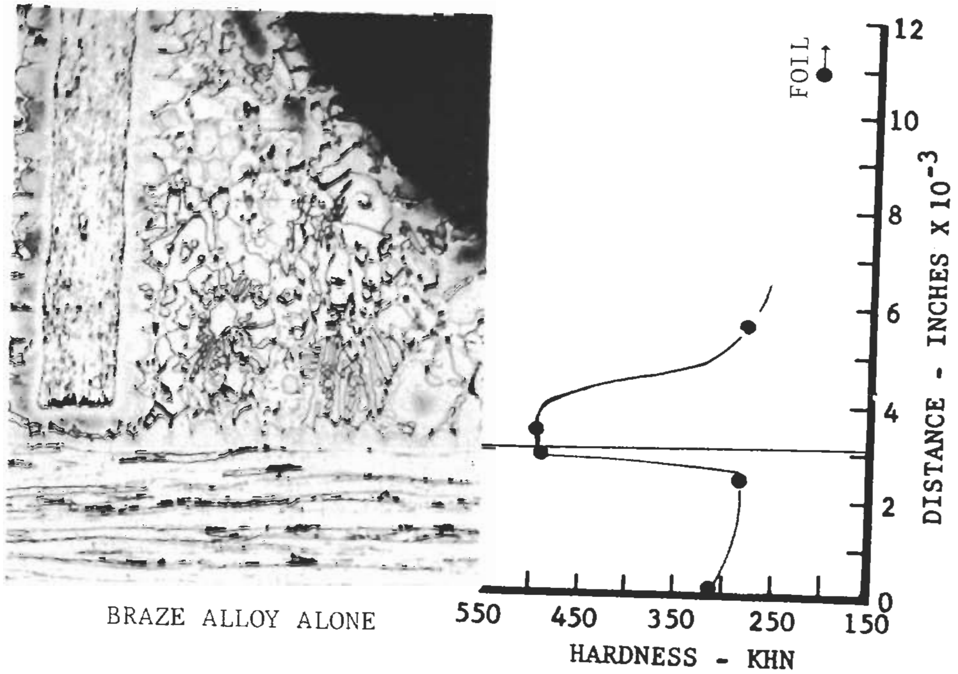
BRAZE CYCLE: 2400F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

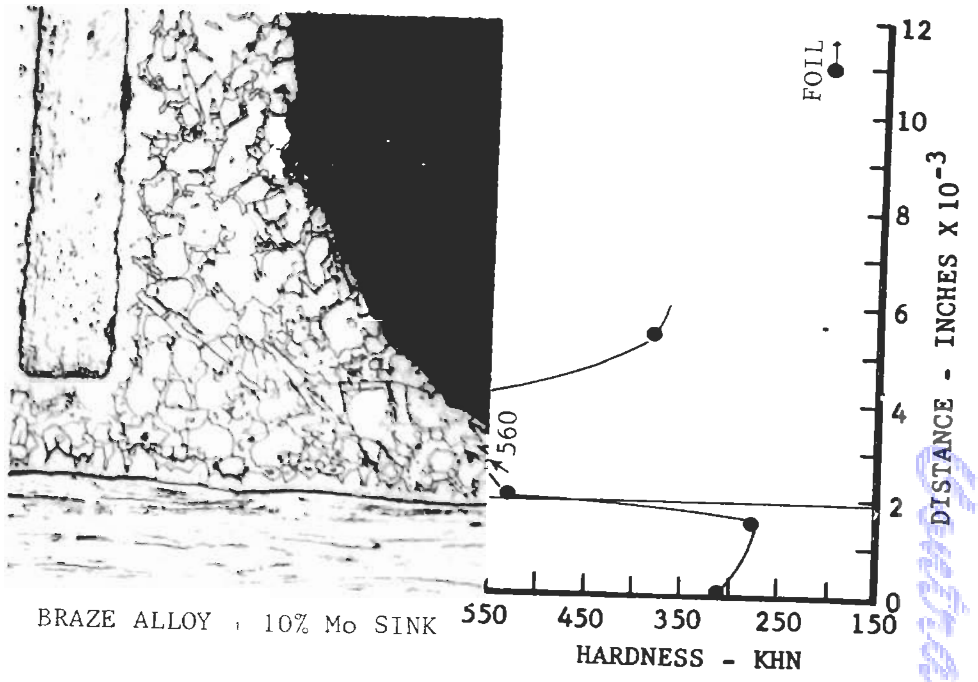
FIGURE C4 TZM TEE JOINTS BRAZED WITH 46Zr-34V-20Ti - DIFFUSED 20 HRS AT 2040F

M10-A

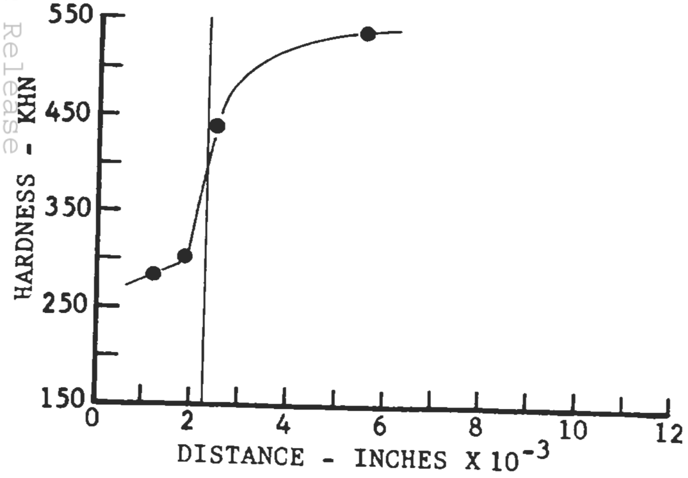


BRAZE ALLOY ALONE

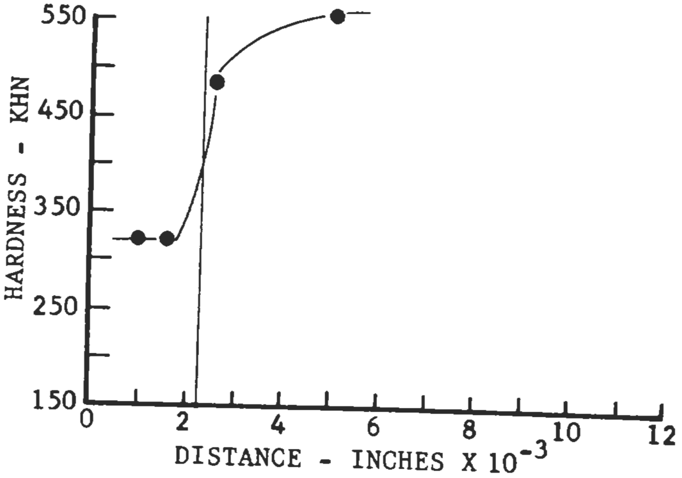
M11-A



BRAZE ALLOY , 10% Mo SINK



BRAZE CYCLE: 2360F - 1 MIN.



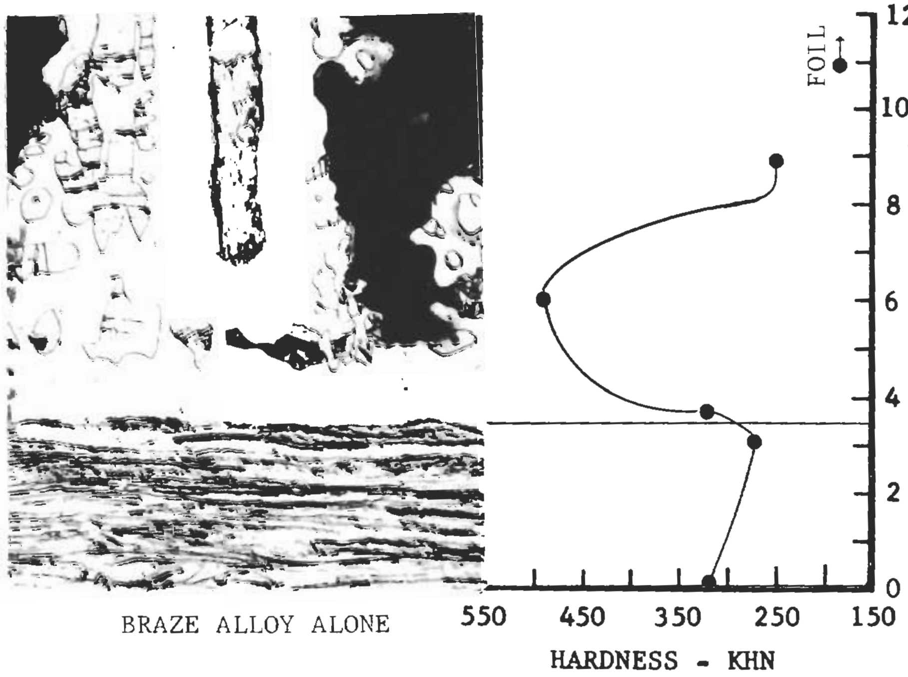
BRAZE CYCLE: 2360F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10 gm. NaOH, 30 gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

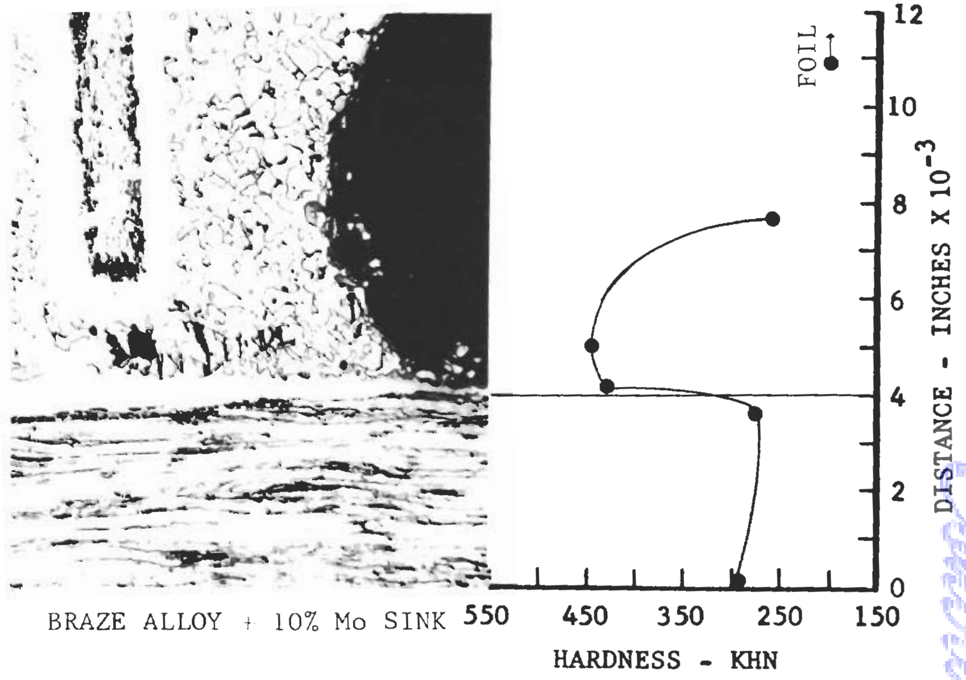
FIGURE C5 TZM TEE JOINTS BRAZED WITH Ti-8Ni-7Si - AS BRAZED

M10-C-D2

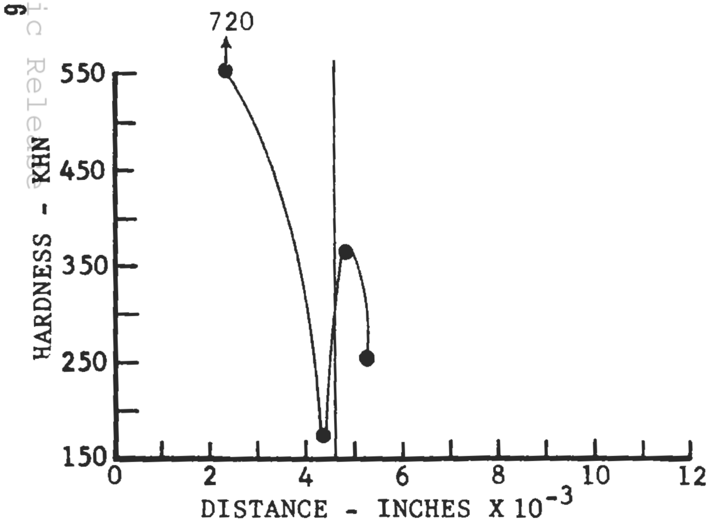


BRAZE ALLOY ALONE

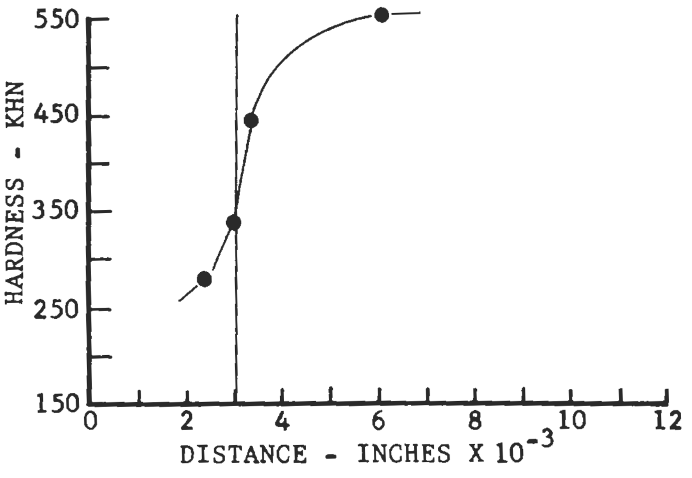
M11-C-D2



BRAZE ALLOY + 10% Mo SINK



BRAZE CYCLE: 2360F - 1 MIN



BRAZE CYCLE: 2360F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10 gm. NaOH, 30 gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE C6 TZM TEE JOINTS BRAZED WITH Ti-8Ni-7Si - DIFFUSED 20 HRS AT 2040F

3. Diffusion treatment of tees with and without sink showed significant fillet-base metal diffusion. However, the degree of diffusion appears insufficient to develop high remelt temperature due to a continuous low melting phase remaining between the foil and base sheet.

Results obtained with Ti-25Cr-10Ni are shown in Figures C7 and C8, and summarized as follows:

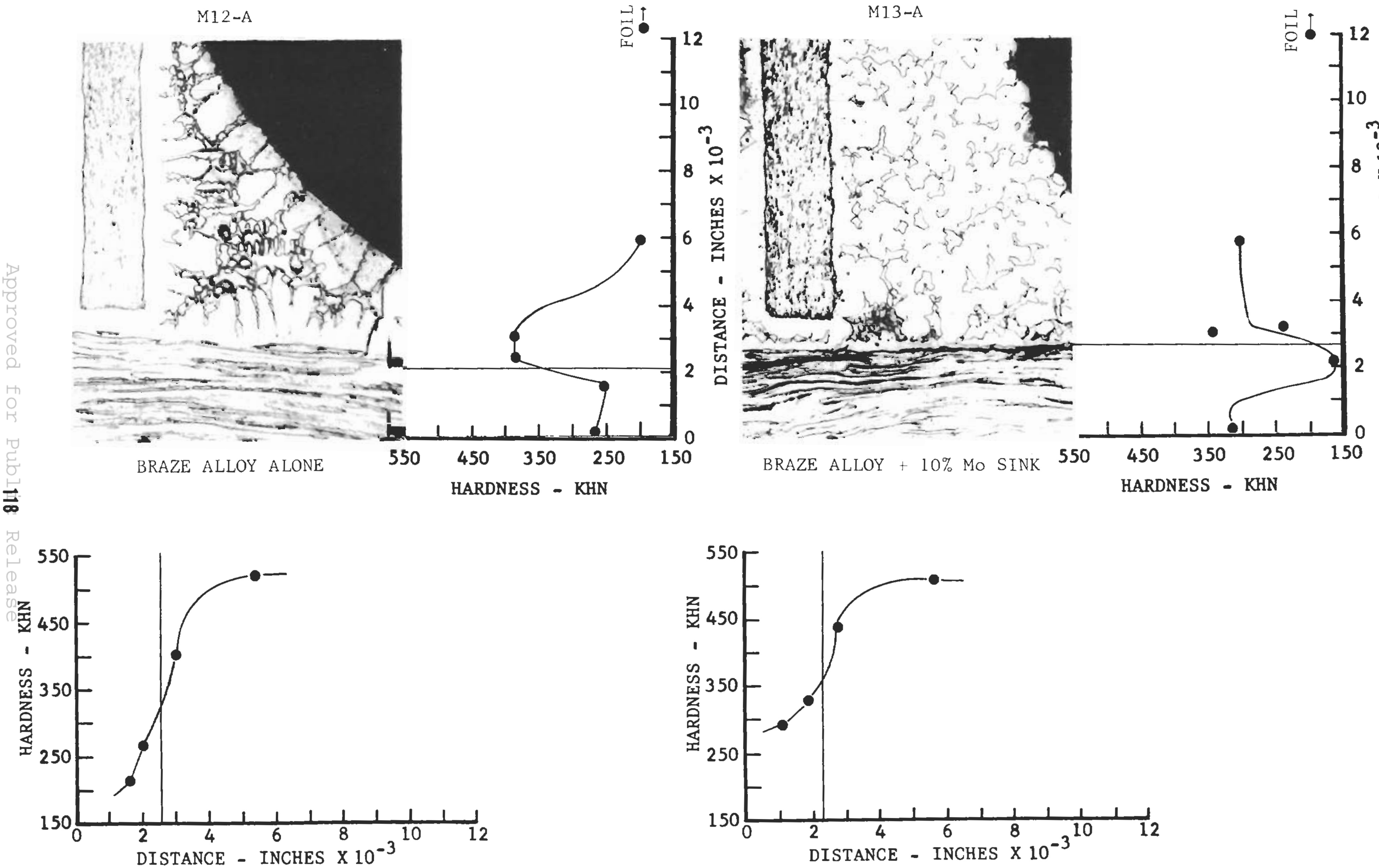
1. The diffusion treatment produced a substantial single phase solid solution fillet-base metal diffusion zone in joints with and without sink powder.

2. The degree of diffusion appeared sufficient to produce a significant remelt temperature increase.

Results obtained with 33Zr-34Ti-33V are shown in Figures C9 and C10. This higher melting braze alloy was selected on a criterion of almost complete foil recrystallization, but no appreciable sheet recrystallization.

1. The one-minute braze cycle at 2580F produced complete foil recrystallization and unacceptable embrittlement. However, the face sheet exhibited minimal recrystallization and acceptable ductility.

2. The diffusion treatment produced little fillet-base metal diffusion in the joints with and without Ta sink powder.



BRAZE ALLOY ALONE

BRAZE ALLOY + 10% Mo SINK

BRAZE CYCLE: 2420F - 1 MIN.

BRAZE CYCLE: 2420F - 1 MIN.

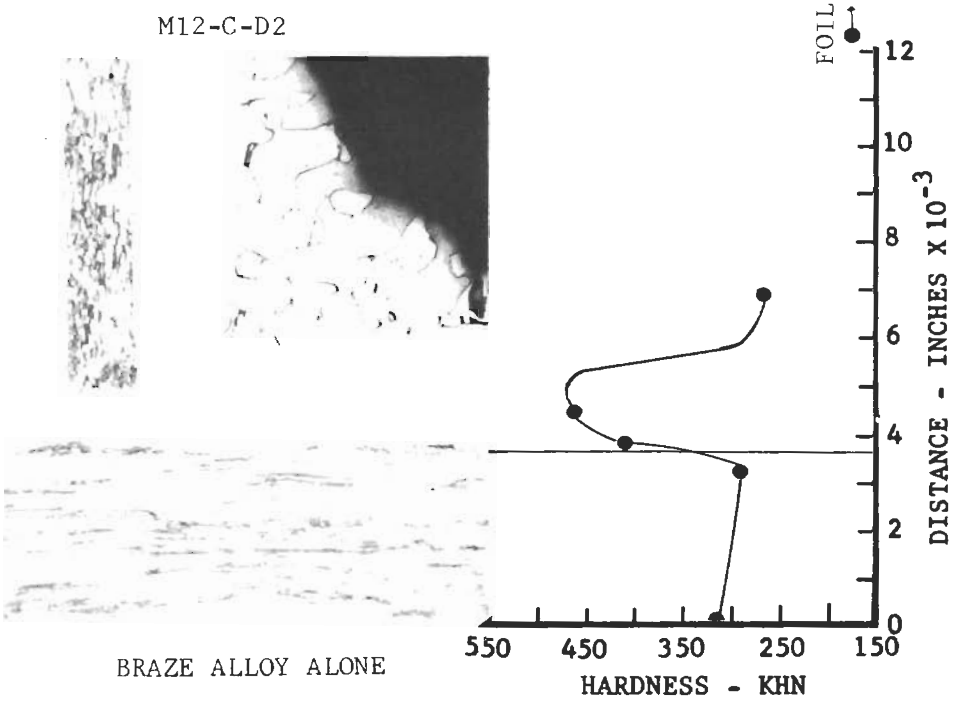
MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O

BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

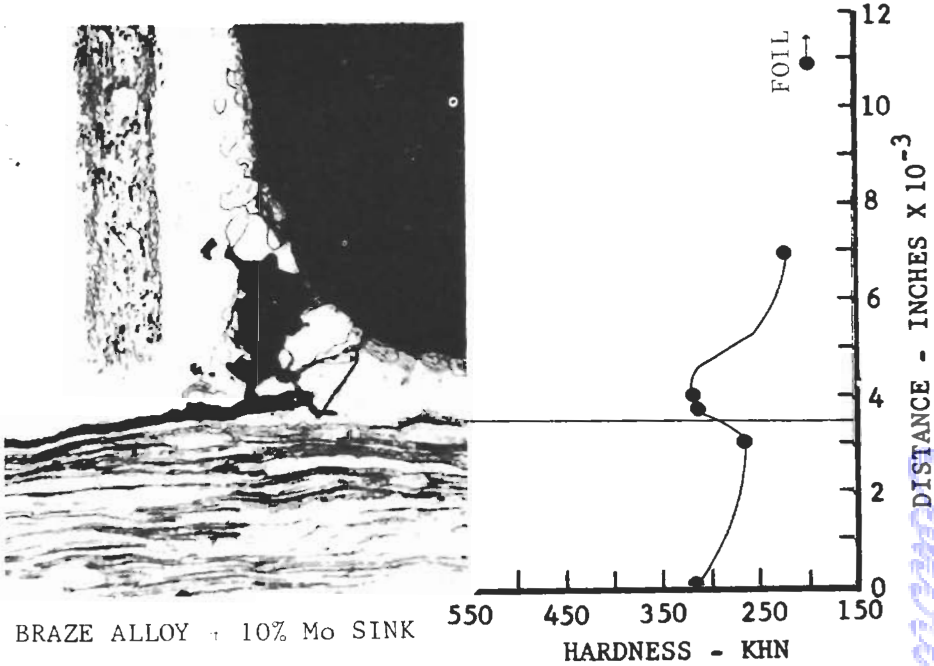
FIGURE C7 TZM TEE JOINTS BRAZED WITH Ti-25Cr-10Ni - AS BRAZED

M12-C-D2

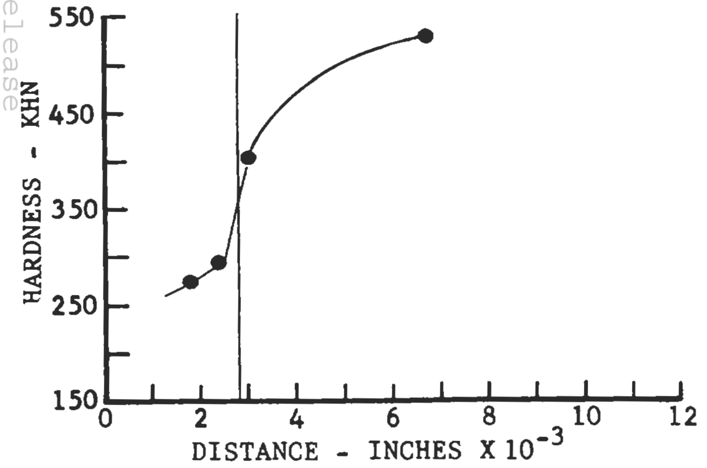


BRAZE ALLOY ALONE

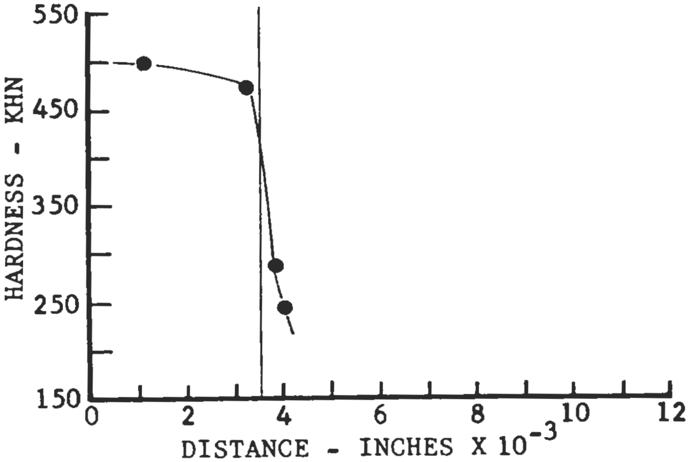
M13-C-D2



BRAZE ALLOY + 10% Mo SINK



BRAZE CYCLE: 2420F - 1 MIN.



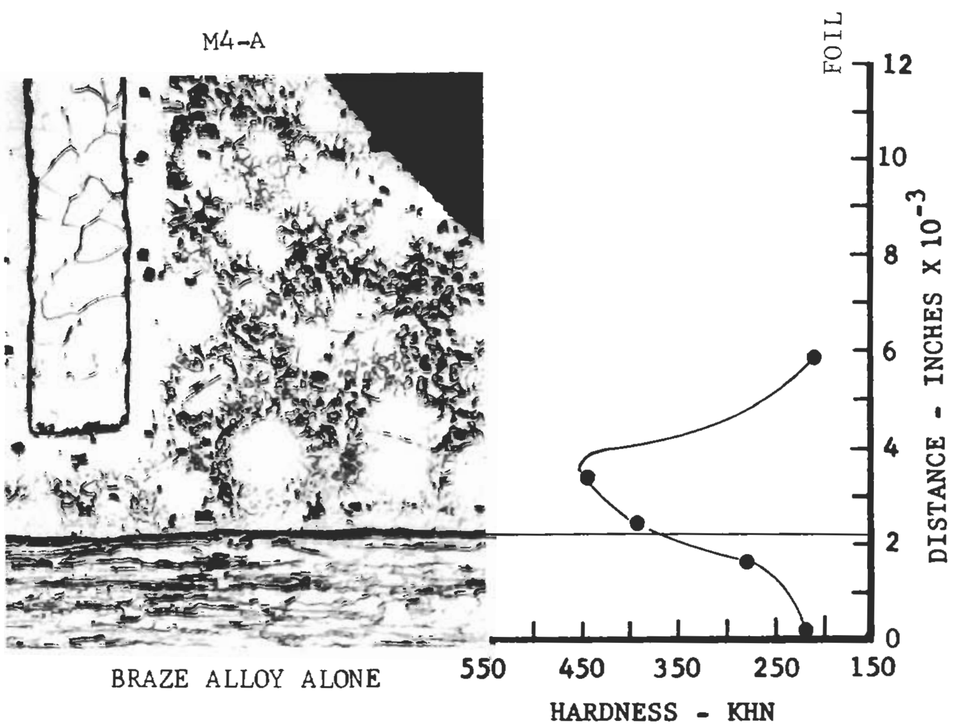
BRAZE CYCLE: 2420F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

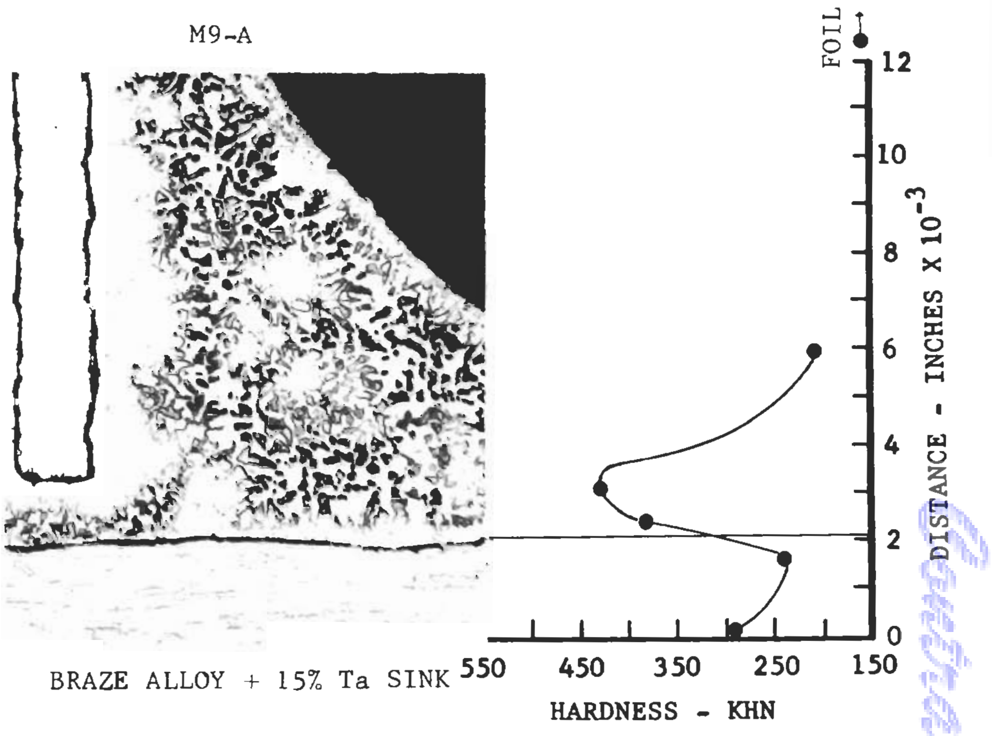
FIGURE C8 TZM TEE JOINTS BRAZED WITH Ti-25Cr-10Ni - DIFFUSED 20 HRS AT 2040F

M4-A

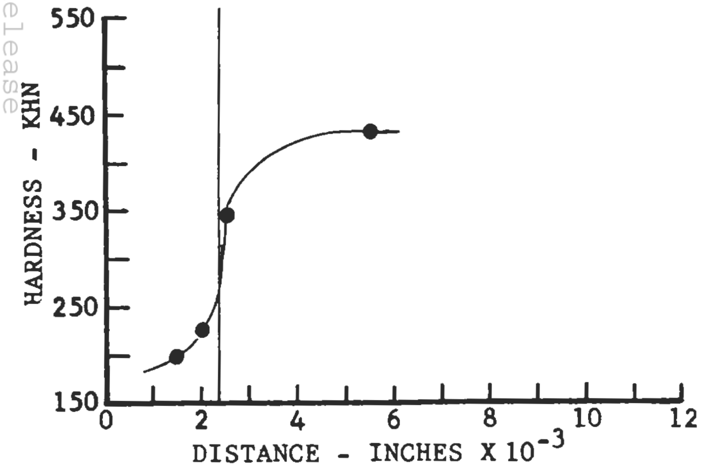


BRAZE ALLOY ALONE

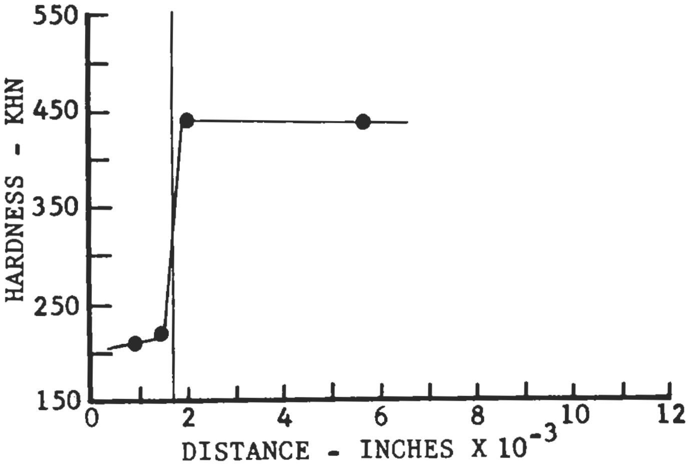
M9-A



BRAZE ALLOY + 15% Ta SINK



BRAZE CYCLE: 2580F - 1 MIN.

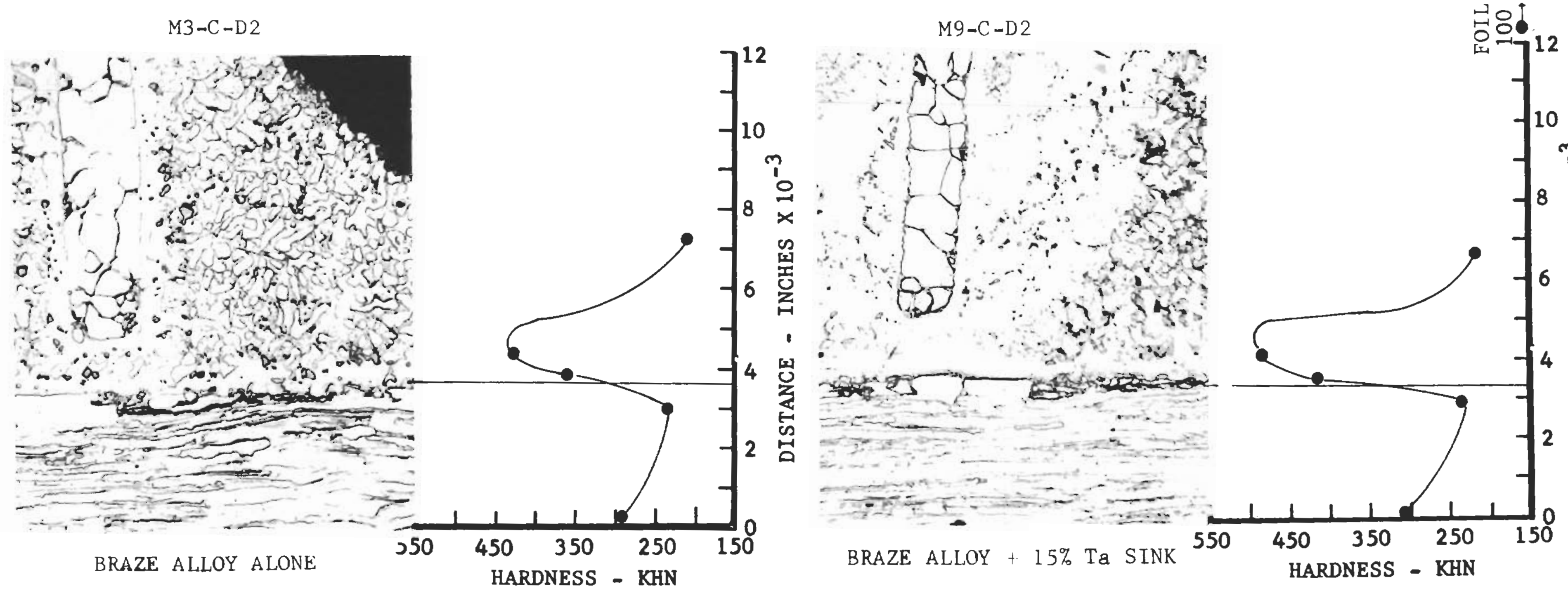


BRAZE CYCLE: 2580F - 1 MIN.

MAG. 250 x

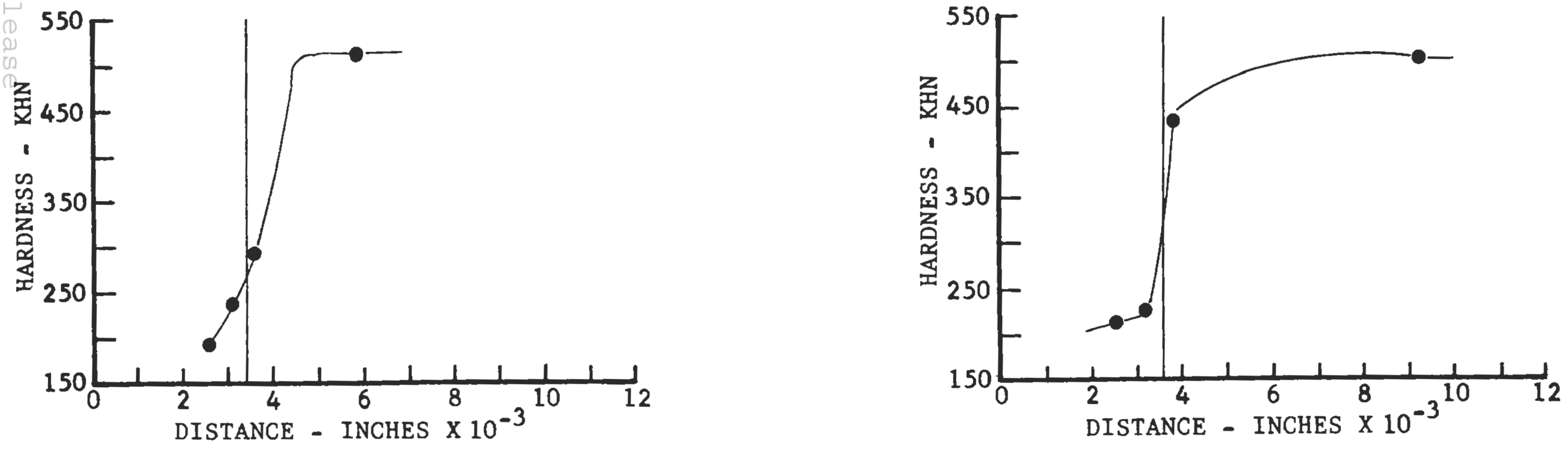
BASE MATERIAL ETCHANT: 10 gm. NaOH, 30 gm. $K_3Fe(CN)_6$, 100 ml. H_2O
BRAZE ALLOY ETCHANT: 25% HF, 12.5% H_2SO_4, 12.5% HNO_3, 50% H_2O

FIGURE C9 TZM TEE JOINTS BRAZED WITH 33Zr-34Ti-33V - AS BRAZED



BRAZE ALLOY ALONE

BRAZE ALLOY + 15% Ta SINK



BRAZE CYCLE: 2580F - 1 MIN.

BRAZE CYCLE: 2580F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 10gm. NaOH, 30gm. $K_3Fe(CN)_6$, 100ml. H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE C10 TZM TEE JOINT BRAZED WITH 33Zr-34Ti-33V - DIFFUSED 20 HOURS AT 2040F

APPENDIX D

EVALUATION OF Ta-10W TEE JOINTS

An analysis of the braze alloys evaluated on Ta-10W tee joints is presented in this Appendix along with hardness and photomicrographs. The two microhardness curves for each tee represents (1) a traverse along the foil centerline from above the fillet extending into the face sheet and (2) a traverse approximately 0.003 inch above and parallel to the face sheet-fillet interface.

The results obtained with the Cb-26V alloy are shown in Figure D1 and summarized as follows:

1. The as-brazed structure obtained with Cb-26V shows little braze alloy-base metal interaction. After a one hour exposure at 3500F, significant fillet-base metal diffusion was observed. However, this effect was not necessarily harmful.
2. Both as-brazed and thermally exposed joints showed the braze alloy, base metal, and their interactions to be solid solutions.
3. Fillet hardness was higher than observed in other systems. This was reflected in somewhat lower but acceptable joint ductility.

Results obtained with D36 are shown in Figure D2 and summarized as follows:

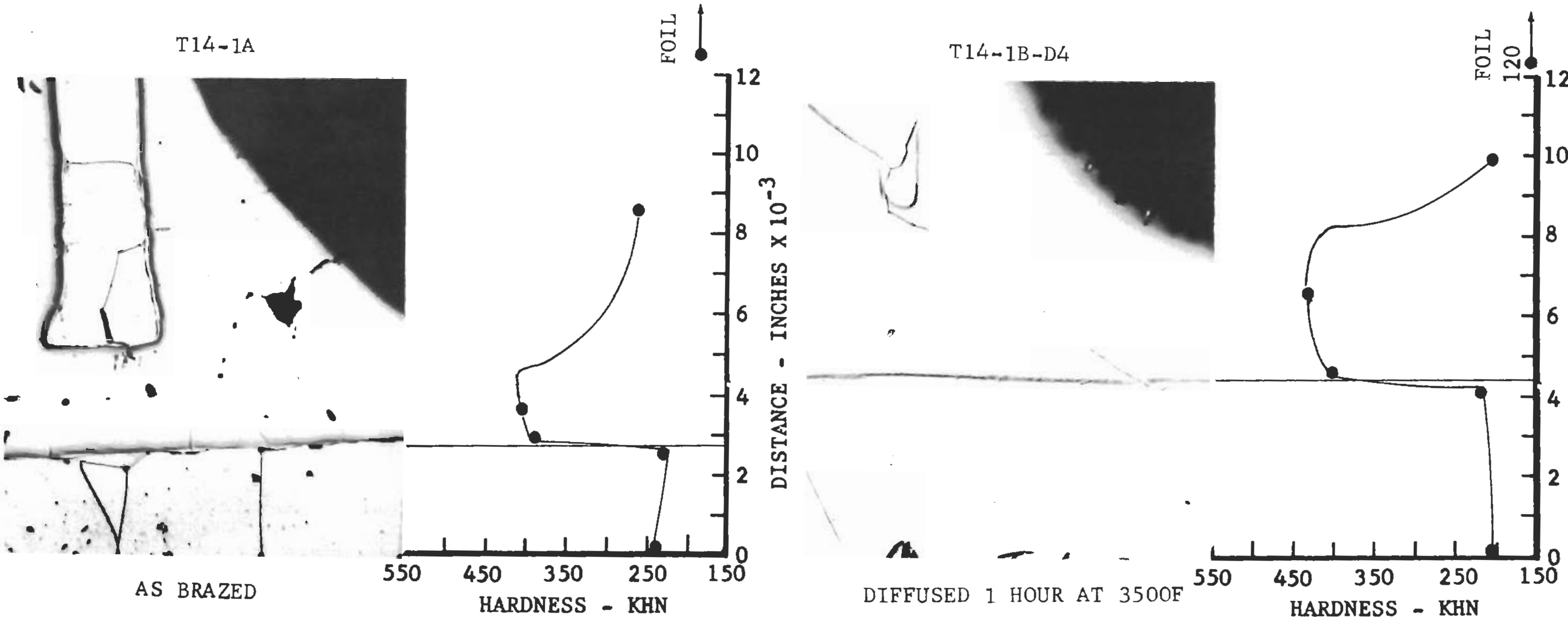
1. The as-brazed joint exhibited more braze alloy-base metal interaction than obtained with Cb-26V. However, less fillet-base metal diffusion was observed after one hour at 3500F.
2. The as-brazed fillet contained a dark-etching second phase which increased in quantity during thermal exposure.
3. Joint ductility was good in the as-brazed and thermally exposed conditions.

Tee joints brazed with Cb-1.8B are shown in Figure D3. Results are summarized below:

1. The as-brazed fillet showed boron depletion adjacent to the base metal interfaces. The boron diffused into the base metal.
2. Boron diffusion into the base metal produced a Ta-B compound on the base metal side of the base metal-fillet interfaces.
3. During thermal exposure, the quantity and continuity of the Ta-B compound increased.
4. The high hardness, lack of ductility, and distribution of the Ta-B compound caused poor joint ductility in the as-brazed and thermally exposed conditions.

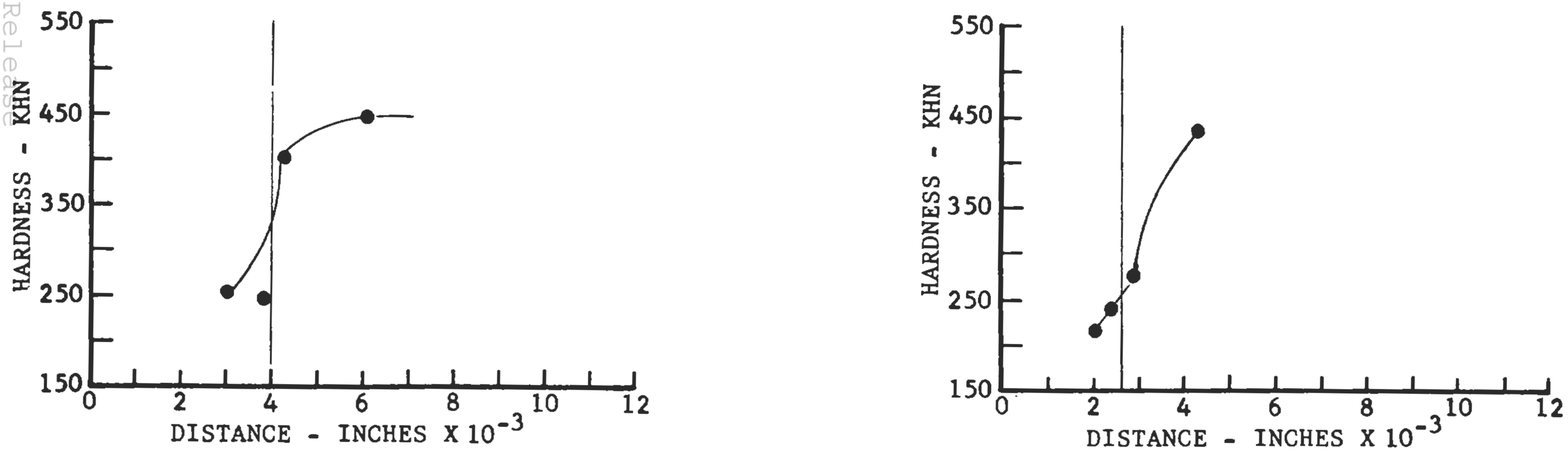
Results obtained with Cb-1.3B are shown in Figure D4 and summarized as follows:

1. Reduction in boron content of the braze alloy eliminated the brittle Ta-B interface compound, resulting in ductile joints both in the as-brazed and thermally exposed conditions.
2. The as-brazed structure shows that boron rapidly diffused into the base material. Discontinuous borides were observed in base metal grain boundaries and as a Widmanstatten structure within the grains.



AS BRAZED

DIFFUSED 1 HOUR AT 3500F



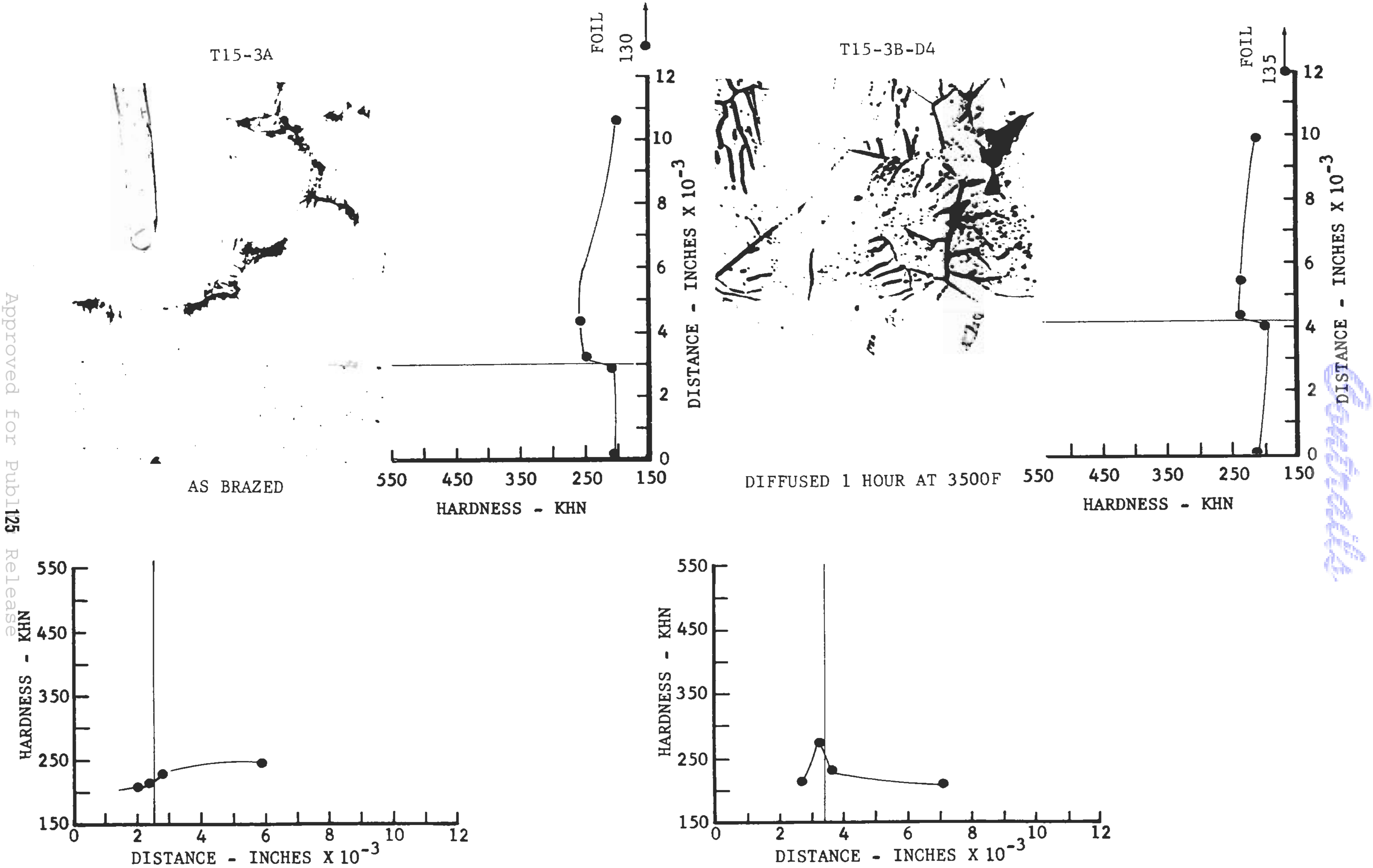
BRAZE CYCLE: 3800F - 1 MIN.

BRAZE CYCLE: 3800F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE D1 Ta-10W TEE JOINTS BRAZED WITH Cb-26V



AS BRAZED

DIFFUSED 1 HOUR AT 3500F

BRAZE CYCLE: 4240F - 1 MIN.

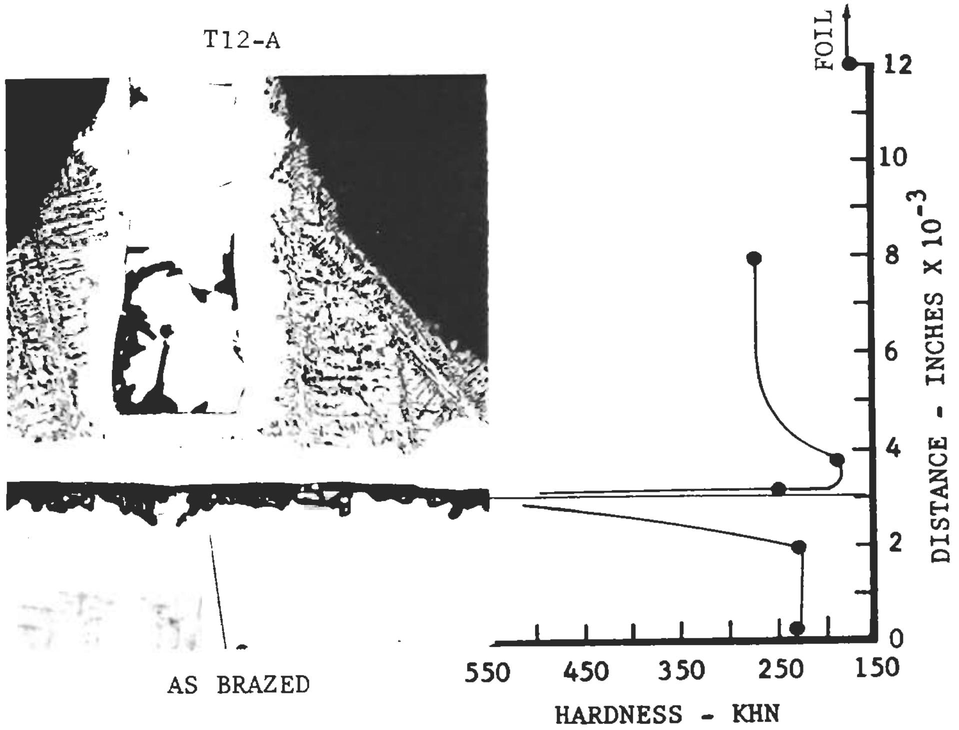
BRAZE CYCLE: 4240F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

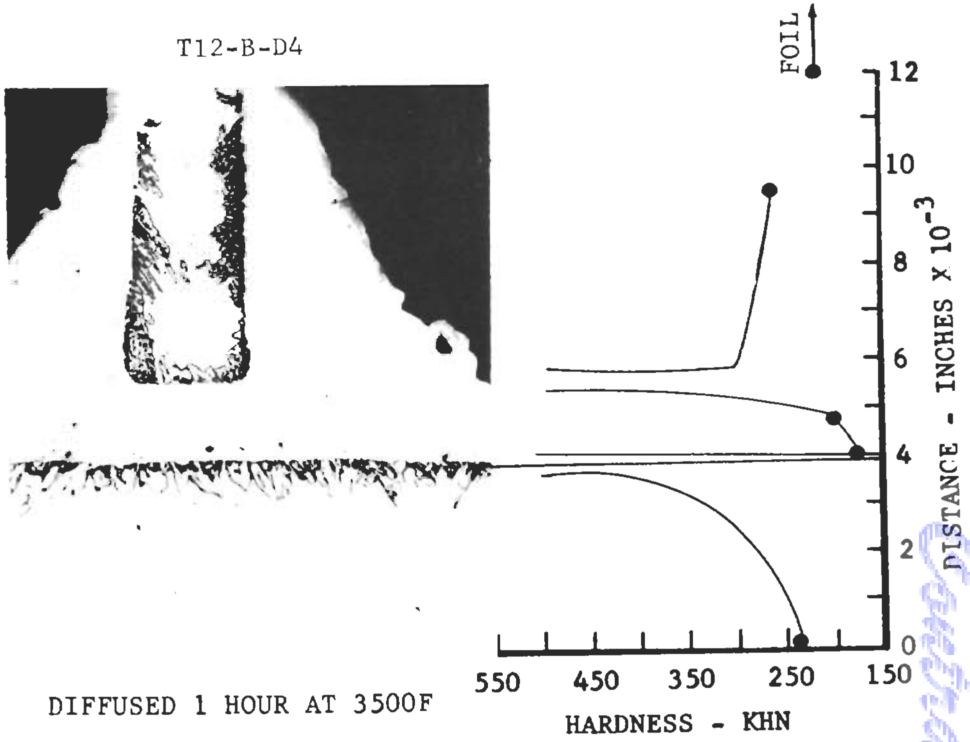
FIGURE D2 Ta-10W TEE JOINTS BRAZED WITH Cb-10Ti-5Zr

T12-A

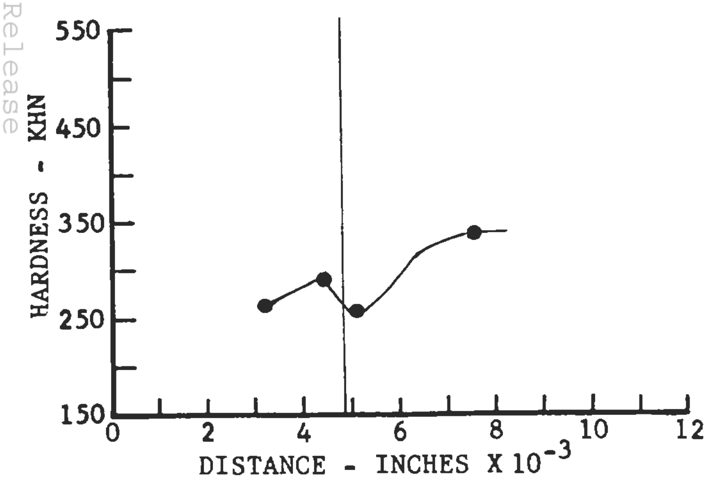


AS BRAZED

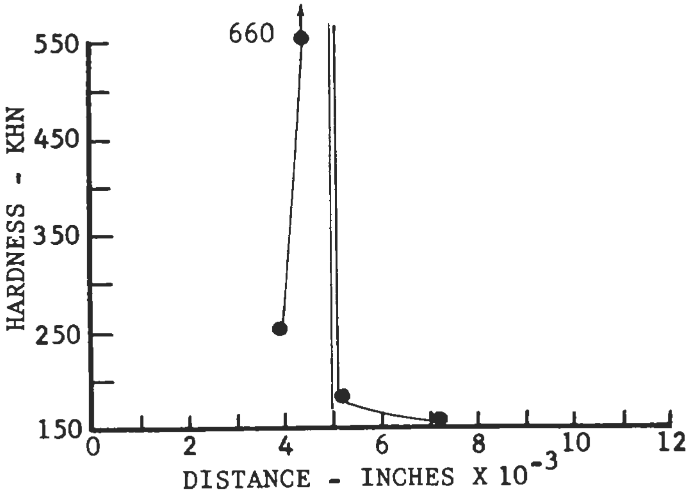
T12-B-D4



DIFFUSED 1 HOUR AT 3500F



BRAZE CYCLE: 4100F - 1 MIN.



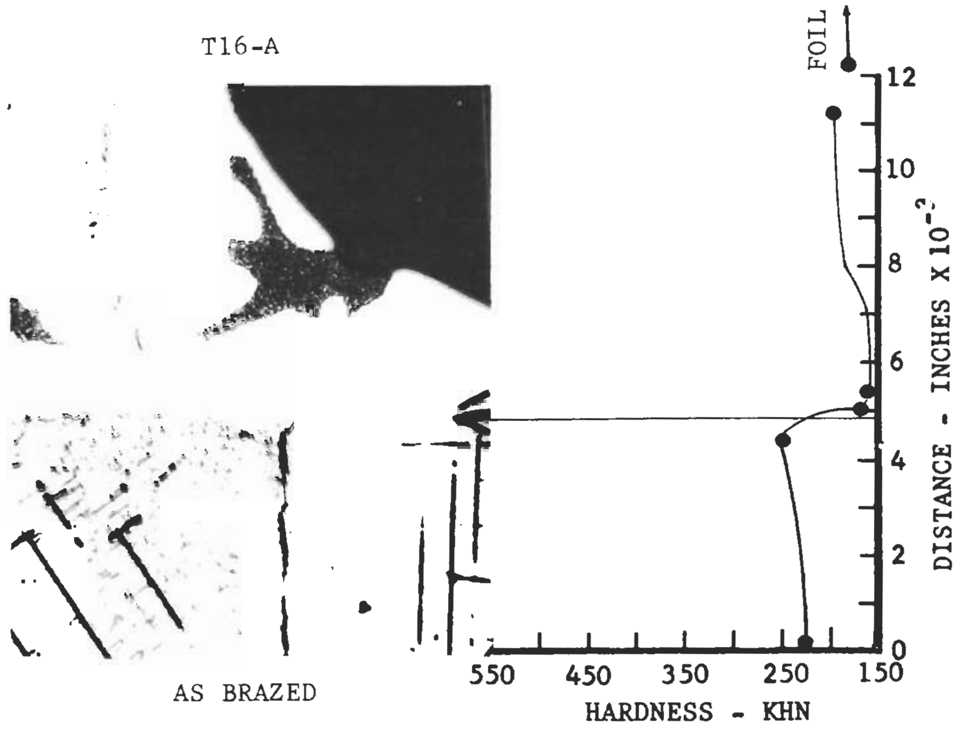
BRAZE CYCLE: 4100F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

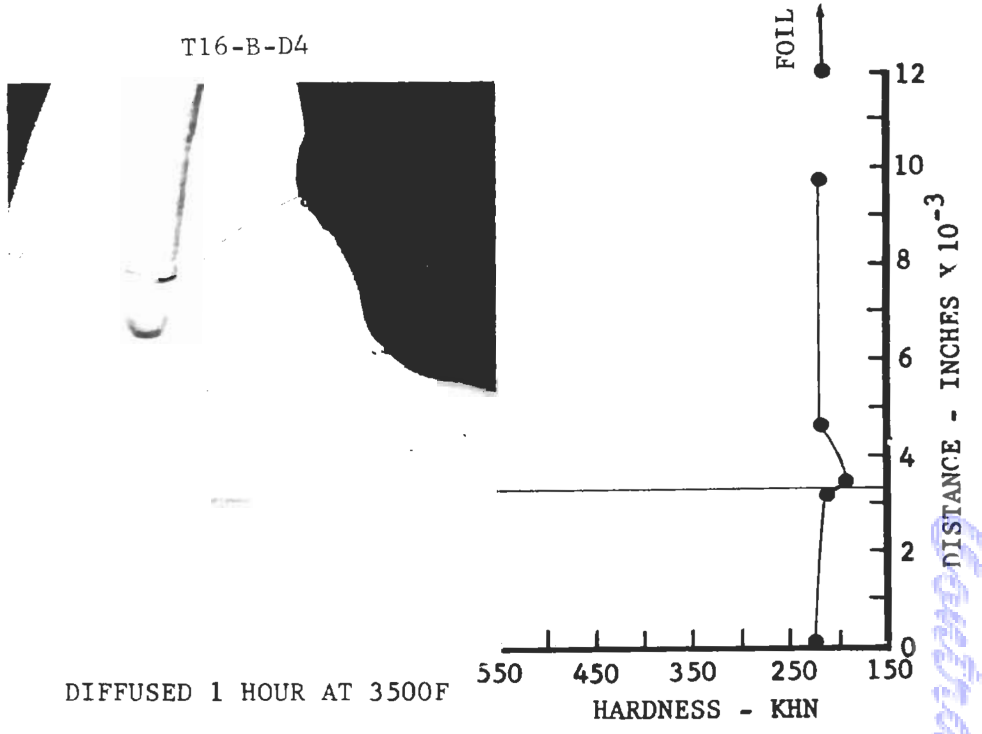
FIGURE D3 Ta-10W TEE JOINTS BRAZED WITH Cb-1.8B

T16-A

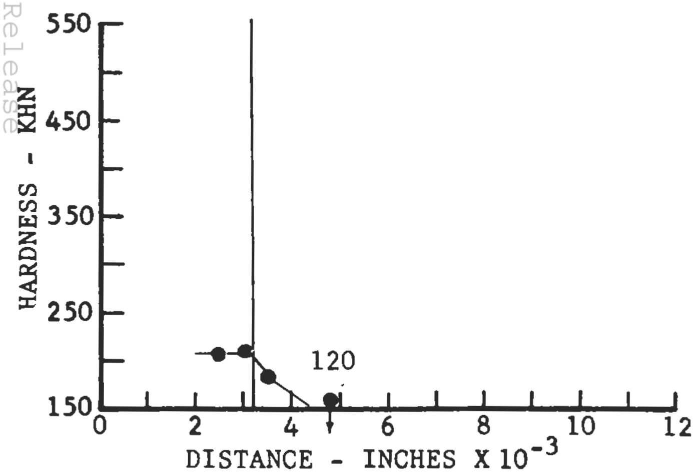


AS BRAZED

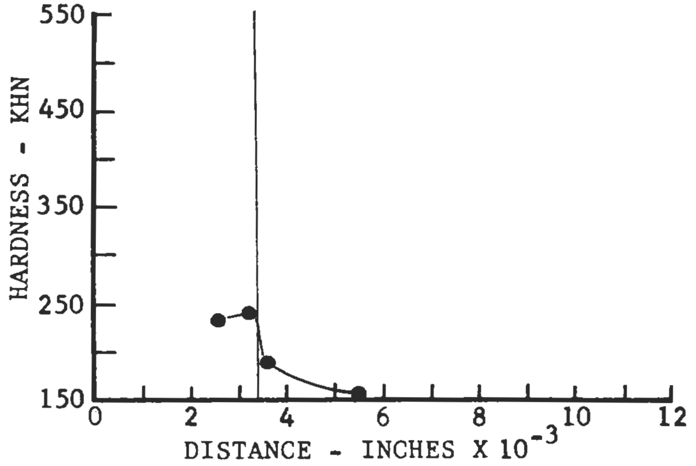
T16-B-D4



DIFFUSED 1 HOUR AT 3500F



BRAZE CYCLE: 4200F - 1 MIN.



BRAZE CYCLE: 4200F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE D4 Ta-10W TEE JOINTS BRAZED WITH Cb-1.3B

3. During the exposure at 3500F, the borides apparently dissolved in the base metal. No grain boundary borides or Widmanstatten structure remained.

Figures D5 and D6 show results obtained with Ti-28Zr-15Mo-10Ta with and without tantalum sink powder. The joint brazed with no sink powder and diffused 10 hours at 2850F shows sufficient fillet-base metal diffusion to indicate remelt potential. However, joints with and without sink powder exhibited formation of additional phases and high fillet hardnesses after diffusion. It is doubtful that these joints would possess adequate ductility. Therefore, no further effort was devoted to this system.

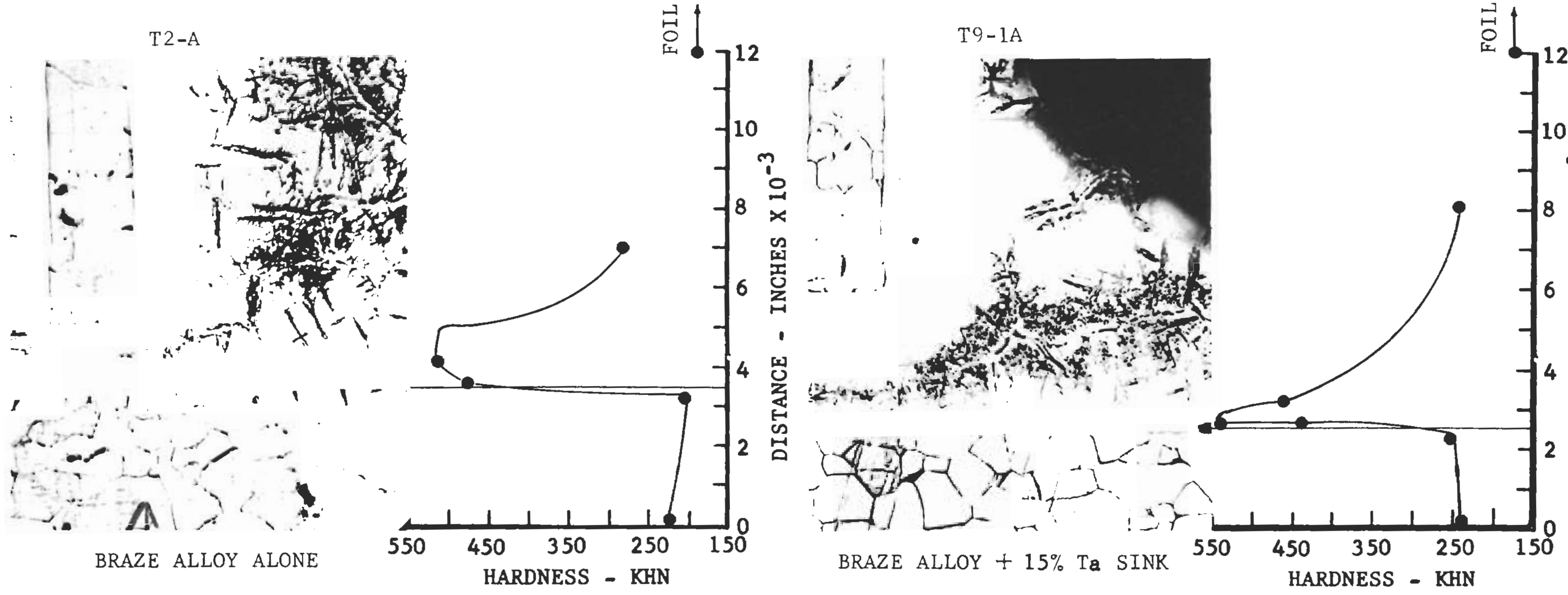
Results obtained with Ti-21.5V-1.5Si-25Ta are shown in Figures D7 and D8. As-brazed joints with and without sink powder show a eutectic structure in the fillets. Both as-brazed and diffused joints exhibited a trend toward increased hardness with diffusion in joints with and without sink powder. However, some loss of fillets by melting and/or evaporation occurred during the diffusion treatment.

Results obtained with the Ti-27V-7Fe system are shown in Figures D9 and D10. A diffusion treatment of 85 hours at 2050F produced substantial fillet-base metal diffusion. Sufficient diffusion was observed in the joint without sink powder to indicate remelt potential. A continuous phase also formed in the base metal at the base metal-braze alloy interfaces. However, the diffusion treatment produced a substantial increase in fillet hardness. Microstructures of tee joints brazed with 33Zr-34Ti-33V are shown in Figures D11 and D12. The 40 hour diffusion treatment at 2130F produced substantial fillet-base metal diffusion in joints with and without Ta sink powder. However, the diffused microstructures showed that somewhat greater diffusion would be required to develop high remelt temperatures. In addition, the diffused joint containing Ta sink powder showed a significant increase in hardness over the diffused joint with braze alloy alone.

The 33Zr-34Ti-33V braze alloy exhibited a solidus of approximately 2200F which was the limiting diffusion treating temperature to prevent fillet run-off. Very long diffusion times would have been necessary at this temperature. It was found that holding 15 minutes at the braze temperature (2600F) produced sufficient diffusion to raise the solidus above 2400F. Figure D13 shows the structure of a tee (honeycomb) fillet after this braze cycle and a stepped diffusion treatment of 20 hours at 2400F plus 44 hours at 2500F plus 24 hours at 2600F. This treatment produced complete alloying between the fillet and Ta-10W foil.

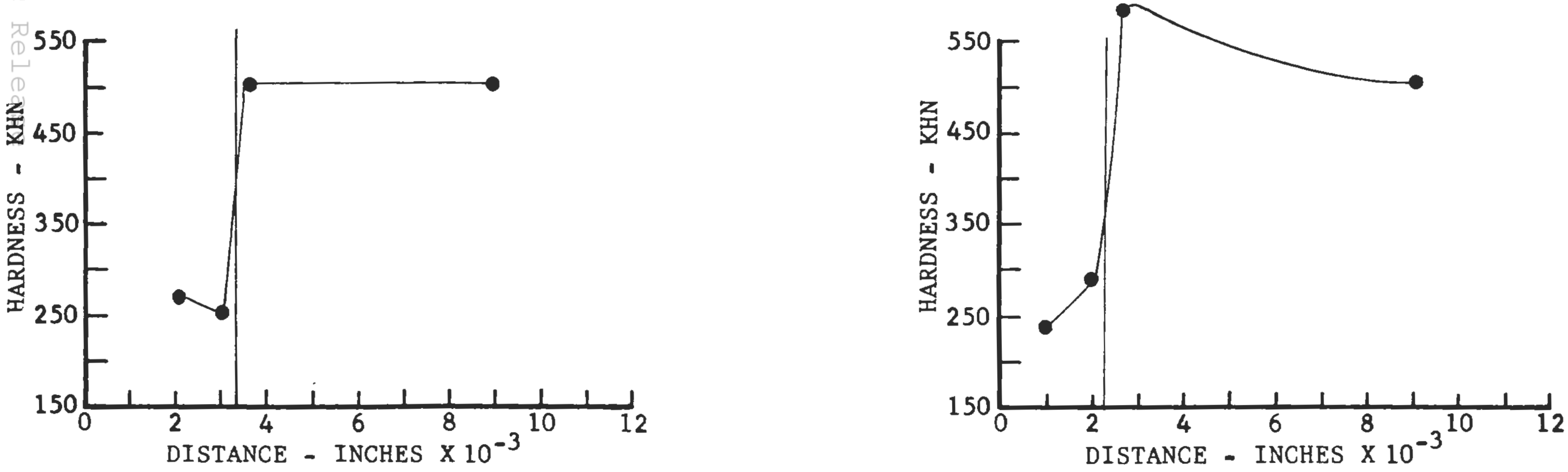
The 46Zr-34V-20Ti alloy was not evaluated extensively because results were similar to those observed with 33Zr-34Ti-33V. In addition, the low liquidus temperature required long impractical diffusion treatments to produce desired remelt temperatures.

Figure D14 shows as-brazed results obtained with Ti-29V-2Si. These microstructures show a eutectic phase and, in general, appear quite similar to the as-brazed Ti-21.5V-1.5Si-25Ta microstructures of Figure D7.



BRAZE ALLOY ALONE

BRAZE ALLOY + 15% Ta SINK



BRAZE CYCLE: 3100F - 1 MIN.

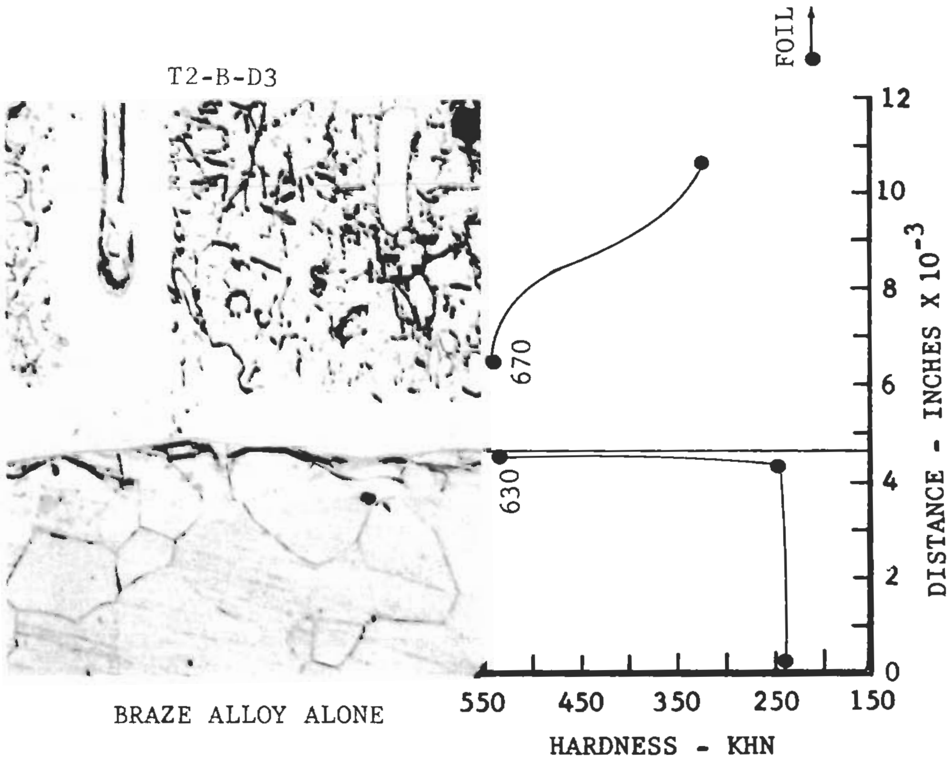
BRAZE CYCLE: 3100F - 1 MIN.

MAG 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

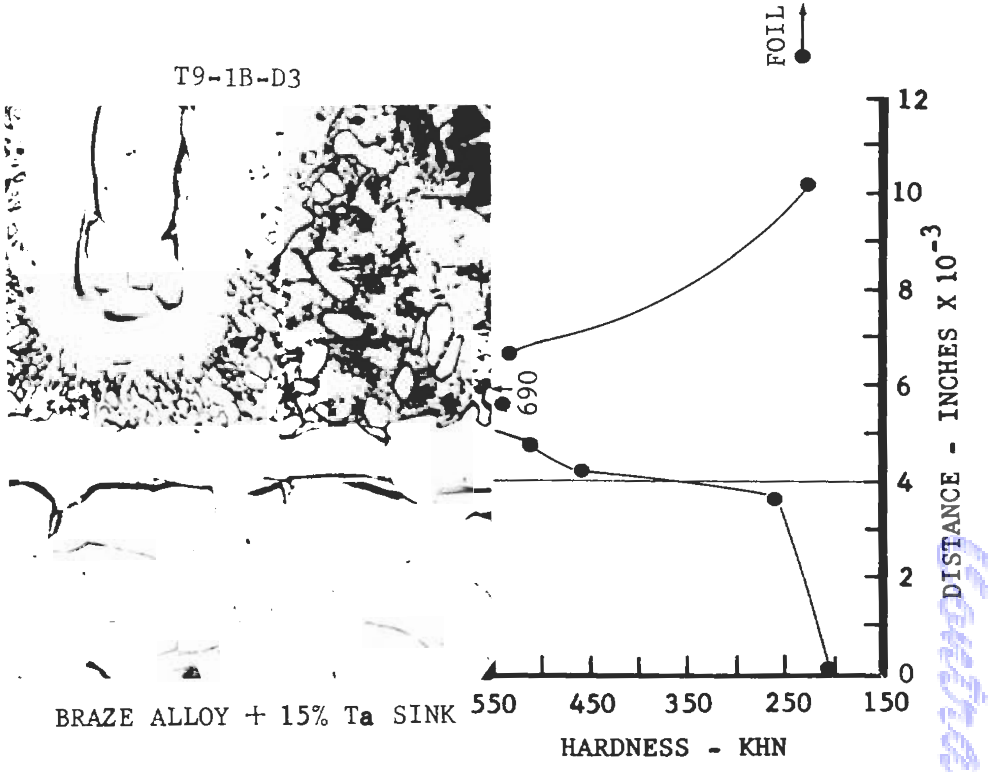
FIGURE D5 Ta-10W TEE JOINTS BRAZED WITH Ti-28Zr-15Mo-10Ta - AS BRAZED

T2-B-D3

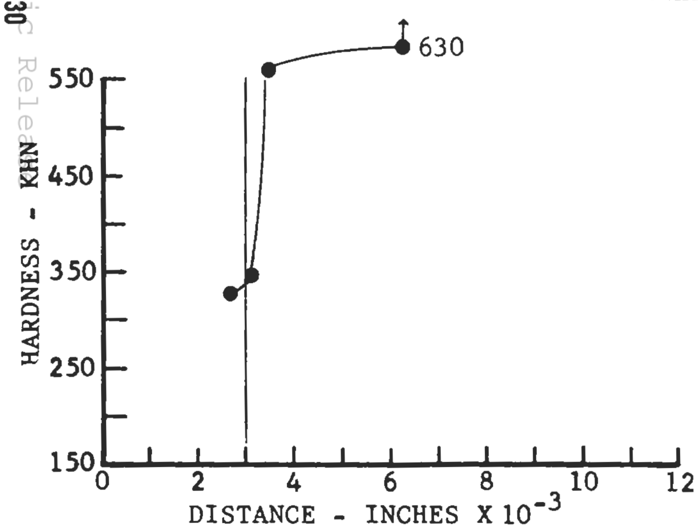


BRAZE ALLOY ALONE

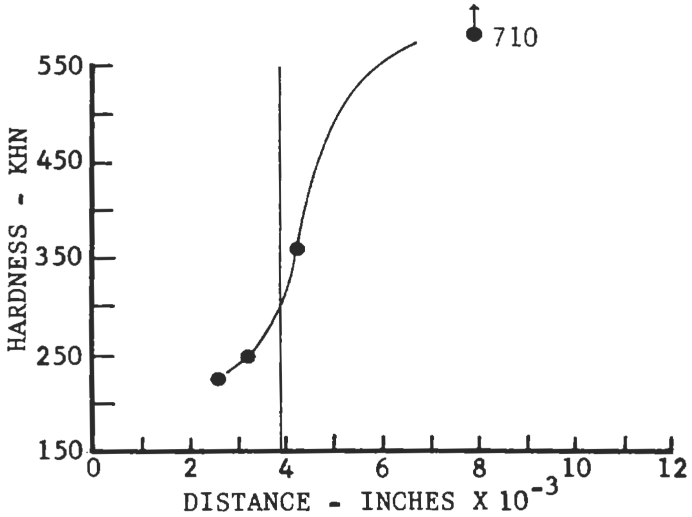
T9-1B-D3



BRAZE ALLOY + 15% Ta SINK



BRAZE CYCLE: 3100F - 1 MIN.

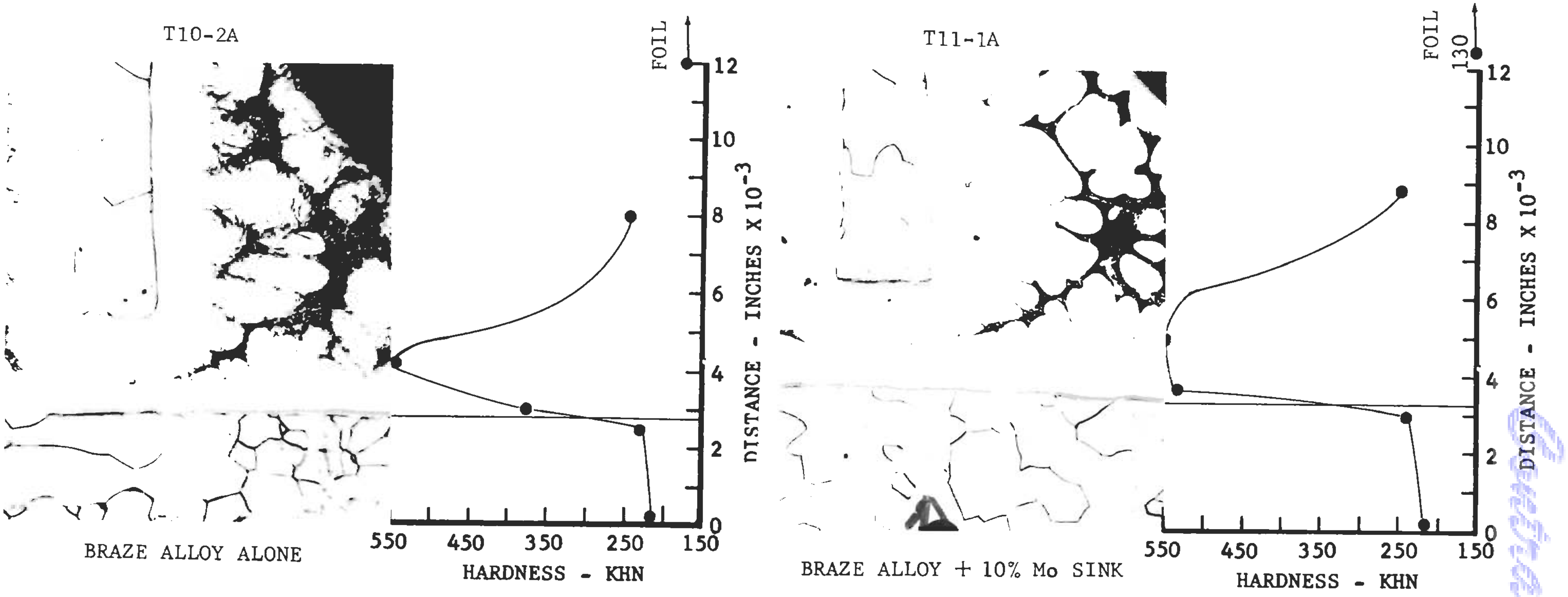


BRAZE CYCLE: 3100F - 1 MIN.

MAG. 250 x

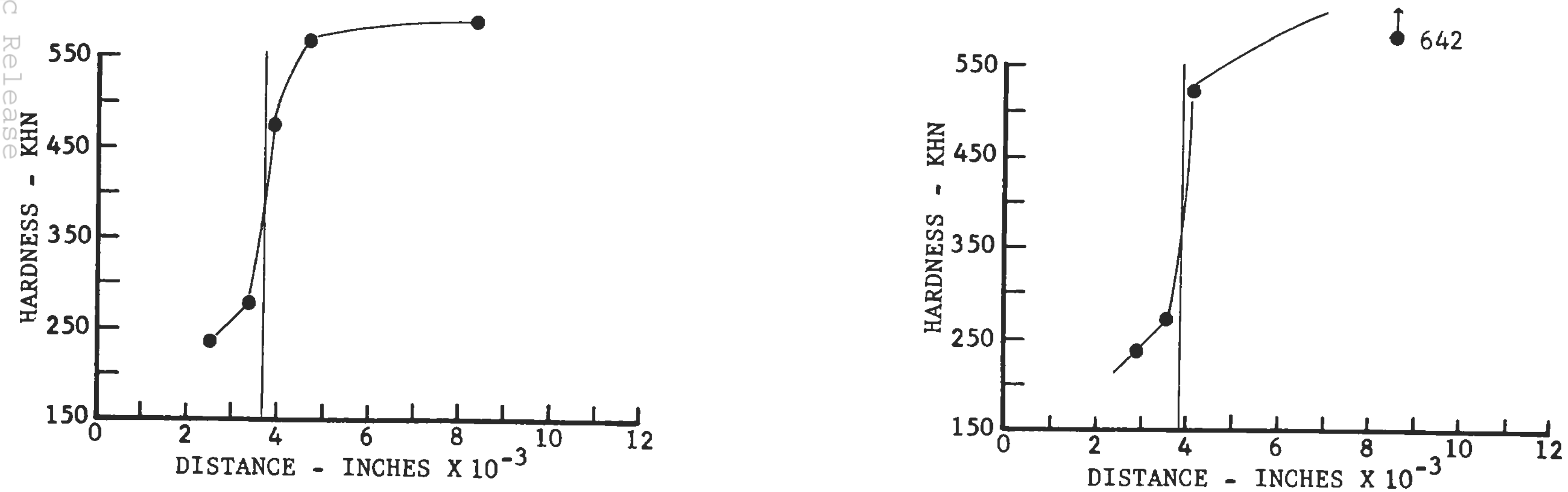
BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE D6 Ta-10W TEE JOINTS BRAZED WITH Ti-28Zr-15Mo-10Ta - DIFFUSED 10 HOURS AT 2850F



BRAZE ALLOY ALONE

BRAZE ALLOY + 10% Mo SINK



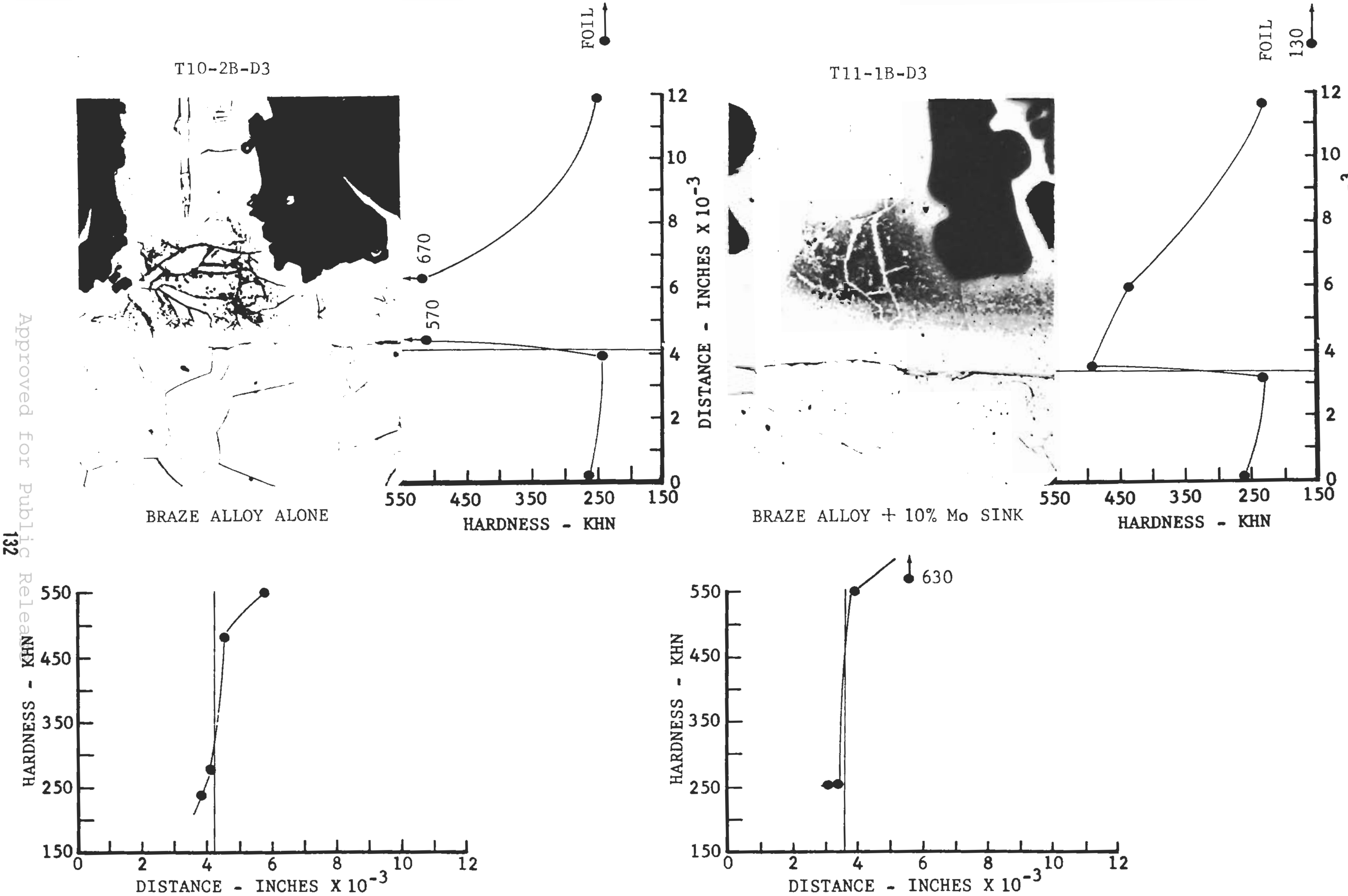
BRAZE CYCLE: 3120F - 1 MIN.

BRAZE CYCLE: 3120F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT:	70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT:	1 HF, 2 HNO_3, 97 H_2O

FIGURE D7 Ta-10W TEE JOINTS BRAZED WITH Ti-21.5V-1.5Si-25Ta - AS BRAZED



BRAZE ALLOY ALONE

BRAZE ALLOY + 10% Mo SINK

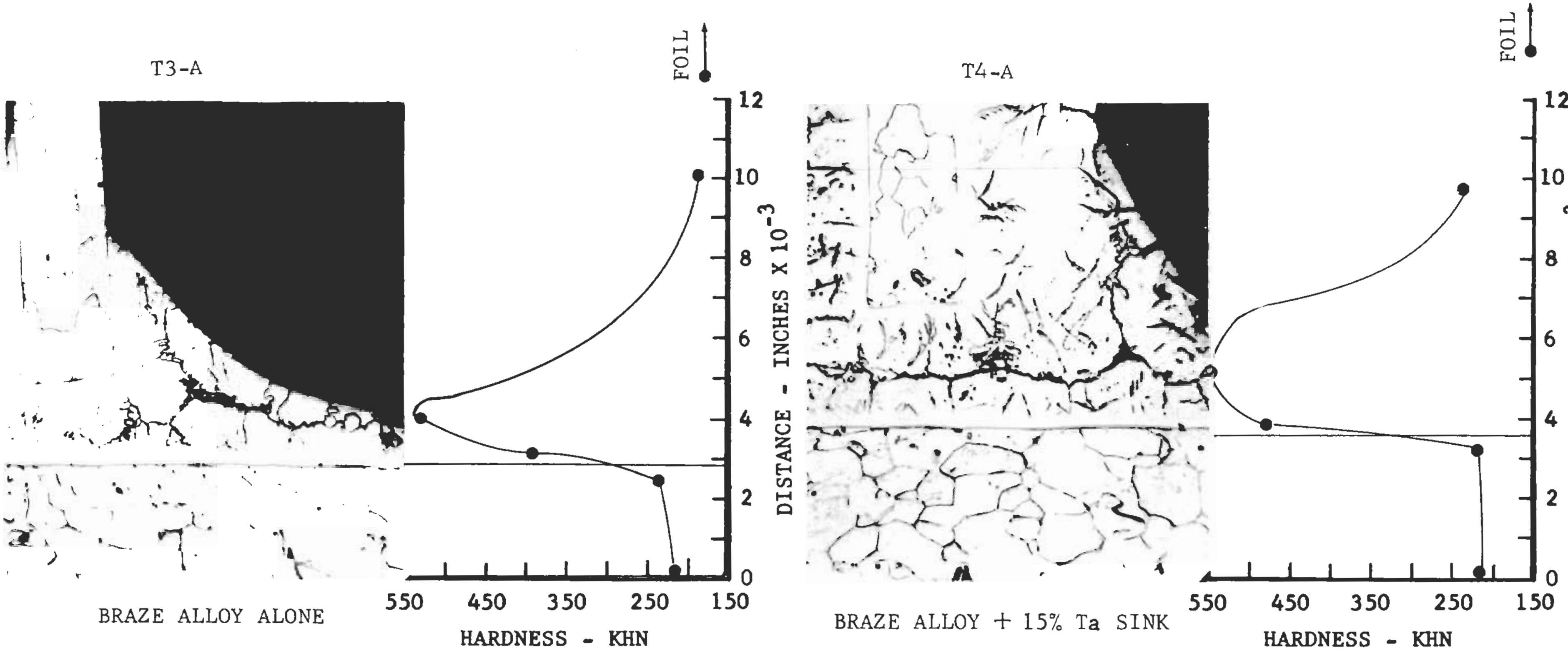
BRAZE CYCLE: 3120F - 1 MIN.

BRAZE CYCLE: 3120F - 1 MIN.

MAG. 250 x

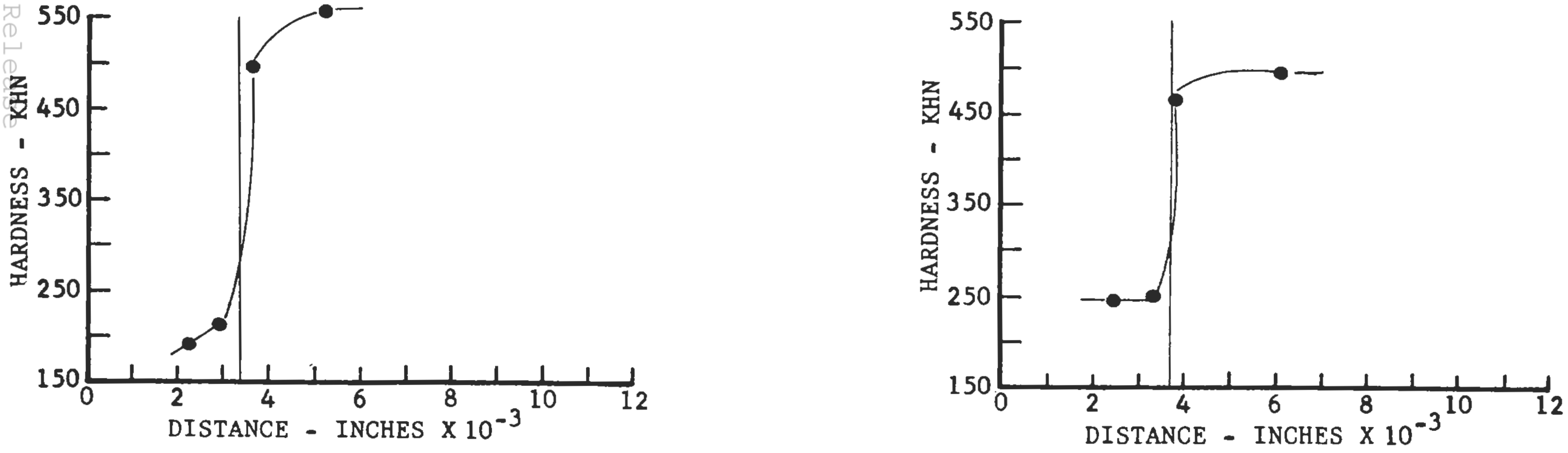
BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE D8 Ta-10W TEE JOINTS BRAZED WITH Ti-21.5V-1.5Si-25Ta - DIFFUSED 10 HOURS AT 2850F



BRAZE ALLOY ALONE

BRAZE ALLOY + 15% Ta SINK



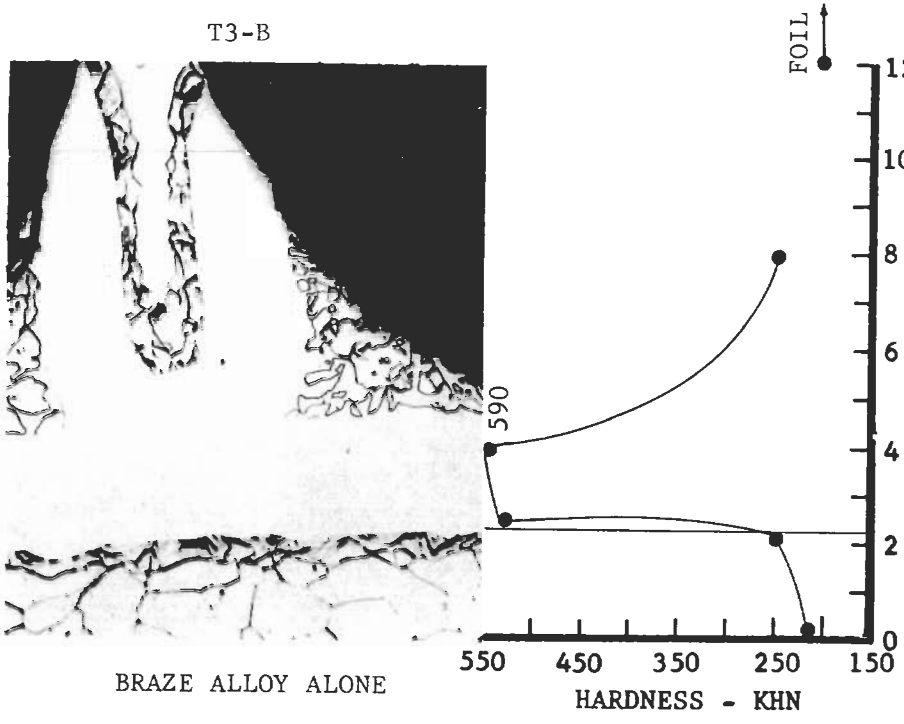
BRAZE CYCLE: 2820F - 1 MIN.

BRAZE CYCLE: 2820F - 1 MIN.

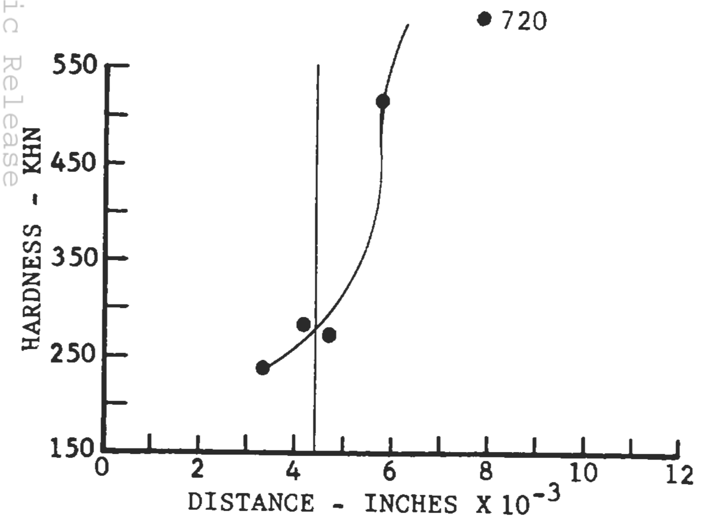
MAG. 250 x

BASE MATERIAL ETCHANT: 25 HF, 12.5 H_2SO_4, 12.5 HNO_3, 50 H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

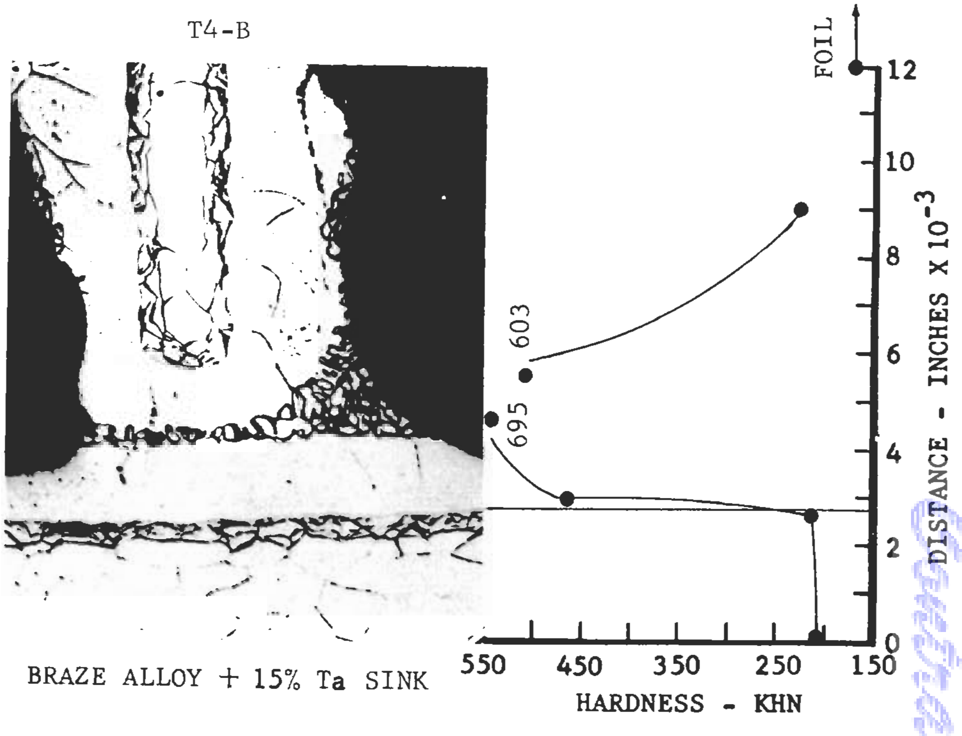
FIGURE D9 Ta-10W TEE JOINTS BRAZED WITH Ti-27V-7Fe - AS BRAZED



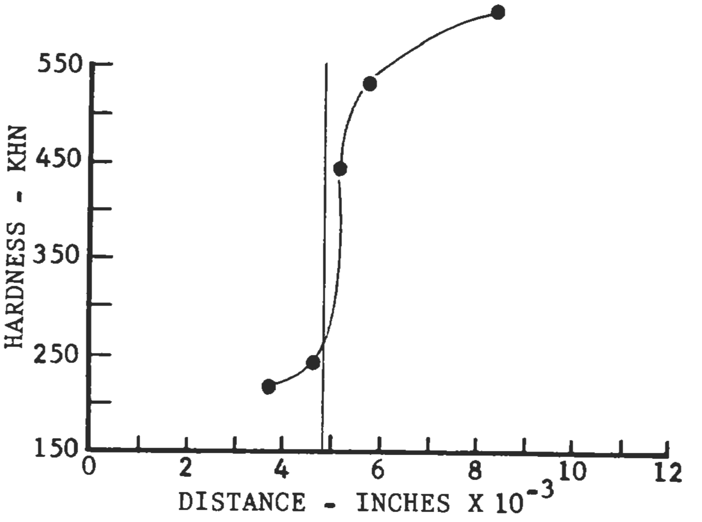
BRAZE ALLOY ALONE



BRAZE CYCLE: 2820F - 1 MIN.



BRAZE ALLOY + 15% Ta SINK

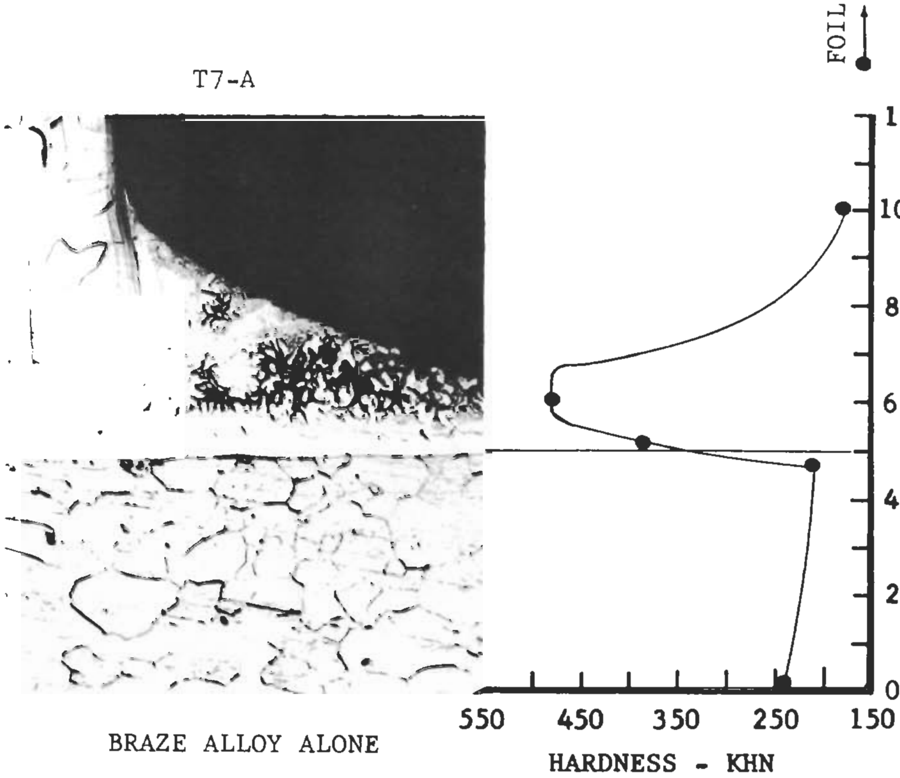


BRAZE CYCLE: 2820F - 1 MIN.

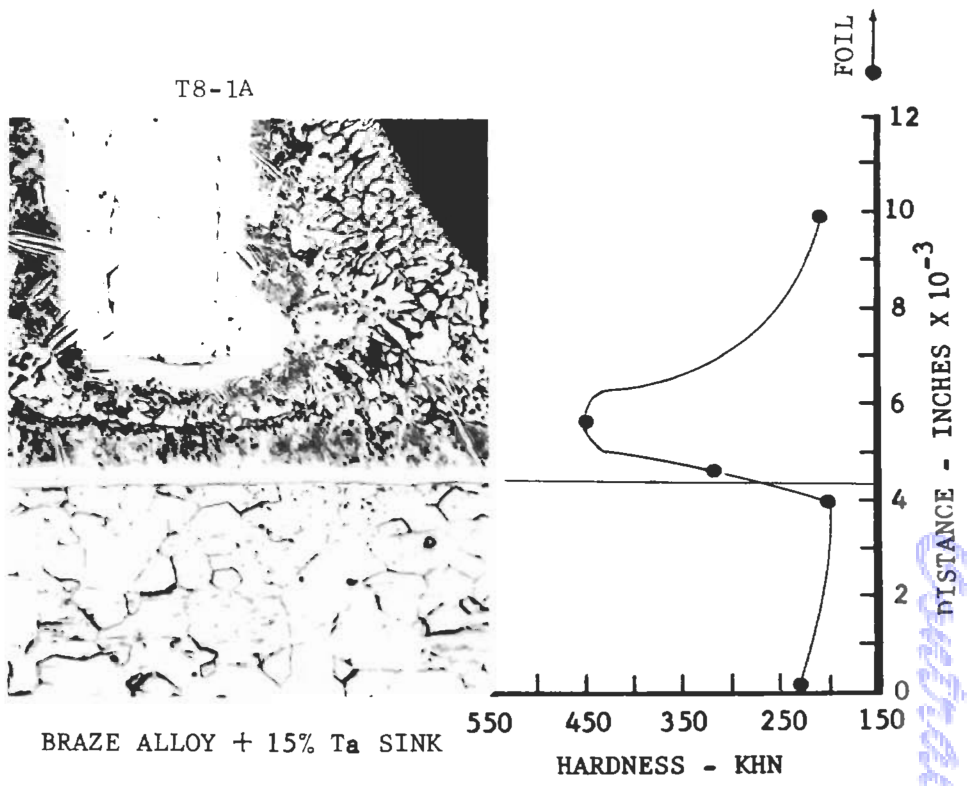
MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

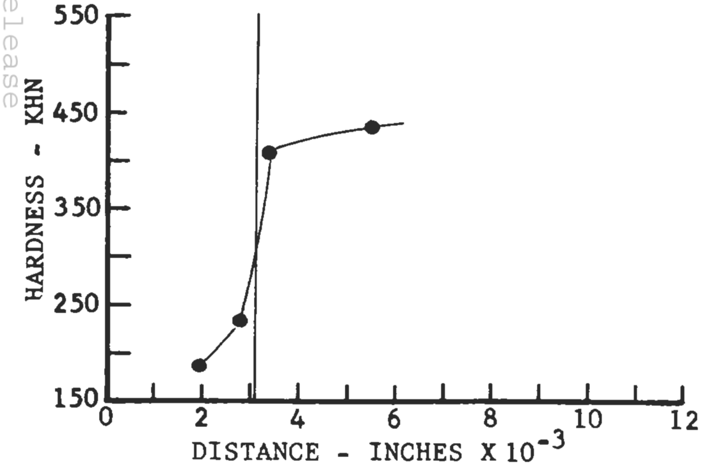
FIGURE D10 Ta-10W TEE JOINTS BRAZED WITH Ti-27V-7Fe - DIFFUSED 85 HOURS AT 2050F

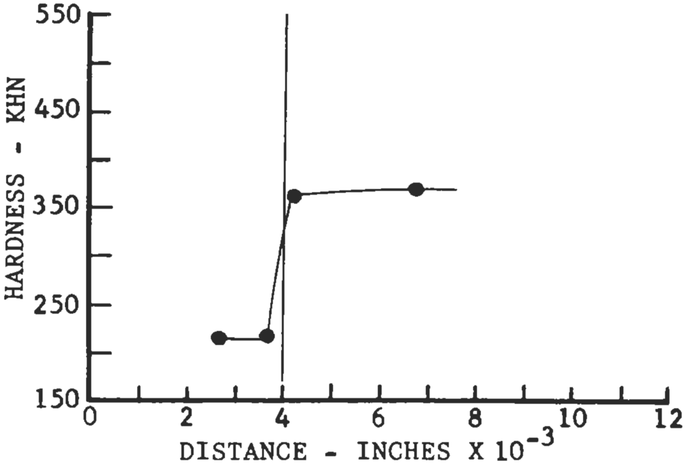


BRAZE ALLOY ALONE



BRAZE ALLOY + 15% Ta SINK





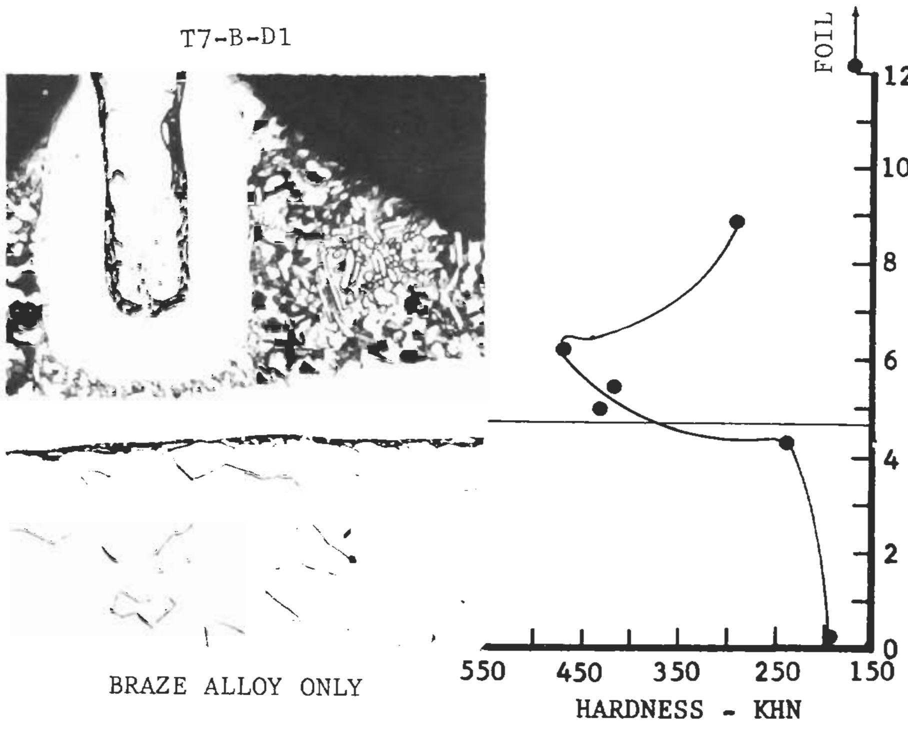
BRAZE CYCLE: 2600F - 1 MIN.

BRAZE CYCLE: 2600F - 1 MIN.

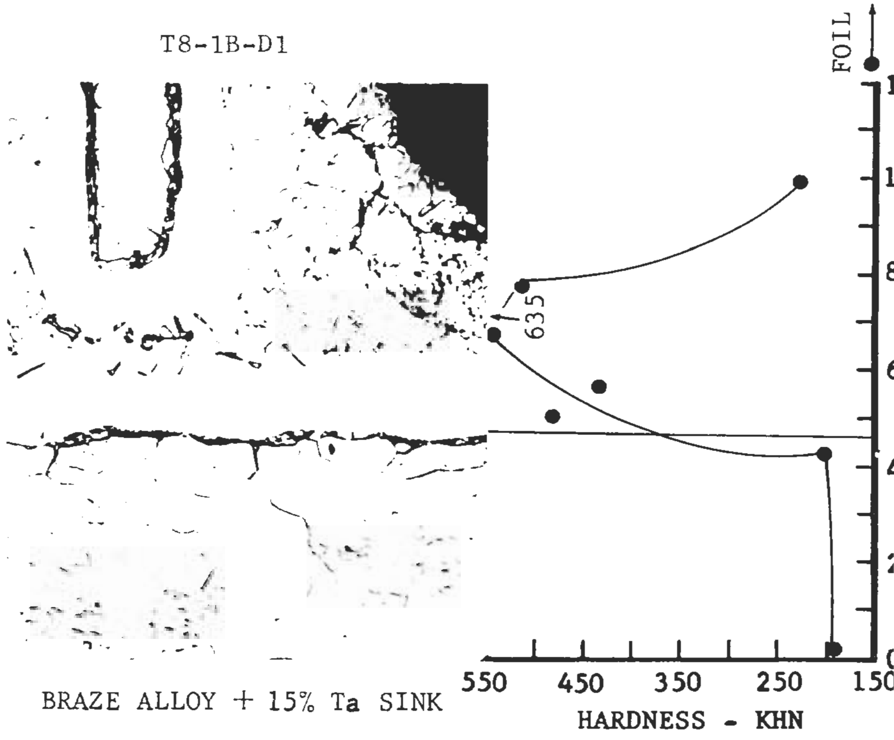
MAG. 250 x

BASE MATERIAL ETCHANT: 25 HF, 12.5 H_2SO_4, 12.5 HNO_3, 50 H_2O
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

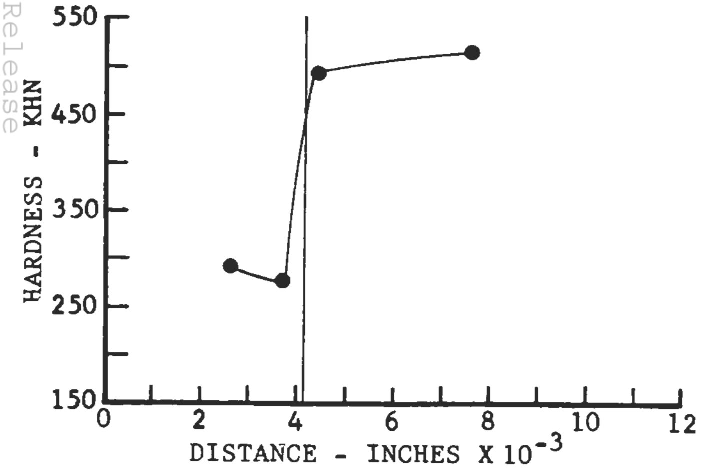
FIGURE D11 Ta-10W TEE JOINTS BRAZED WITH 33Zr-34Ti-33V - AS BRAZED



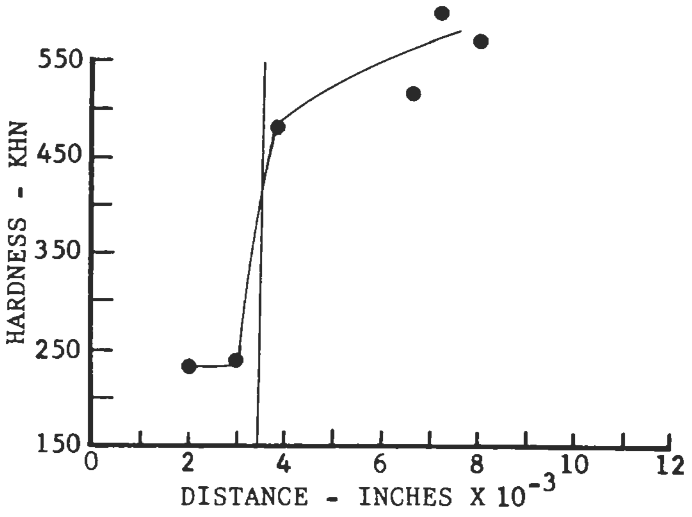
BRAZE ALLOY ONLY



BRAZE ALLOY + 15% Ta SINK



BRAZE CYCLE: 2600F - 1 MIN.

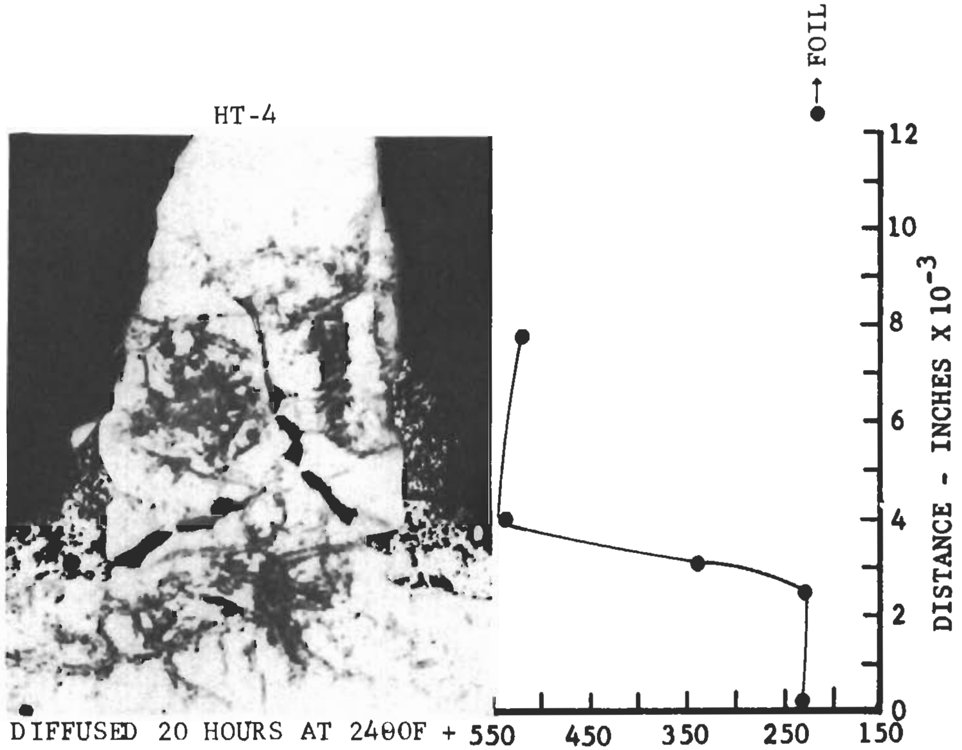


BRAZE CYCLE: 2600F - 1 MIN.

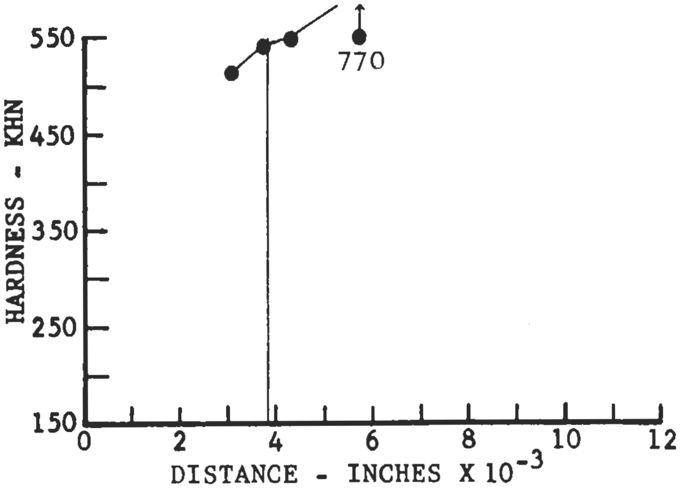
MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

FIGURE D12 Ta-10W TEE JOINTS BRAZED WITH 33Zr-34Ti-33V - DIFFUSED 40 HOURS AT 2130F



DIFFUSED 20 HOURS AT 2400F + 44 HOURS AT 2500F + 24 HOURS AT 2600F



BRAZE CYCLE: 2600F - 15 MINUTES

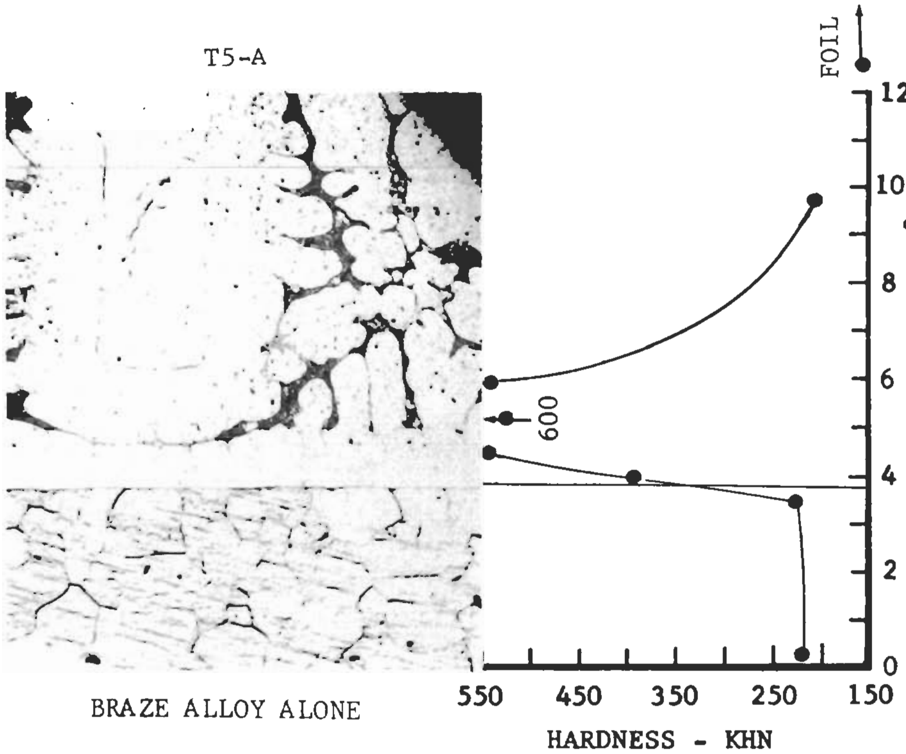
MAG. 250X

BASE MATERIAL ETCHANT: 25 HF, 12.5 H_2SO_4, 12.5 HNO_3, 50 H_2O

BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

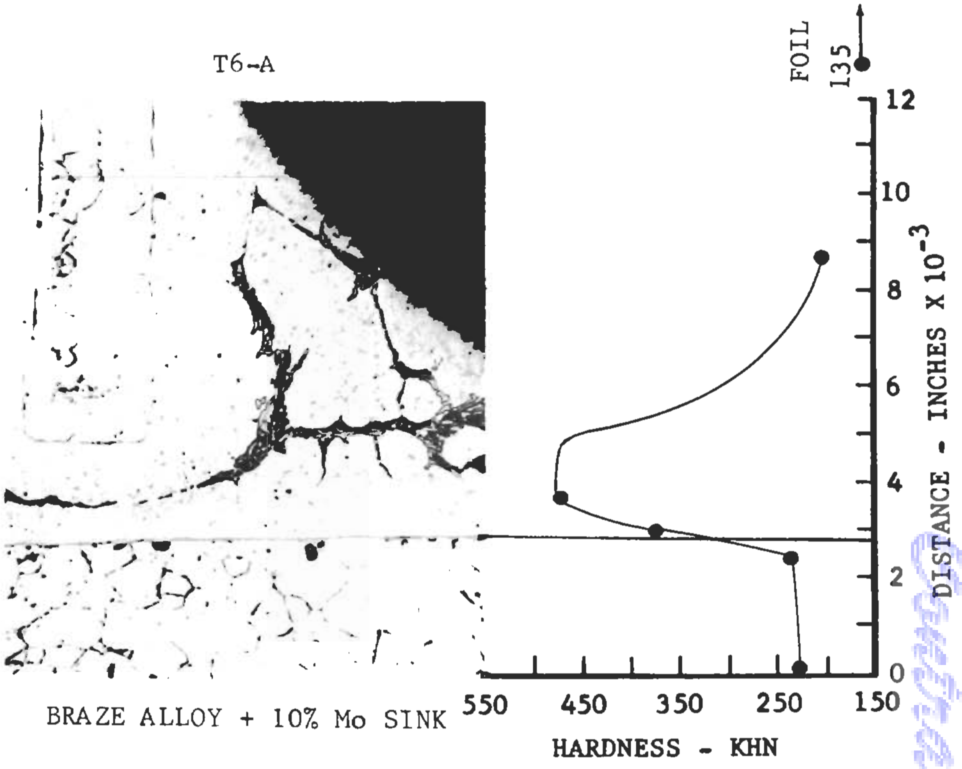
FIGURE D13 Ta-10W TEE (HONEYCOMB) JOINT BRAZED WITH 33Zr-34Ti-33V - STEP DIFFUSION TREATED

T5-A

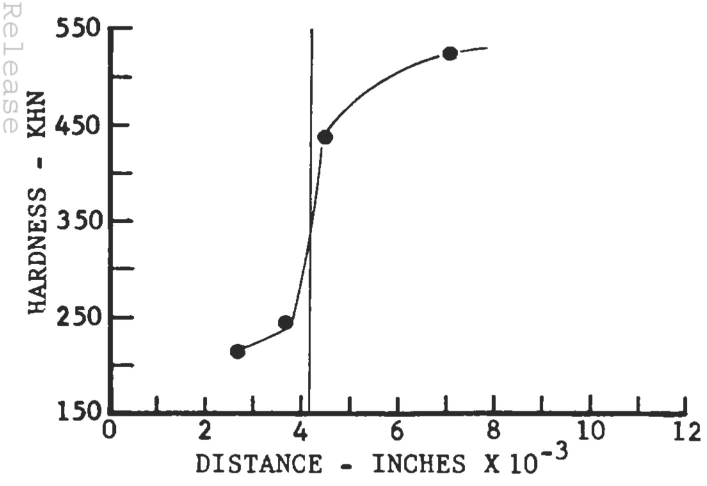


BRAZE ALLOY ALONE

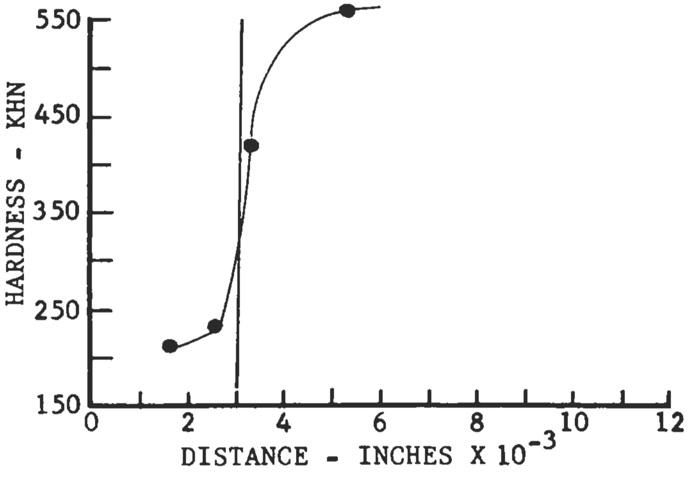
T6-A



BRAZE ALLOY + 10% Mo SINK



BRAZE CYCLE: 2900F - 1 MIN.



BRAZE CYCLE: 2900F - 1 MIN.

MAG. 250 x

BASE MATERIAL ETCHANT: 70 HF, 30 H_2O_2
BRAZE ALLOY ETCHANT: 1 HF, 2 HNO_3, 97 H_2O

RE D14 Ta-10W TEE JOINTS BRAZED WITH Ti-29V-2Si - AS BRAZED