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RESEARCH ON GAS PLATED REFRACTORY METAL COATINGS FOR LIQUID METAL COMPATIBILITY INVESTIGATION

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Fred A. Glaski

San Fernando Laboratories

TECHNICAL REPORT AFML-TR-66-72

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Wright-Patterson Air Force Base, Ohio

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RESEARCH ON GAS PLATED REFRACTORY METAL COATINGS FOR LIQUID METAL COMPATIBILITY INVESTIGATION

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FOREWORD

This report was prepared by San Fernando Laboratories, 10258 Norris Avenue, Pacoima, California, under USAF Contract AF33(615)-2226. The contract was initiated by Mr. M. Wannemacher and funded under Project No. 3145, Task No. 314511, Aerospace Power Division, Air Force Aeropropulsion Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. The work was under the direction of the Physical Metallurgy Branch, Metals and Ceramics Division, Air Force Materials Laboratory, Mr. J. Jay Crosby, Project Engineer.

This report covers work conducted from 1 November 1964 through 1 November 1965.

Publication of this technical report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

ABSTRACT

A means of possibly preventing potential dissimilar metal corrosion in stainless steel/Cb-1% Zr liquid metal systems is by coating the stainless steel portions of the systems with Cb-1% Zr thus exposing only Cb-1% Zr to the liquid metal. Consequently, a technique has been developed for depositing columbium-1% zirconium corrosion barrier coatings on the internal surfaces of type 316 stainless steel tubing assemblies. Configurations approximating those which might be used in liquid metal space power systems were coated with uniform and adherent deposits of Cb-1% Zr ranging in thickness from 0.002 to 0.006 inches. A chemical system employing the hydrogen reduction of mixed chlorides at reduced pressure proved to be the most suitable. A bond was not attained directly between Cb-1% Zr alloy and 316 stainless steel. However, a diffusion bond was attained between columbium and 316 stainless steel, and it was demonstrated that plating Cb-1% Zr over a 5-to-10 micron interlayer of Cb gave adherent coatings. The integrity of the bonding was demonstrated in comprehensive physical tests.

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SECTION I

INTRODUCTION AND SUMMARY

The development of an interesting technique for possibly preventing potential dissimilar metal corrosion in 316 SS/Cb-1% Zr systems such as those which have been considered for the SNAP 50/SPUR nuclear power system was pursued in this program. The technique is that of internally coating all stainless steel portions of a SS/Cb-1% Zr system with Cb-1% Zr thus presenting only Cb-1% Zr to the liquid metal working fluid or heat transfer fluid as the case may be. However, the development of a satisfactory method for coating stainless with Cb-1% Zr has proven difficult. In recent years substantial effort has been concentrated on the co-extrusion of Cb-1% Zr tubing within stainless steel tubing. Although this process has merit, problems have been encountered in forming bimetallic tubes which are concentric and crack-free. Furthermore, the co-extrusion process seems inherently limited to simple linear components rather than entire assemblies. The joining of these bimetallic components also presents certain problems. The search for a simple alternate method of depositing thin, impermeable, uniform and adherent coatings of Cb-1% Zr on stainless parts of random sizes and shapes led directly to the consideration of metal deposition through chemical vapor plating.

Vapor-phase plating is now particularly attractive because of the rapidly expanding technology of this field. San Fernando Laboratories and other investigators have in recent years made the process routine for many applications. Additionally, SFL has deposited various refractory metals inside of tubing, including columbium and columbium-zirconium alloys.

This report summarizes SFL's first year of effort in the development of the technique of internally plating Cb-1% Zr on 316 SS tubing. The work is sponsored under Air Force Contract AF33(615)-2226.

Cb-1% Zr has been deposited on the inner surface on 316 stainless steel tubing, and tubing assemblies of configurations which might be used in liquid metal power systems. Straight and "S" shaped tubing as well as manifolds have been plated. Various chemical systems have been evaluated for the deposition reaction. The hydrogen co-reduction of $CbCl_5$ and $ZrCl_4$ at reduced pressures has been found to be

most promising and development of this system has been pursued. Bonding of deposited metal to the 316 SS substrate was obtained from pure columbium systems but not from mixed Cb-Zr systems. A very thin columbium layer was therefore deposited on all 316 SS substrates to effect a diffusion bond prior to depositing Cb-1% Zr alloy.

The bond, although an intermetallic which under other conditions could be expected to be hard and brittle, was proved sound in 170° bend tests and tensile tests. Testing was carried out on flat rectangular coupons of Cb and Cb-1% Zr plate, Cb plated on plain and butt welded 316 SS, and Cb-1% Zr plated on plain and butt welded 316 SS. Tests of coupons were made both without heat treatment and also after a 200 hour heat treatment at 800°F which included 5 minute temperature excursions to 1200°F, followed by a 5 minute dwell at 1200°F and a 5 minute cool to 800°F, every 6 hours. Internally plated 316 SS plain and butt-welded tubular specimens were tensile tested with and without the same heat treatment. The integrity of the bond in its as-deposited condition was demonstrated. The ductility of the bond was found to be improved in the heat treated specimens. Heat treatment did not appear to cause any widening of the zone of the originally deposited diffusion bond.

Among the items internally plated with Cb or Cb-1% Zr alloy were 5 ft. long "S" loops, manifolds with multiple legs, test capsules for alkali metal corrosion static testing, and a special mock-up of a portion of a corrosion loop assembly.

SECTION II

DETERMINATION OF OPTIMUM CHEMICAL SYSTEM FOR PLATING COLUMBIUM

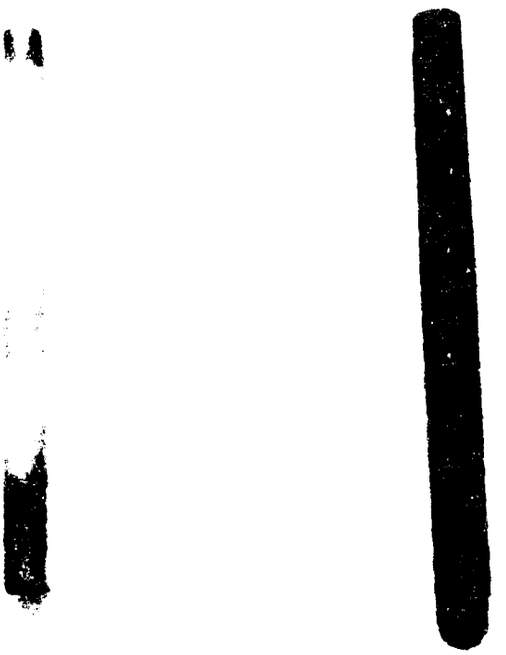
CbF_5, CbI_5, $CbBr_5$ and $CbCl_5$ were considered potential plating species for both pyrolytic decomposition and hydrogen reduction reactions. Bonding of the deposit to the 316 SS substrate and optimum decomposition temperature within the limits of the substrate were the primary considerations that led to the choice of the $CbCl_5/H_2$ reduction system.

A thermochemical analysis of the deposition of columbium from columbium fluoride was conducted. On the basis of this analysis, the fluoride system appeared to be workable. However CbF_5 is not readily available and it is difficult to handle and cannot be readily generated in situ. Other halide systems were subsequently found to be more suitable and therefore deposition via the hydrogen reduction of CbF_5 was dismissed from further consideration.

The deposition of columbium was attempted by the pyrolysis of columbium iodide. A smooth crystalline deposit was obtained but at a very low deposition rate. Since the melting point of 316 SS prevented operation at the higher temperatures necessary to obtain an acceptable plating rate, the pyrolytic iodide system was deemed unsuitable.

Deposition using the hydrogen reduction of columbium bromide was also considered. $CbBr_5$ was generated by passing bromine vapor, in an argon carrier gas stream, through a columbium charge pot. It was found that a specimen temperature of at least 1600°F (indicated brightness temperature) was necessary to obtain a detectable plating rate; the plate became quite bumpy when the temperature was taken to the 1900°F-1950°F range. The optimum temperature which resulted in a smooth, adherent, ductile plate was found to be approximately 1850°F.

Figure 1 shows two specimens, as-plated, that were prepared at excessive temperatures. The specimen to the left was at a suitable plating temperature everywhere but at the center, which operated at over 1900°F. A coarser grain is apparent in the central portion of the specimen. The specimen to the right suffered an excursion to 2000°F in the central portion; severe coarseness is evident.



1900°F-1950°F

2000°F

FIGURE 1

COLUMBIUM DEPOSITS FROM BROMIDE SYSTEM

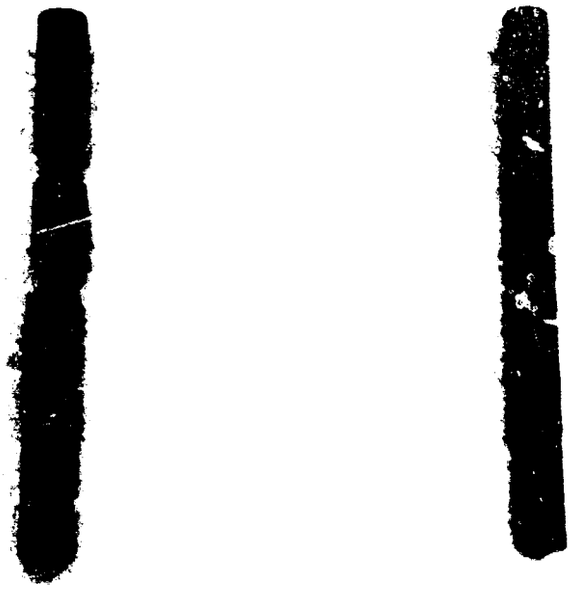
The specimen on the left in Figure 2 was deposited at 1600°F. The grains are very fine, the deposit adherent, but the plating rate was quite low, almost negligible. The specimen on the right in Figure 2 was deposited at the optimum temperature of 1850°F, measured in the mid-section. The grains are fine (135 grains/mm^2) and the plating rate was satisfactory. The specimens were photographed in the as-plated condition.

The later (best) bromine runs were made at bromine feed rates and brominator temperatures sufficient to ignite the columbium. All of the bromine runs produced considerable amounts of condensed oxy- and sub- bromides in the reaction chamber. The unignited runs produced yellow oxy- and/or sub-bromides while the ignited runs produced a reddish-violet crystal condensate, probably the desirable $CbBr_5$.

Plating rates between 0.25 and 0.34 mils per minute were attained in the ignited runs, yielding a good, metallic, adherent plate. Figure 3 is a photomicrograph of a section of one of these specimens showing a thin diffusion bond between the columbium and the 316 stainless steel mandrel.

The plating rate and bond quality appeared to be as good as that eventually obtained in chloride systems. However, the Cb + Br_2 reaction was more difficult to promote to completion than, for example, the Cb + Cl_2 reaction. The measured burn-up rate in the brominator was found to be repeatedly above 100 percent of theoretical when calculations were based upon only $CbBr_5$ formation. This indicated that lower bromides were being formed in the brominator; these species are believed not to contribute to the plating reaction but are less volatile than $CbBr_5$ and greatly increase the danger of plugging the plating chamber exhaust line with bromide condensates.

The major system explored was the hydrogen reduction of columbium pentachloride to Cb and HCl. The remainder of this report is devoted to this system.



1600°F 1850°F

FIGURE 2

COLUMBIUM DEPOSITS FROM BROMIDE SYSTEM

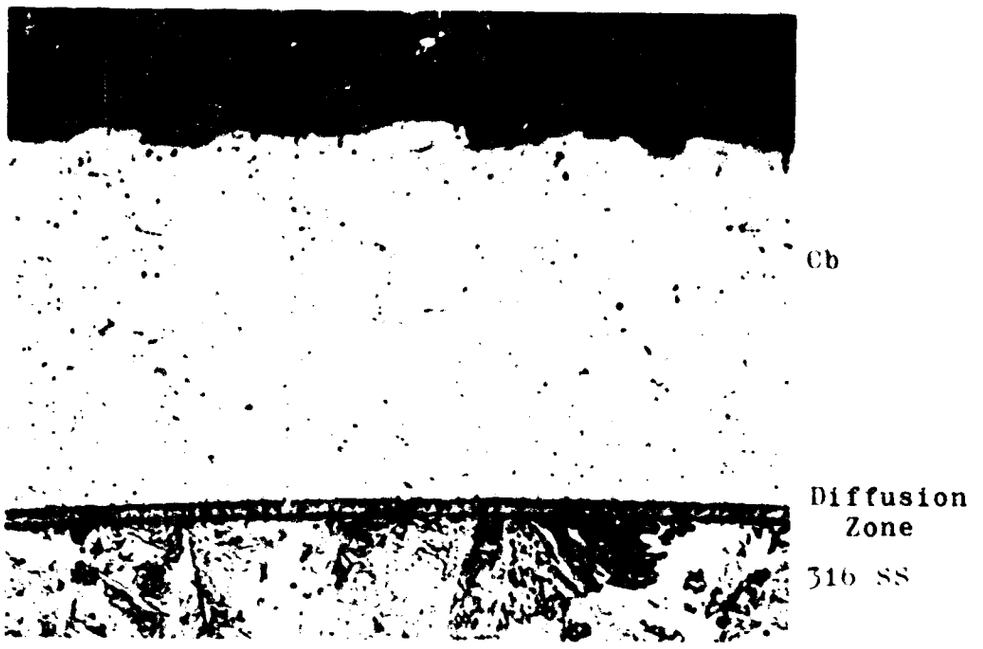


FIGURE 5

COLUMBIUM DEPOSIT FROM BROMIDE SYSTEM (240X)

SECTION III

DESIGN AND FABRICATION OF EXTERNAL PLATING SYSTEM

A deposition rig was designed and built for the purpose of exploring the parameters involved in Cb and Cb-Zr alloy deposition. A single and double chloride generation system was included. Induction heating of the specimen was employed.

A plating system suitable for the deposition of Cb-Zr alloys on the outside surface of 316 SS tubing was designed. A sketch of the system is shown in Figure 4. Figure 5 is a photograph of the assembled system. A summary of the rig's operation follows below.

A cylindrical 316 SS test specimen was inductively heated in a 38 mm vycor glass chamber. The specimen was supported on a pedestal which was turned at approximately 8 rpm; since the reactant gases flowed past the specimen at very low Reynolds numbers (200-300) resulting in negligible radial mixing of the gases, rotation of the part was employed to insure circumferential plate uniformity. Two concentric vycor cylinders, one filled with columbium metal feed stock and the other filled with zirconium metal feed stock, were suspended above the specimen, in the reaction chamber.

Separately controlled chlorine gas flows were directed through the concentric columbium and zirconium chlorinators, which were externally heated by a resistance clamshell heater. (See Figure 6.)

Columbium and zirconium chlorides were generated in the chlorinators and flowed into the reaction chamber toward the specimen. Hydrogen was supplied to the chamber in a separate stream between the chlorinators and the outer chamber wall. Argon could also be supplied to the system mixed with the hydrogen gas stream for the purpose of adjusting partial pressures of the reactant gases and/or adjusting the overall velocity of the gases past the specimen.

A "subchloride knock-out pot" was incorporated downstream of the reaction chamber to trap condensible metal chlorides and prevent plugging of the vacuum pumping system which was farther downstream. Figure 7 depicts a typical condensate "knock-out pot" assembly.

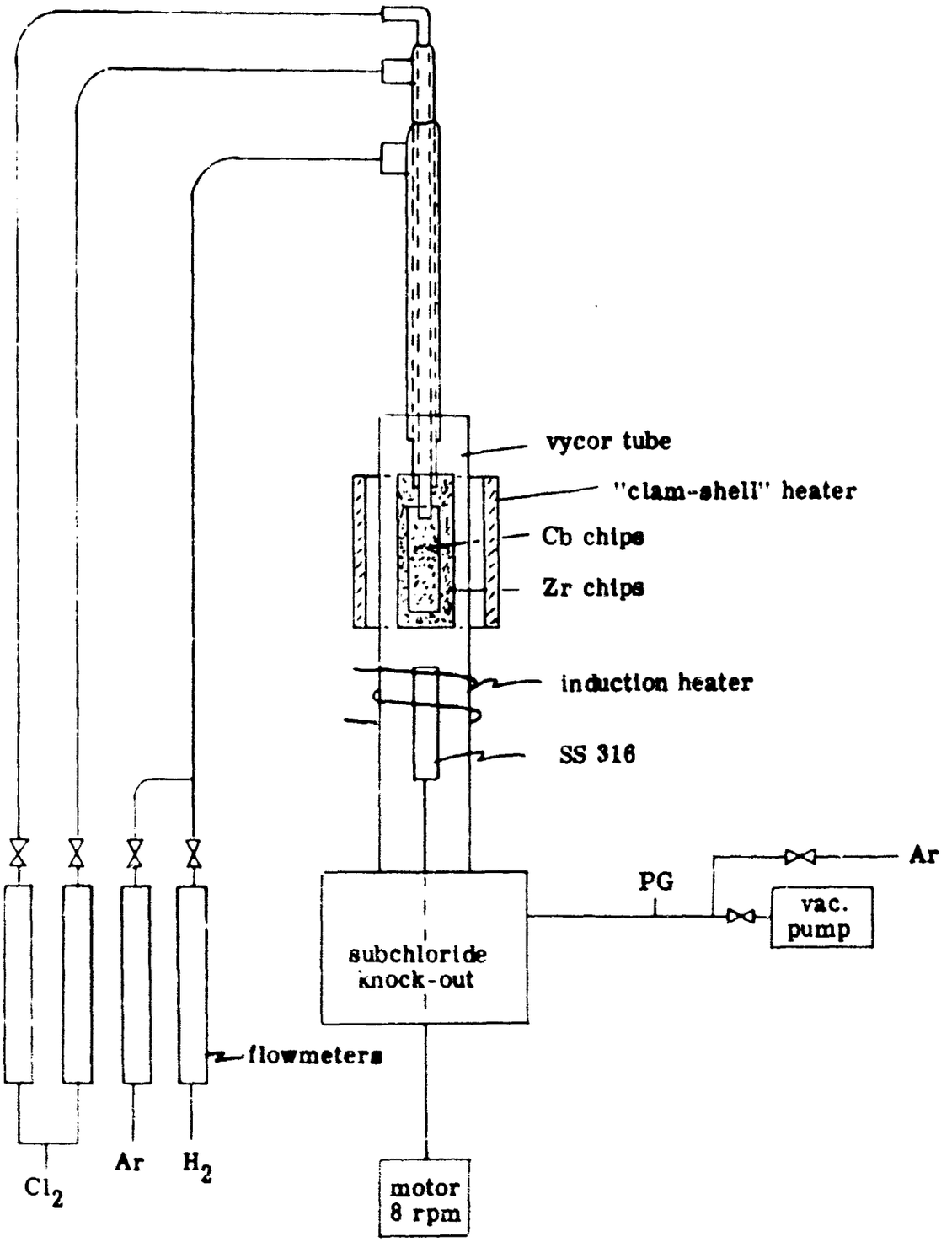


FIGURE 4

SKETCH OF PLATING SYSTEM

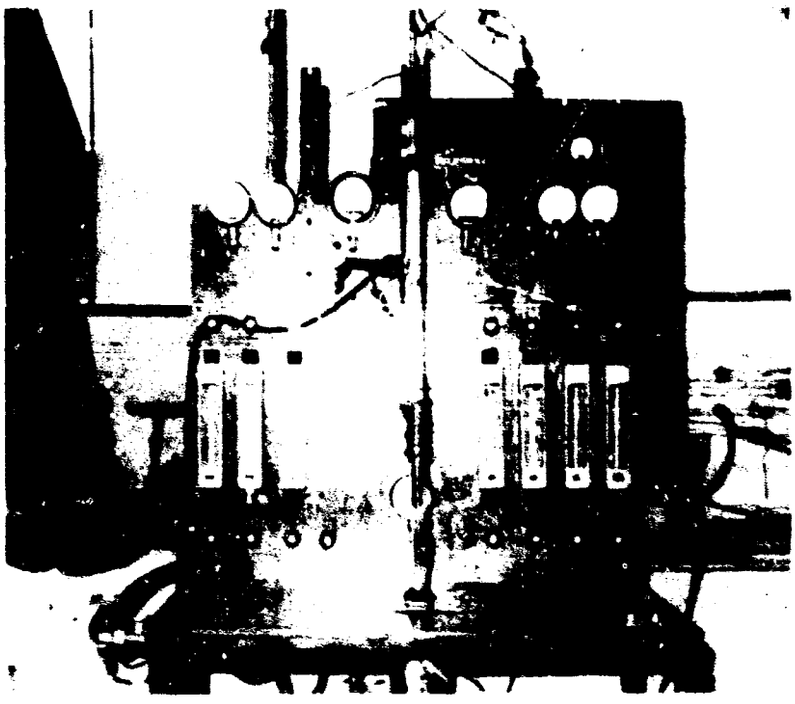


FIGURE 5

EXTERNAL PLATING SYSTEM

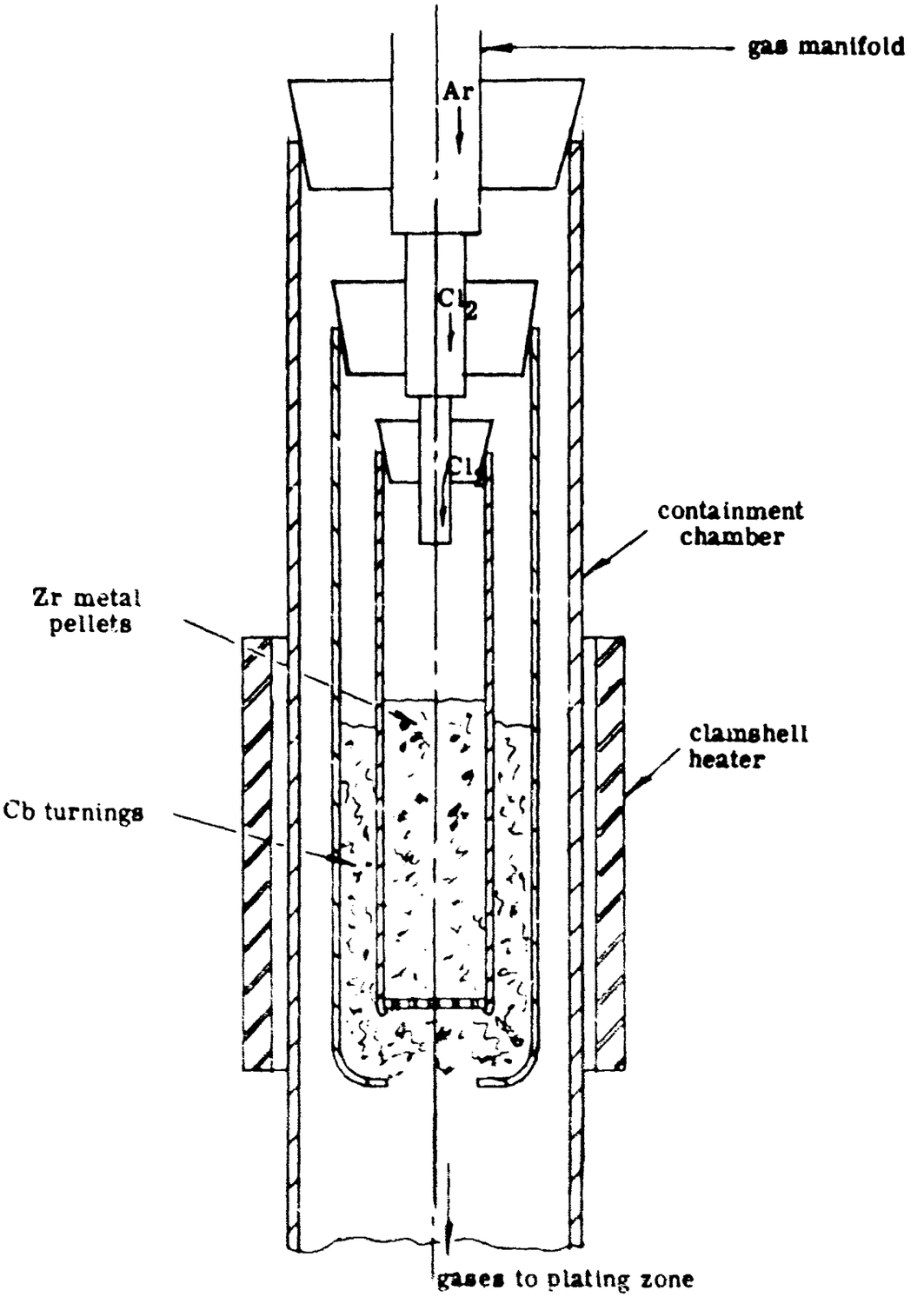


FIGURE 6

CONCENTRIC COLUMBIUM AND ZIRCONIUM CHLORINATORS

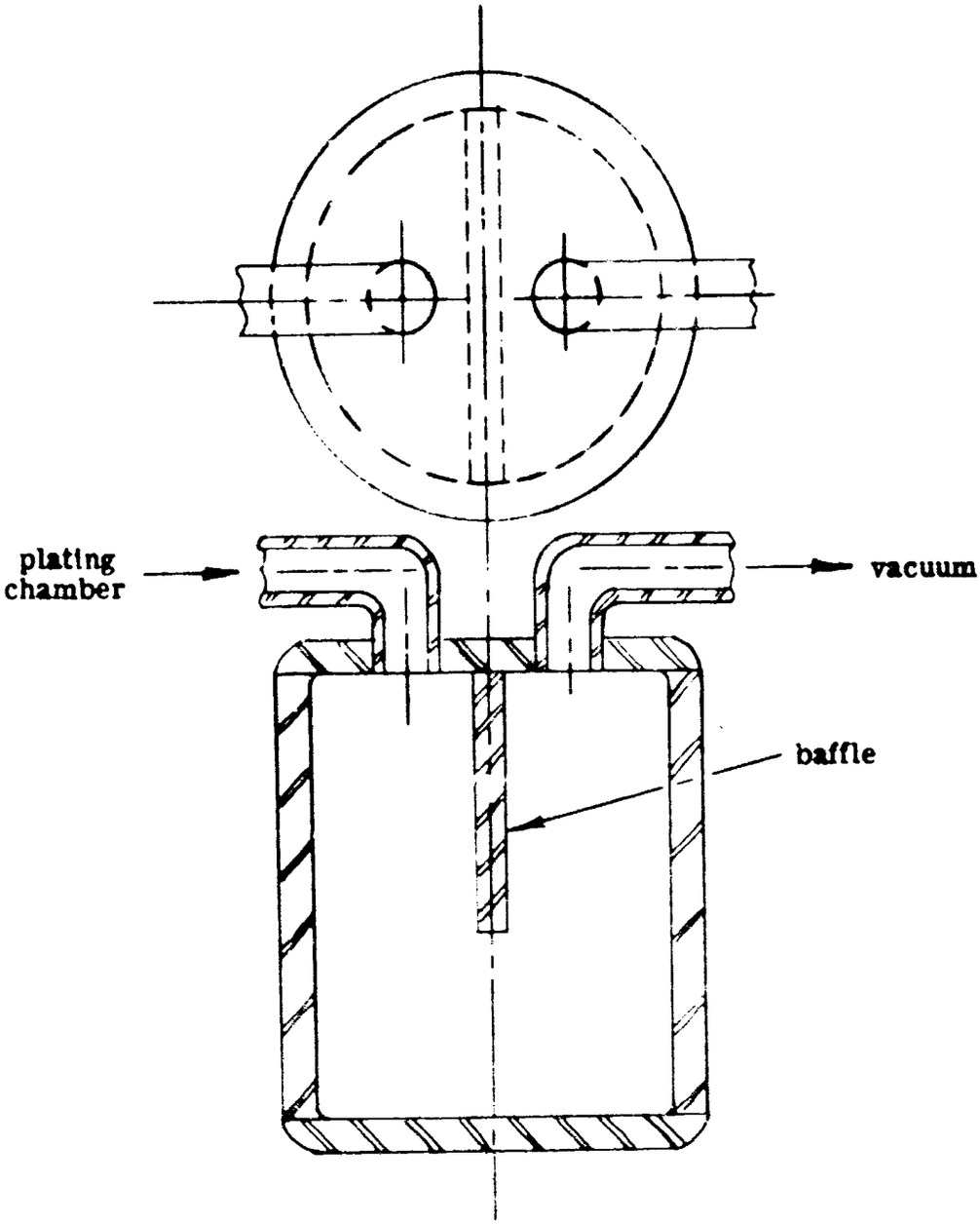


FIGURE 7

KNOCK-OUT POT
No Scale

SECTION IV

INVESTIGATION TO DETERMINE THE OPTIMUM RUN CONDITIONS FOR THE DEPOSITION OF COLUMBIUM FROM THE CHLORIDE SYSTEM

The characteristics of chloride generation and the effects of specimen temperature and pressure were investigated. The sources of non-plating chloride species were determined and methods to decrease their generation were developed resulting in increased deposition rate and efficiency. The optimum deposition temperature was found to be 1850°F. Deposition rate was not found to be a strong function of total pressure over a wide pressure range.

The "O $_2$" deposition system, described above and shown in Figure 5, was used to deposit columbium on the outside surface of 316 SS test specimens. $CbCl_5$ was generated by passing chlorine gas through a bed of hot columbium chips. Ignition of the exothermic chlorination reaction occurred quite readily.

$$2\ Cb_{(s)} + 5\ Cl_{2(g)} \xrightarrow{1000°F} 2\ CbCl_{5(g)} + HEAT$$

The $CbCl_5$ was hydrogen-reduced to Cb on the hot specimen (1800°F $\stackrel{2}{-}$ 1950°F indicated brightness temperature).

$$2\ CbCl_{5(g)} + 5\ H_{2(g)} \xrightarrow{1800°F} 2\ Cb_{(s)} + 10\ HCl_{(g)}$$

The chlorination reaction was found to be very efficient, repeatably 99% of theoretical. The reduction reaction was found to be approximately 10% of theoretical.

1. EFFECT OF PRESSURE ON DEPOSITION RATE

Preliminary investigations included a number of trial depositions at -10" Hg and -29.9" Hg. Constant specimen temperature and gas mass flow rates were employed for all of these depositions. A deposition rate between 0.35 and 0.4 mils/minute was obtained at the higher pressure and a negligible rate was obtained at the lower pressure. Subsequent determinations of plating rate for depositions carried out at intermediate pressures indicated that a constant (within the limits of the data) rate was obtained over the entire pressure range of 0 to -20" Hg. Below -20" Hg the deposition

rate decreased very rapidly. The primary reason for a lowering of rate with lower pressures was found to be the accompanying increase in gas velocity which sped the reactants past the specimen before they could be heated to plating temperature. An important study related to these data will be conducted during the second year of this program; the lower pressure regime (high gas velocity) will be explored as a means of extending "I.D." plate penetration down the length of long tubing assemblies.

2. EFFECT OF TEMPERATURE ON DEPOSITION RATE

The specimen temperature for all of the "effect of pressure" depositions was 1850°F ± 30°F. Temperature was measured pyrometrically for the exterior surface depositions and by thermocouple for interior depositions. This temperature was found to be the optimum through a separate series of "O.D." trial depositions conducted at a constant system pressure of -10" Hg. In this series of depositions temperature profiles were taken pyrometrically (brightness temperatures were measured) over the length of the specimens, which were inductively heated. The plate thickness was then measured at each temperature measurement point at the conclusion of a timed run. A 2-3 inch plating zone was used in each trial deposition and variance in plating rate due to reactant gas depletion down the length of the plating zone was found to be negligible. Data from these runs, indicated an expected upward trend in plating rate with temperature, from 0.15 mils/minute at 900°C to 0.45 mils/minute at 1050°C.

When the temperature of the specimen was taken into the 1950-2000°F range the plating rate increased rapidly and a very nodular large-grained deposit (20 grains/mm^2) was obtained. The optimum plating temperature, considering the criteria of maximum rate and quality of deposit finish, was found to be 1850°F.

The deposit obtained at 1850°F appeared to be of high quality with a smooth, small-grained surface, and was shiny and ductile. A continuous bond between the columbium and the 316 SS substrate was observed. (See Figure 8)

It was found that a minimum H_2:$CbCl_5$ molal ratio of twice stoichiometric was necessary to maximize plating rate and plate quality. This no doubt stemmed from the extreme laminar nature of the reactant gas flow past the heated specimen (Reynolds Number = 200-500) which resulted in very little radial mixing. The $CbCl_5$ impinged directly upon the

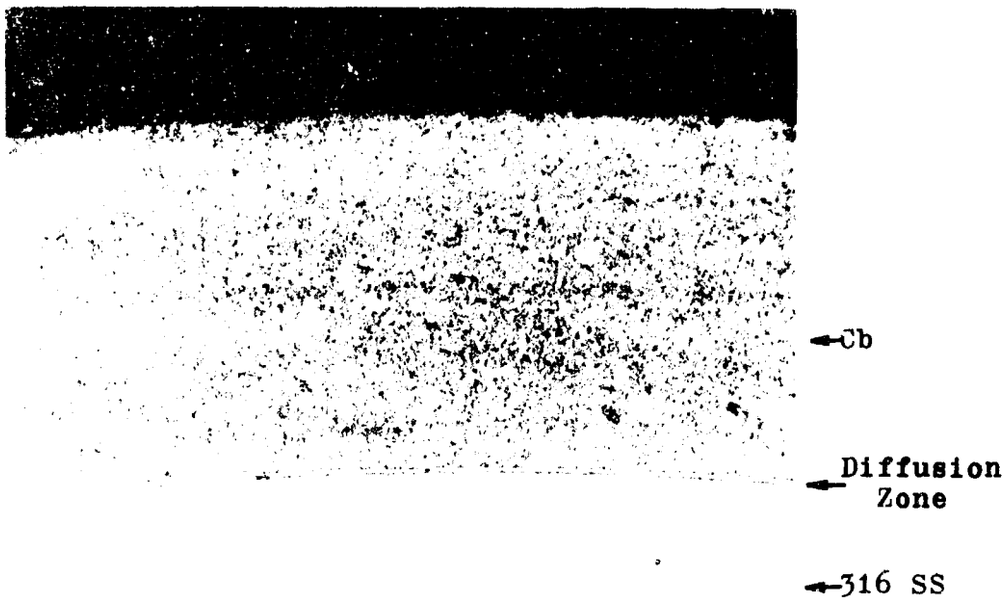


FIGURE 8

COLUMBIUM DEPOSIT FROM CHLORIDE SYSTEM

specimen in the center of the reaction chamber, while the hydrogen was injected outside of the chlorinator along the chamber wall. A certain amount of mixing was forced to occur by tapering the end of the chlorinator inward. However, use of an excess hydrogen flow did assure a stoichiometric supply of the reducing agent at the surface of the specimen.

The heat transfer characteristics of the columbium chlorinator were found to dictate rather precise requirements for chlorinator control. Initially it was required to heat the columbium metal to approximately 800°F before chlorine would react with it in a sustaining manner. At this temperature the metal ignited visibly and the burning metal rose in temperature to approximately 1300°F. The top of the metal charge in the chlorinator, once ignited, sustained the exothermic reaction $2\ Cb + 5\ Cl_2 \longrightarrow 2\ CbCl_5$. However, if the lower portion of the chlorinator was not heated externally solid $CbCl_5$ readily condensed in it. Care had to be exercised not to overdrive the chlorination reaction through an excessive external heat input. This led to the thermal decomposition of $CbCl_5$ to $CbCl_3$ as the pentachloride passed through the overheated, fresh, reactive columbium metal downstream of the ignition zone. This trichloride product was less volatile than $CbCl_5$, and therefore condensed, and produced a pluggage in the chlorinator; $CbCl_3$ appears to be totally useless as a plating species.

3. CONDENSATE FORMATION

It is interesting to note that thermodynamic considerations indicate that, at comparable run conditions, columbium should plate more readily than tantalum from a chloride system. The reverse, in fact, had been observed. Based upon observations of the columbium plating runs there appeared to be a number of possible explanations (and corresponding corrections) for this reversal. Yellow, white and black solid condensates had been observed in the plating system. These species were presumably $CbCl_5$, $CbOCl_3$, and $CbCl_3$, respectively. The black residue had been observed to form in the exhaust portion of the columbium chlorinator as well as downstream of the specimen. The other two species had been found throughout the chamber.

Both $CbCl_3$ and $CbOCl_3$ are theoretically more stable than the corresponding tantalum compounds. If these compounds form in sufficient abundance the generation of the preferred plating species ($CbCl_5$) could be reduced to a point where plating rate is dramatically reduced.

Besides being generated in an excessively heated chlorinator the $CbCl_3$ also appeared to be a significant reaction product when the $CbCl_5$ reacted with H_2 to deposit Cb on the specimen. While carefully controlling the chlorination reaction as outlined above a simple study was conducted to determine whether significant subchloride formation was taking place at the specimen as a by-product of the deposition reaction. Columbium and zirconium chlorinators were separately operated without attempting to deposit metal on any hot surface. Only yellow-white $CbCl_5$ or white $ZrCl_4$ was observed to condense in the cooler portions of the chamber or in the chlorinator itself. None of the darker subchlorides were detected; of course the formation of $CbOCl_3$ was not observable against the yellow-white $CbCl_5$.

The specimen was then brought to plating temperature. Dark subchloride condensate was immediately apparent, but only downstream of the specimen. Of course, the primary reaction products were Cb deposit and HCl.

Condensate formation, although formidable from a system pluggage point of view, was found to be less bothersome in the chloride system than in the bromide system.

The above analysis was found to be adequate for the purpose of identifying the major chloride species present in the deposition system. The chloride compounds are reactive in air and transfer of these products from the deposition rig to another location, in vacuum or under an inert atmosphere, for the purpose of detailed analysis would be difficult. A quantitative analysis of the chloride species was felt to be unnecessary since the overabundant presence of the undesirable species was clearly manifested by reduced deposition rates and system condensate pluggages.

An oversupply of chlorine to the chlorinator was adequately controlled by direct reaction with the excess hydrogen supply when the chloride and hydrogen streams combined, immediately below the chlorinator. Etching of the specimen by free chlorine was, therefore, seldom encountered.

For a given chlorinator diameter there was found to be a limiting chlorine flow capacity. Beyond that capacity an overly violent exothermic reaction occurred causing decomposition of the $CbCl_5$. For high $CbCl_5$ generation requirements, a larger chlorinator diameter is recommended. (Of course a shallow bed of metal in the chlorinator, and a high chlorine supply rate will allow a considerable portion of the chlorine to pass through the bed unreacted, thereby greatly reducing chlorinator efficiency. This problem becomes more critical as burning reduces the height of metal in the chlorinator.)

Typically, a chlorine flow rate of 450 cc/min to the chlorinator and a hydrogen flow rate of 2400 cc/min was used for the "O.D." trial depositions. No etching difficulty was encountered either by free chlorine or HCl.

SECTION V

CONTROL OF PURITY OF COLUMBIUM DEPOSITS

Various qualities of columbium metal feed stock were chlorinated in trial depositions using vycor glass or alumina chlorinators. The deposits produced were analyzed for interstitial contaminants. Impurity levels of 150 ppm carbon, 10 ppm hydrogen, 50 ppm oxygen and 50 ppm nitrogen were attained. The analytical results furnished by one subcontracting laboratory for the potentially highest purity system were questionable.

Three sources of columbium feed stock were evaluated in efforts to:

(1) improve the efficiency of the plating system by reducing the formation of the non-plating species $CbOCl_3$,

(2) improve the quality of the plate by reducing interstitial contamination, and

(3) improve the zirconium yield in the Cb/Zr system by increasing pure $CbCl_5$ formation which apparently is involved in a $CbCl_5$-$ZrCl_4$ interaction that yields zirconium.

The sources included machined turnings of high surface oxide content and two sources of high purity pellet stock, one containing 52 ppm oxygen and the other 1200 ppm oxygen.

Use of a metal chlorinator was considered but quickly dismissed due to the reactive nature of chlorine at high temperatures. Inconel, the best candidate for this application would also be subject to attack at the 1000°F columbium ignition temperature.

1. USE OF VYCOR GLASS CHLORINATORS

Sample deposits were made employing each of the three feed materials and the resultant plated specimens were chemically analyzed for interstitial gaseous contaminants and carbon content. The results of the evaluation are summarized below.

(a) Feed Type - Heavy Machined Turnings (High O_2 Content) Plate Analysis:

Sample #1	-	C	-	700 ppm
		H_2	-	29 ppm
		O_2	-	64 ppm
		N_2	-	17 ppm
Sample #2	-	C	-	200 ppm
		H_2	-	35 ppm
		O_2	-	52 ppm
		N_2	-	40 ppm
Sample #3	-	C	-	300 ppm
		H_2	-	29 ppm
		O_2	-	61 ppm
		N_2	-	17 ppm

(b) Feed Type - Pellets with O_2 - 52 ppm Plate Analysis:

Sample #1	-	C	-	1600 ppm
		H_2	-	10 ppm
		O_2	-	214 ppm
		N_2	-	80 ppm
Duplicate Sample #1	-	C	-	1500 ppm
		H_2	-	6.9 ppm
		O_2	-	163 ppm
		N_2	-	68 ppm
Sample #2	-	C	-	800 ppm
Duplicate Sample #2	-	C	-	1100 ppm

(c) Feed Type - Pellets with O_2 - 1200 ppm Plate Analysis:

Sample #1	-	C	-	1600 ppm
		H_2	-	2.6 ppm
		O_2	-	384 ppm
		N_2	-	55 ppm
Duplicate Sample #1	-	C	-	1600 ppm
		H_2	-	2 ppm
		O_2	-	442 ppm
		N_2	-	47 ppm

Feed Type (c) was composed of small diameter granules that tended to pack too tightly in the chlorinator causing an excessive pressure drop across the pack and eventual plugging via inter-granule chloride fusion at temperature. This problem was circumvented by placing the columbium feed pellets in stacked graphite trays lined with graphite or glass cloth. Feed Type (b) was adequately supported by a single graphite plug with a glass cloth liner. All of the samples prepared with Feed Materials (b) and (c) and analyzed (reported above) required the presence of graphite and glass cloth sieve arrangements. (The one exception was Feed Type (b), Sample #2, which used the all-graphite tray and cloth configuration and was analyzed for carbon only.)

The analyses of the specimens made with the Feed Materials (b) and (c) showed at least a two fold increase in carbon content over the specimens made with Feed Material (a). This was not too surprising because of the graphite additions to the small pellet feed systems. The dramatic increase in the oxygen content of the specimens made from the low $-O_2$ feed was not expected. In fact a decrease in oxygen contamination was expected.

It appears that Cb or $CbCl_5$ interaction with the cloth could have been responsible for the increase in oxygen content in the specimen. Cb is known to react to completion with SiO_2, in the presence of a small quantity of hydrogen to form Cb_5Si_3 and CbO at 1000°C. The SiO_2 migrates from the quartz tube or the SiO_2 cloth to the columbium according to the reaction

$$SiO_2 + H_2 \longrightarrow SiO_{(g)} + H_2O_{(g)} \qquad 1000°C \qquad \text{(Ref. 1)}$$

Since the chlorinator was kept in the 700-800°C range no problem was anticipated from Cb and SiO_2 interaction. However, since only quantities less than 0.1 percent O_2 were detected in the specimens, it is possible that the above reactions did take place, at a very low rate, followed by reaction between CbO and Cl_2 to form a columbium oxychloride, probably $CbOCl_3$.

2. USE OF ALUMINA CHLORINATORS

Chlorinators made entirely of 99% Al_2O_3 were then fabricated and used for a series of depositions employing various columbium metal feed materials. Figure 9 shows a cross section of the concentric Cb/Zr Al_2O_3 chlorinator configuration. For pure columbium depositions only the larger Al_2O_3 chamber was used.

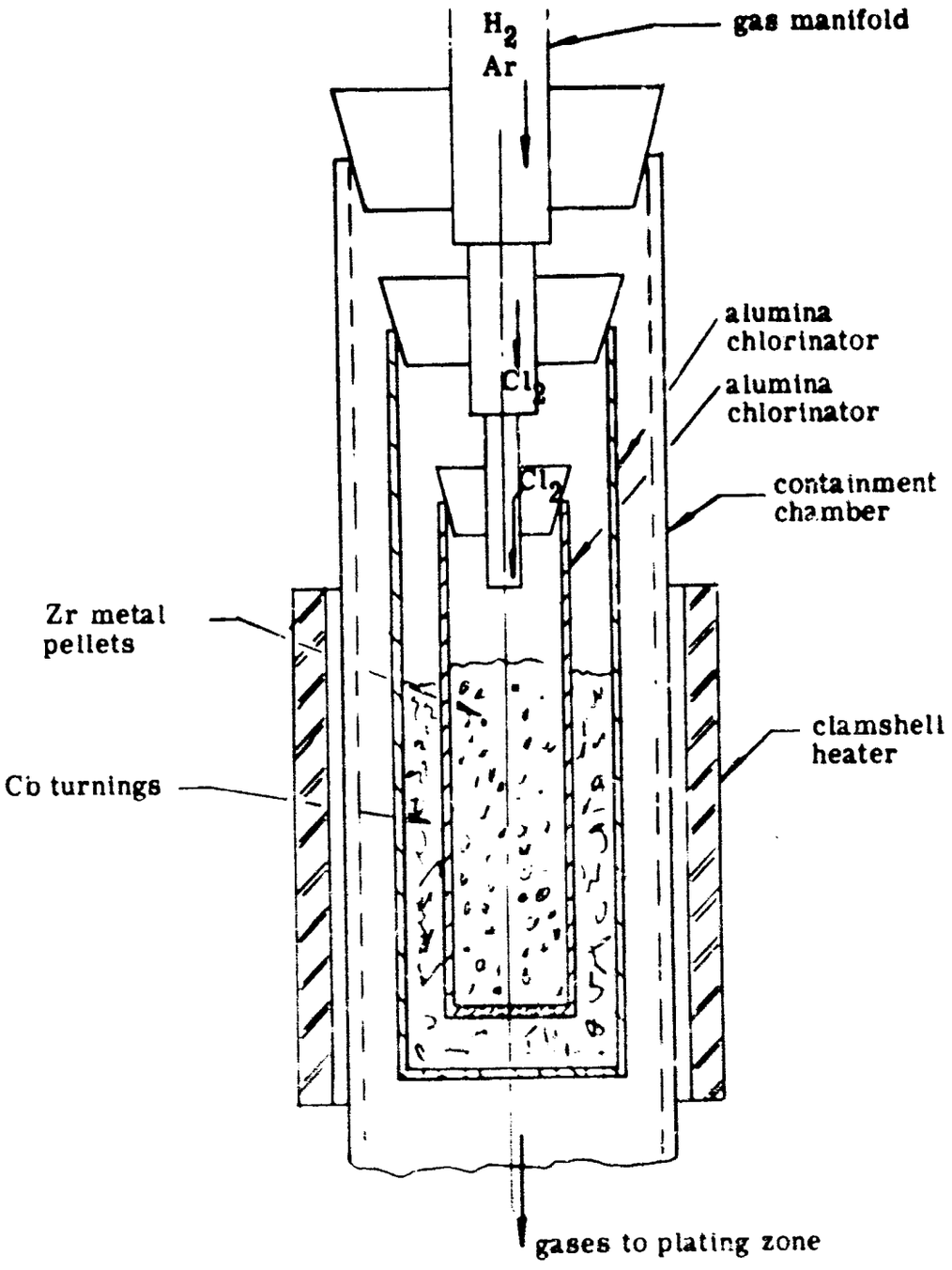


FIGURE 9

CONCENTRIC ALUMINA CHLORINATORS

The chlorinators were initially baked in hydrogen for 60 minutes at 2000°F; they were then filled with the appropriate metal feed charge and used for the trial depositions. The results of chemical analyses are summarized below.

(a) Feed Type - Heavy Machined Turnings (High O_2 Content) Plate Analysis in ppm:

C	-	424, 246, 480
H_2	-	47, 75
O_2	-	1307, 762
N_2	-	66, 210

(b) Feed Type - Pellets with O_2 1200 ppm Plate Analysis in ppm:

C	-	341, 387, 500
H_2	-	107, 195
O_2	-	1060, 1026
N_2	-	107, 87

(c) Feed Type - Pellets with O_2 - 52 ppm Plate Analysis in ppm:

C	-	372, 274, 593
H_2	-	115, 104
O_2	-	225, 107
N_2	-	84, 16

(d) Feed Type - Cb/Zr System with Heavy Machined Cb Turnings and High Purity Zr Pellets Plate Analysis in ppm:

C	-	713, 954, 1600
H_2	-	89, 108
O_2	-	615, 1120
N_2	-	23, 66

Two additional samples were analyzed by another analytical laboratory. They were prepared using columbium turnings in a vycor chlorinator. The plate analyses are:

Sample #1	-	C	- 170
		H_2	- 7
		O_2	- 100
		N_2	- 80
Sample #2	-	C	- 150
		H_2	- 7
		O_2	- 40
		N_2	- 70

Samples (a) through (d), the Al_2O_3 chlorinator runs, were not analyzed by the same vendor as were the last two samples listed above. The former vendor chose to use acetone to degrease the specimens. SFL believes that such treatment could yield erroneously high carbon readings. Such appears to be the case here; the carbon analyses appear to be highly suspect for a plating system consisting only of alumina, columbium, and 316 SS. The oxygen content also appears to be abnormally high; however, oxygen transfer from the Al_2O_3 is not out of the question. During the second year's effort under AF33(615)-2226 SFL will submit duplicate samples to various analytical laboratories to compare the reliability of their techniques.

In summary the following trends can be cited:

(1) Purity of the metal feed effects chlorination efficiency and therefore plating rate. This effect is not prominent compared with other influencing factors.

(2) The presence of graphite in the chlorinator results in a high carbon level in the plate; the level is further increased (as is the oxygen level) when glass sieves, glass cloth, etc. are added to this system.

(3) Use of an Al_2O_3 chlorinator reduces carbon but may increase oxygen content in the deposit.

(4) The optimum system would appear to be the use of a vycor chlorinator without any graphite or glass sieve supports (SiO_2 exposure would be limited to the inner surface of the chlorinator) and high purity columbium metal feed. Because the high purity material has been obtainable only in small pellets requiring a tray or sieve support, and because graphite or glass supports have been discounted, further attempts to employ this optimum system are planned with a columbium sieve tray. Meanwhile machined turnings in a vycor chlorinator will be used in the other portions of the program.

SECTION VI

INVESTIGATION TO DETERMINE THE OPTIMUM CHEMICAL SYSTEM AND RUN CONDITIONS FOR THE DEPOSITION OF COLUMBIUM-1% ZIRCONIUM

Mixed columbium/zirconium fluorides, iodides, bromides, and chlorides were considered as candidate species for pyrolytic decomposition and hydrogen reduction reactions. The $CbCl_5/ZrCl_4$ hydrogen reduction was chosen primarily because of the ease in controlling zirconium content in the 1% range with this system. The 1850°F optimum deposition temperature found for the pure $CbCl_5/H_2$ reduction system was successfully employed for the mixed system. Microprobe techniques were employed to determine the radial and longitudinal uniformity of Cb-1% Zr tubular deposits; a uniform alloy was reproducibly deposited.

1. DETERMINATION OF CHEMICAL SYSTEM

Previous SFL experience was drawn upon to initially compare and evaluate the various chemical systems available for depositing zirconium. Pyrolysis of the iodides at a minimum temperature of 1100°C - 1200°C was deemed unsuitable because of:

(a) the proximity of this temperature range to the melting point of the substrate 316 stainless steel, and

(b) because the mechanism of the reactions are independent and therefore sensitive to the partial pressures of the individual species as well as total pressure and temperature.

Hydrogen reduction of either columbium iodide or zirconium iodide is theoretically impossible.

In a co-deposition system the independent or consecutive independent nature of the reaction is an important consideration. In a system consisting of two depositing species that could also be deposited in a single component system, each species demonstrates individual dependencies on pressure, temperature, gas mixture ratio, etc. In such a system, co-deposition often requires a delicate control of

these parameters to control the composition of the deposit to within 5%. The tungsten/rhenium alloy system is a typical example of such a system. Control of a 99%/1% alloy such as the Cb-1% Zr alloy studied in this program would be most difficult with a chemical system utilizing two independent species. The Cb/Zr iodide system would be this type of deposition system.

Zirconium tetrafluoride is not available commercially. Since columbium tetrafluoride is not readily available and has been found to be reducible at an acceptable rate only at temperatures above the melting point of the 316 SS substrate, the effort required to manufacture the fluorides at SFL was not thought to be worth-while and the fluoride system was set aside. Additionally, ZrF_4 is a very non-volatile material. In a ZrF_4 system the feed system would need to be maintained at the impractical level of only 100° to 200°C below the specimen temperature.

Neither zirconium tetrabromide nor tetrachloride could be readily hydrogen reduced to plated metal as a single component. However, both halides become involved in a consecutive reaction in the presence of the columbium halide whereby the $CbCl_5$ or $CbBr_5$ participates as a reducing agent for the $ZrCl_4$ or $ZrBr_4$. This is in contrast to the independent character of the mixed iodide system discussed above. In the mixed Cb/Zr bromide or chloride system the amount of zirconium deposited is dependent upon the columbium halide availability and a rather large fluctuation in zirconium halide would result in a much smaller fluctuation in zirconium content in the deposit. For example, a 20% change in $ZrCl_4$:$CbCl_5$ ratio would yield only a 1-2% zirconium variance in the Cb/Zr alloy. A system of this type is well suited for control of a 99%/1% alloy.

Because of the greater subhalide condensate problem experienced with the bromide system (discussed in Section II of this report) and the somewhat greater difficulty encountered in accurately controlling bromine vapor flow to the brominators, the columbium/zirconium mixed chloride system was deemed most promising and therefore explored in the most detail.

2. OPTIMIZATION OF CHLORIDE SYSTEM

The same plating apparatus used for the columbium runs was used to co-deposit columbium and zirconium. Separate chlorinators were employed for the two metals; the arrangement is described in Section III of this report. Columbium

metal chips and zirconium sponge were used as chlorinator feed materials. A series of depositions was made to plate the Cb/Zr alloy on the outside surface of 316 SS tubes using the optimum chamber pressure and specimen temperature developed in the columbium runs. Chlorine flow rate ratios of 4.5:1 and 100:1 (Cb:Zr) produced Cb:Zr metal weight burnup rate ratios ranging from 4.2:1 at the lowest Cl_2 ratio to 30:1 at the highest Cl_2 ratio. A large excess hydrogen flow was used in each case.

Microprobe analyses of all of the specimens produced in these initial runs indicated the presence of less than 0.1% zirconium. The zirconium sponge feed stock used in these runs was found to be highly suspect with regard to oxygen contamination. All attempts to plate significant quantities of zirconium, using zirconium sponge feed stock in the chlorinator were unsuccessful.

Oxygen contamination of the zirconium metal feed to the chlorinator could be catastrophic to the zirconium plating potential. The low volatility and stability of ZrO_2 would exclude thermal outgassing or hydrogen reduction as methods for removing the oxide impurity. Furthermore, ZrO_2 is soluble in zirconium, especially at elevated temperatures. This would homogenize ZrO_2 surface contamination with the bulk zirconium metal, further deteriorating the zirconium metal feed material. At normal chlorinator temperatures the oxygen that is present as ZrO_2 would be available to form $ZrOCl_2$, a non-plating species.

It would be possible to include carbon in the zirconium chlorinator to convert the ZrO_2 to ZrC. The ZrC would then readily convert to $ZrCl_4$ when reacted with chlorine. Unfortunately a temperature substantially above normal chlorinator temperature is required for this reaction and carbon contamination of the specimen deposit would probably result from such a system. The best solution is to employ the highest possible quality of zirconium metal in the chlorinator.

A series of trial Cb-1% Zr specimens were prepared using electron beam melted zirconium bar stock as the chlorinator feed material. Small pellets suitable for packing into the chlorinator were cut from the bar stock in an inert atmosphere to reduce the possibility of oxygen contamination of the cut surfaces. Three types of trial runs were made. One used a $ZrCl_5$:CbC_4 ratio of 50:50; another used a ratio of 30:70. Radial microprobe analyses were conducted on cross sectional samples taken at two different longitudinal points on each specimen. The data for the 50:50 samples, plotted as percent zirconium versus radial thickness of the plate in

microns, are shown in Figure 10. Similar data for the 70:30 samples is given in Figure 11. No appreciable zirconium concentration was detected in the 30:70 runs; the microprobe data for these runs are not included here. The above results were qualitatively confirmed by SFL chemical analyses.

The 1850°F optimum plating temperature found for the columbium system was found to apply to the Cb/Zr system as well. The characteristics of low plating rate at lower temperatures and coarse plate at higher temperatures were nearly identical for the Cb and Cb/Zr systems. However, a coarse deposit was encountered at a lower temperature in the Cb/Zr system than it was in the Cb system.

A 70:30 specimen was prepared for the purpose of determining the composition uniformity of this material. The center of the sample was cut into three 1/2 inch long sections and each of these sections was cut into "D" halves. The outer (plated) surface of the bottom of one of the "D's" was mounted and polished flat for longitudinal probing; approximately 0.001" of the radius was removed in polishing. The other "D" was mounted on end and polished flat for radial probing. Figure 12 is a drawing which depicts the configuration of the "D" samples.

The three longitudinal sections, their corresponding radial sections, plus an additional ring radial section (taken from just below the others) were microprobed. The data are shown in Figure 13. T, M, and B refer to "top", "middle", and "bottom" portions of the specimen, referenced from the plating gas inlet end. Percentage zirconium is plotted versus position down the length of the three sections, with an approximate allowance made for the width of the sawcut between each section. Plots of composition versus radial plate thickness are positioned in Figure 13, relative to their respective axial cross sectional points of measurement. The specimen plating temperature profile (pyrometrically measured brightness temperatures) is given in the last page of Figure 13-I. The radial point at which each longitudinal probe was made is indicated on its respective radial plot.

There is an uncertainty with regard to the exact location at which the first radial probe data point appears totally on the deposit, i.e., the first point shown to be zero percentage zirconium is not necessarily on the deposit but could be on the 316 SS or on the Cb-SS bond (refer to Section VII of this report). Therefore, any initial point on Figure 13 is positioned to within ± the width of a step — between points — 10 microns for the radial data and 250 microns for the longitudinal data.

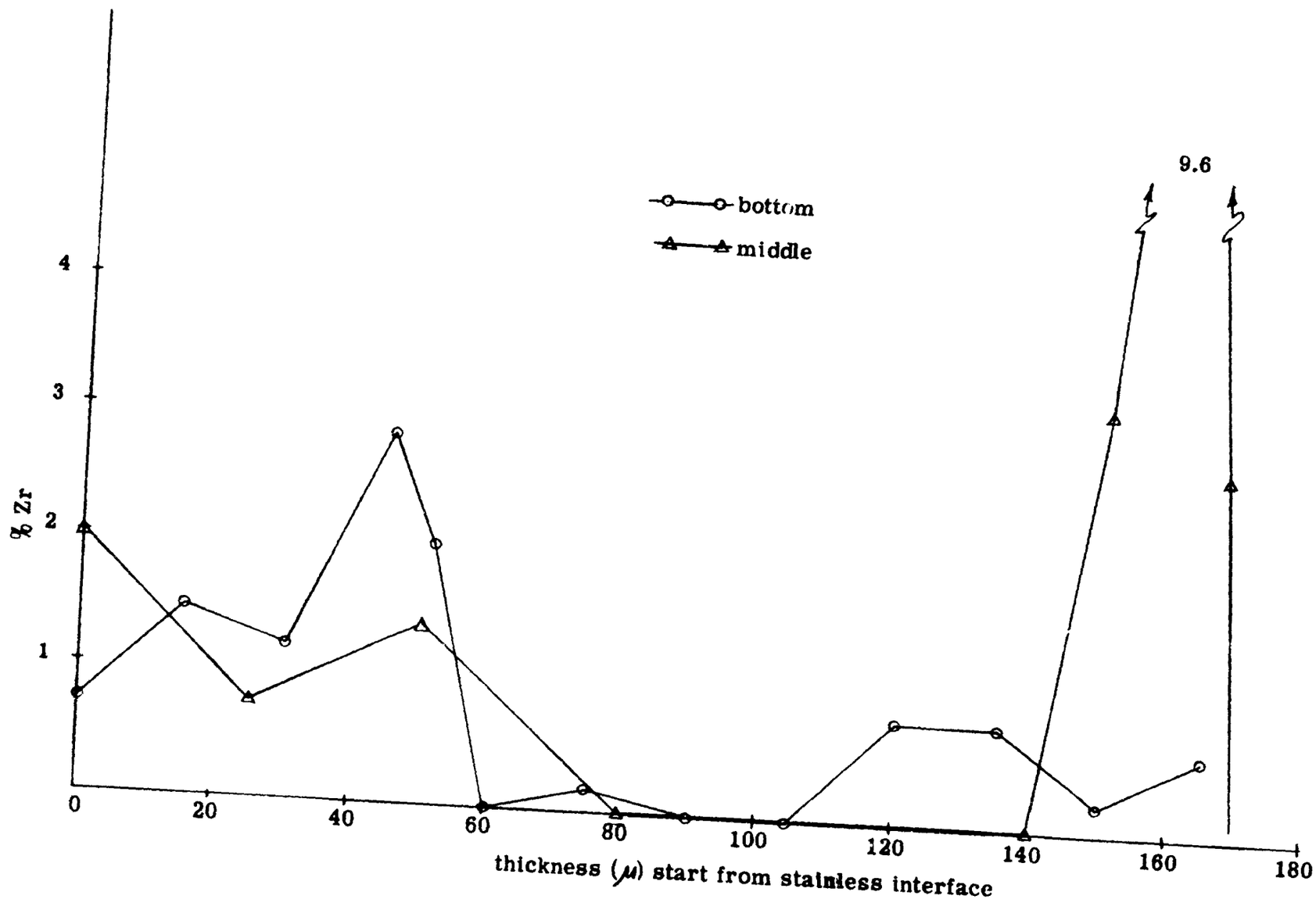


FIGURE 10

Cb-Zr ALLOY (MICROPROBE DATA)

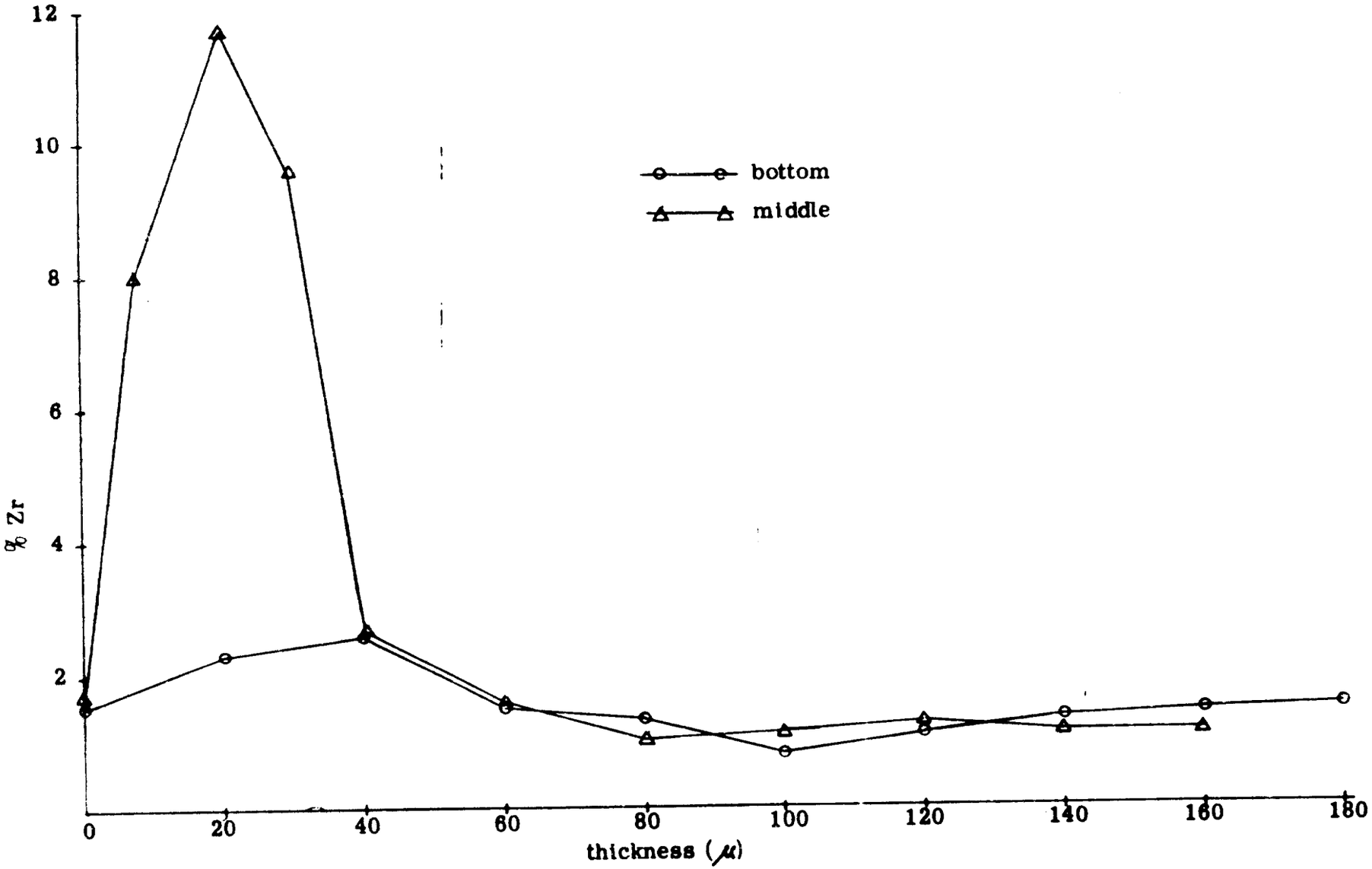


FIGURE 11

Cb-Zr ALLOY, DUPLICATE RUN (MICROPROBE DATA)

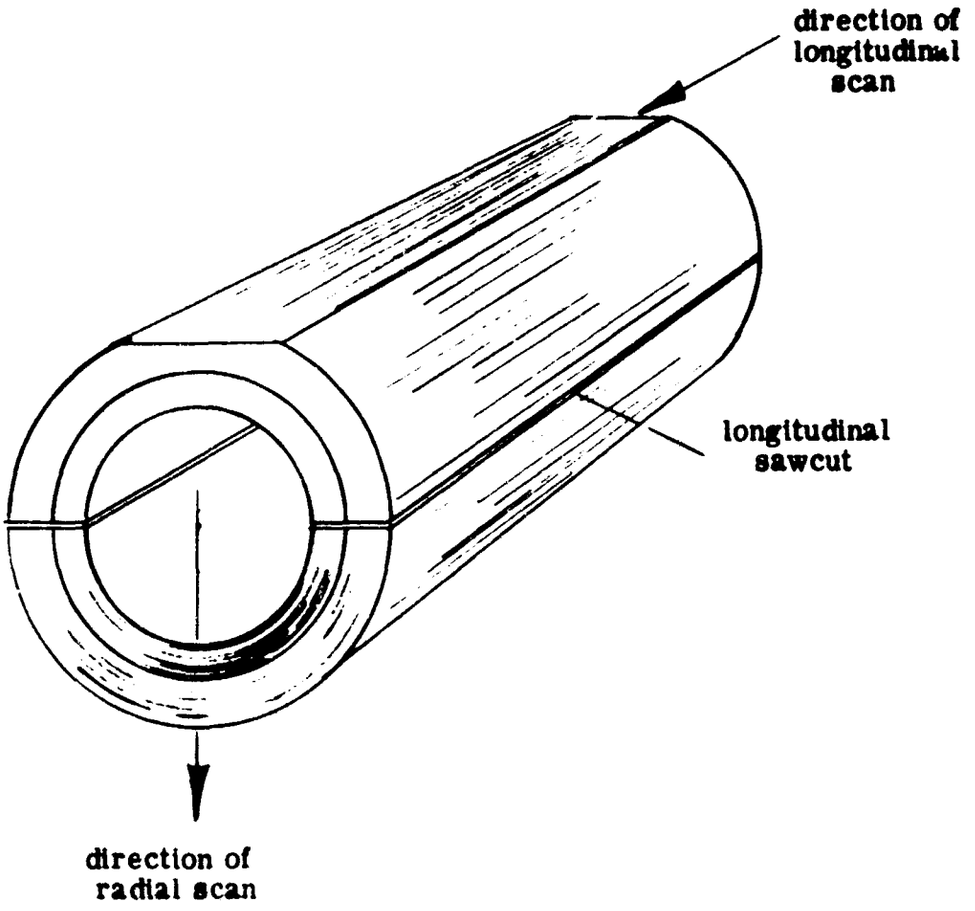


FIGURE 12

Cb-Zr SAMPLE AS PREPARED FOR
MICROPROBE (SKETCH)

FIGURE 13

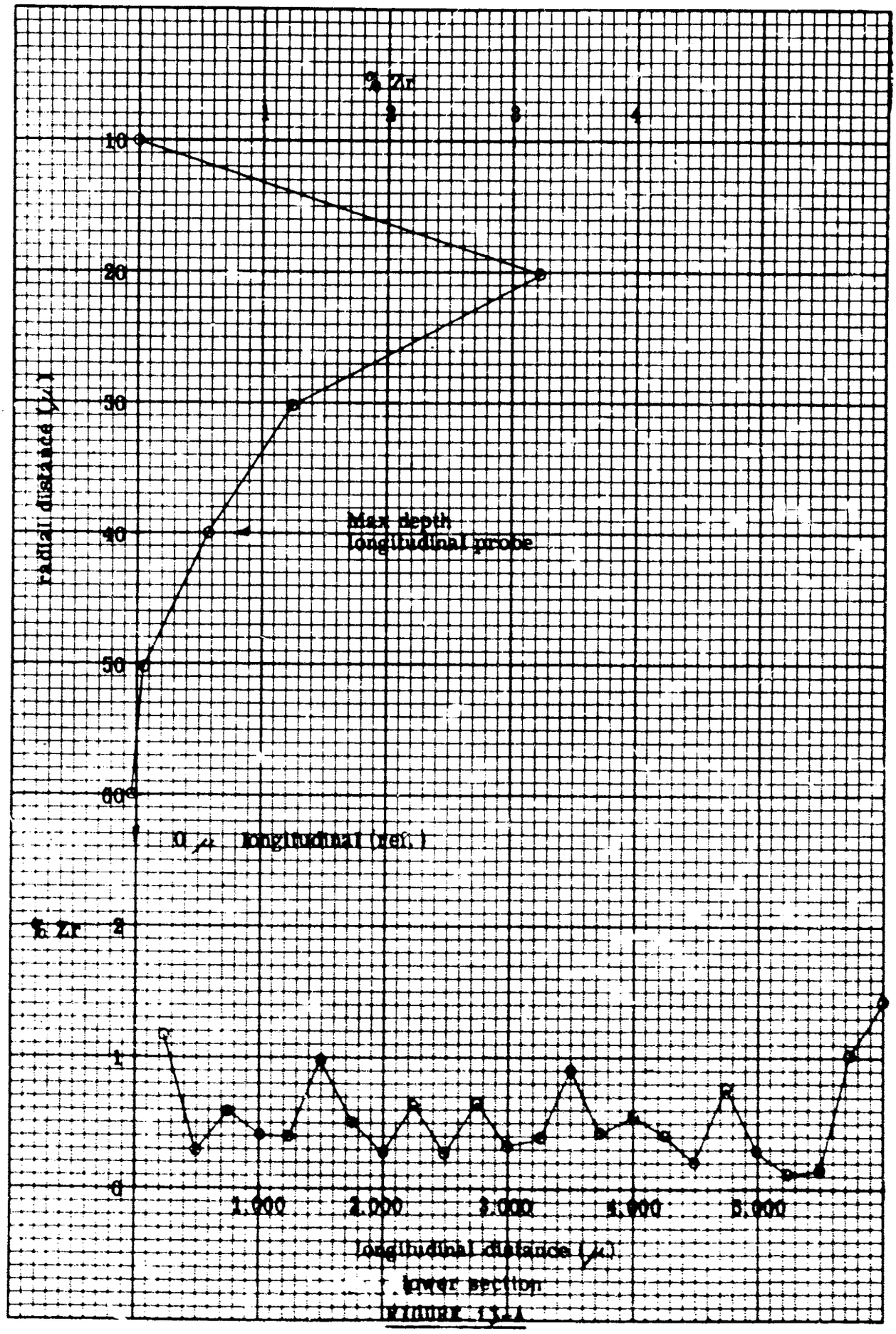
COLUMBIUM/ZIRCONIUM ALLOY SPECIMEN

Radial and Longitudinal Composition Profiles,

Microprobe Data ---------- A through H

Longitudinal Deposition Temperature Profile,

Pyrometer Data ---------- I


% Zr
1
2
3
4
10
20
30
40
50
60
Radial distance (μ)
Max depth
longitudinal probe
0 μ longitudinal (ref.)
% Zr
2
1
0
1.000
2.000
3.000
4.000
5.000
longitudinal distance (μ)
lower section
Figure 13.A

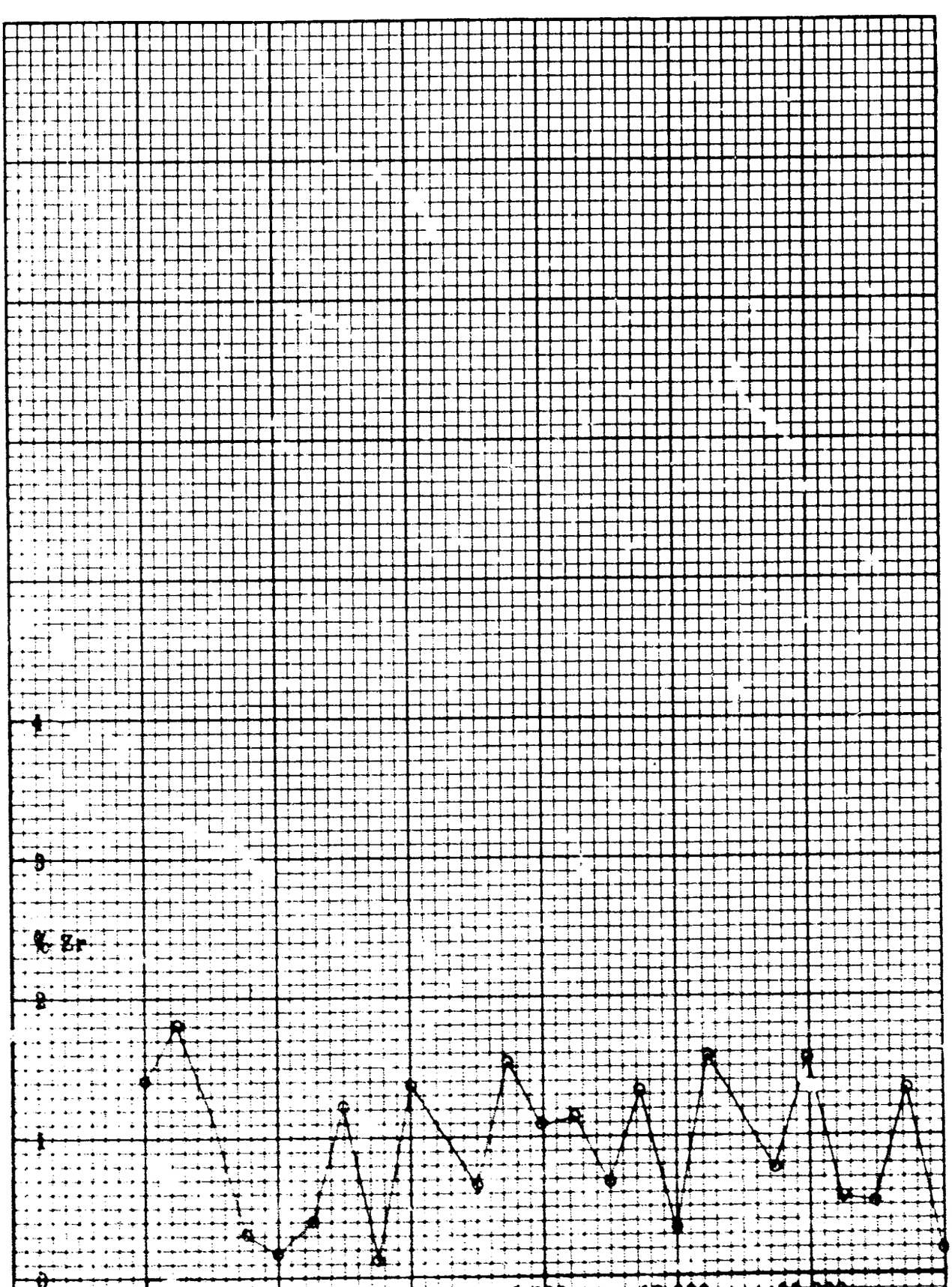

% Zr
2
1
0
6,000
7,000
8,000
9,000
10,000
11,000
longitudinal distance (x)
lower section

FIGURE 13.8

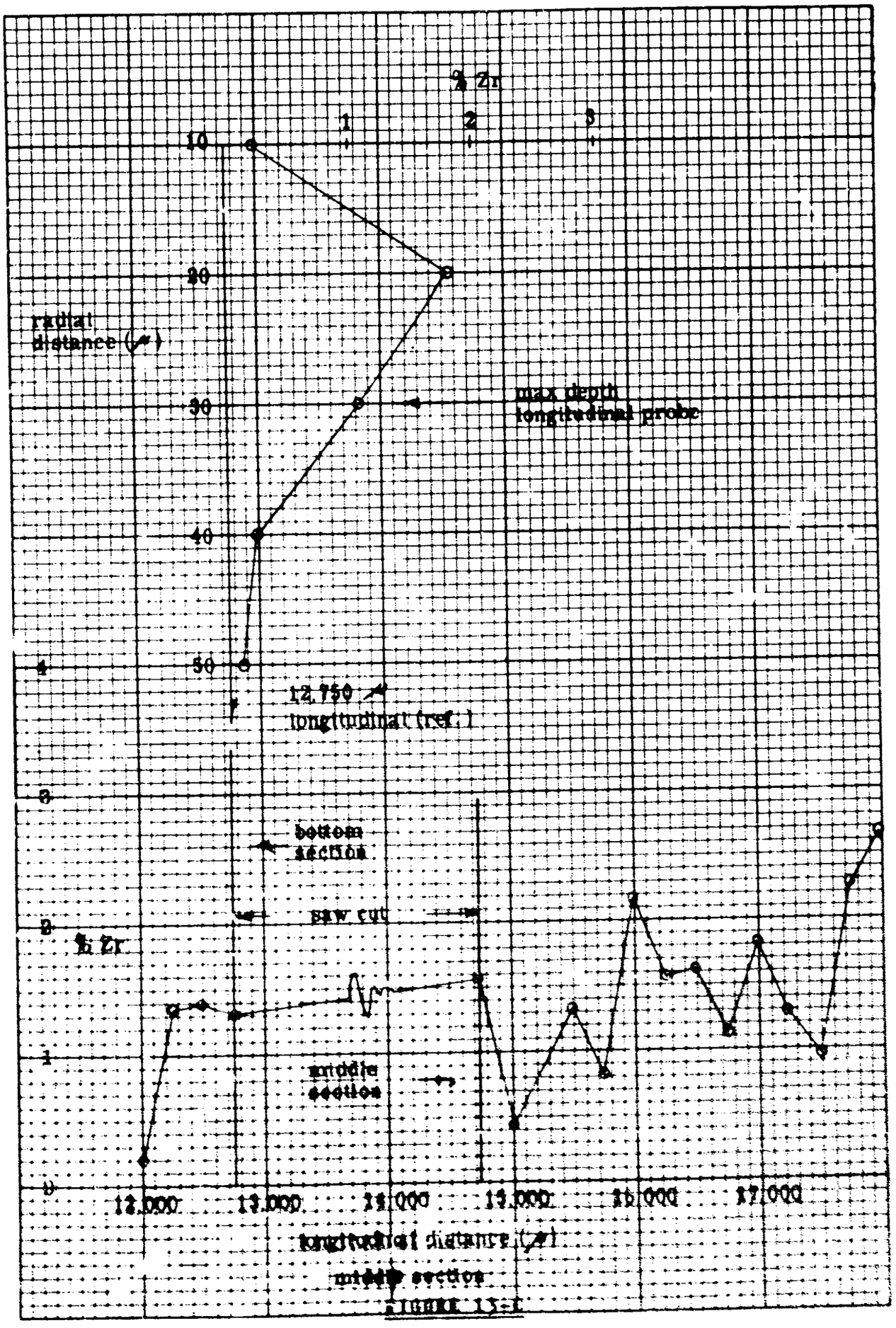

% Zr
1
2
3
10
20
radial distance (in)
30
max depth longitudinal probe
40
50
12.750
longitudinal (ref. 1
bottom section
saw cut
% Zr
middle section
12.000
13.000
14.000
15.000
16.000
17.000
longitudinal distance (in)
middle section

FIGURE 13-1

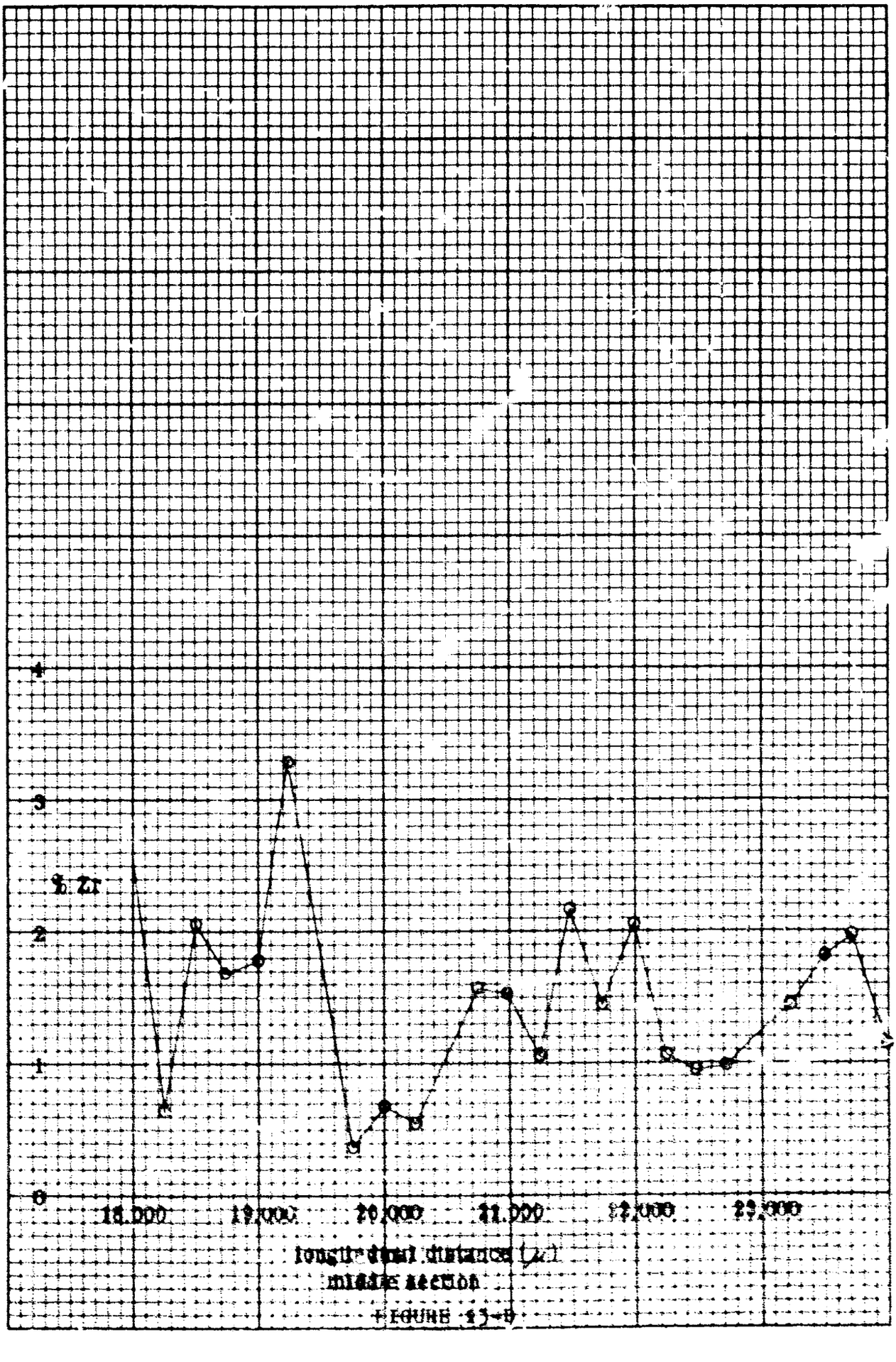


FIGURE 13-9

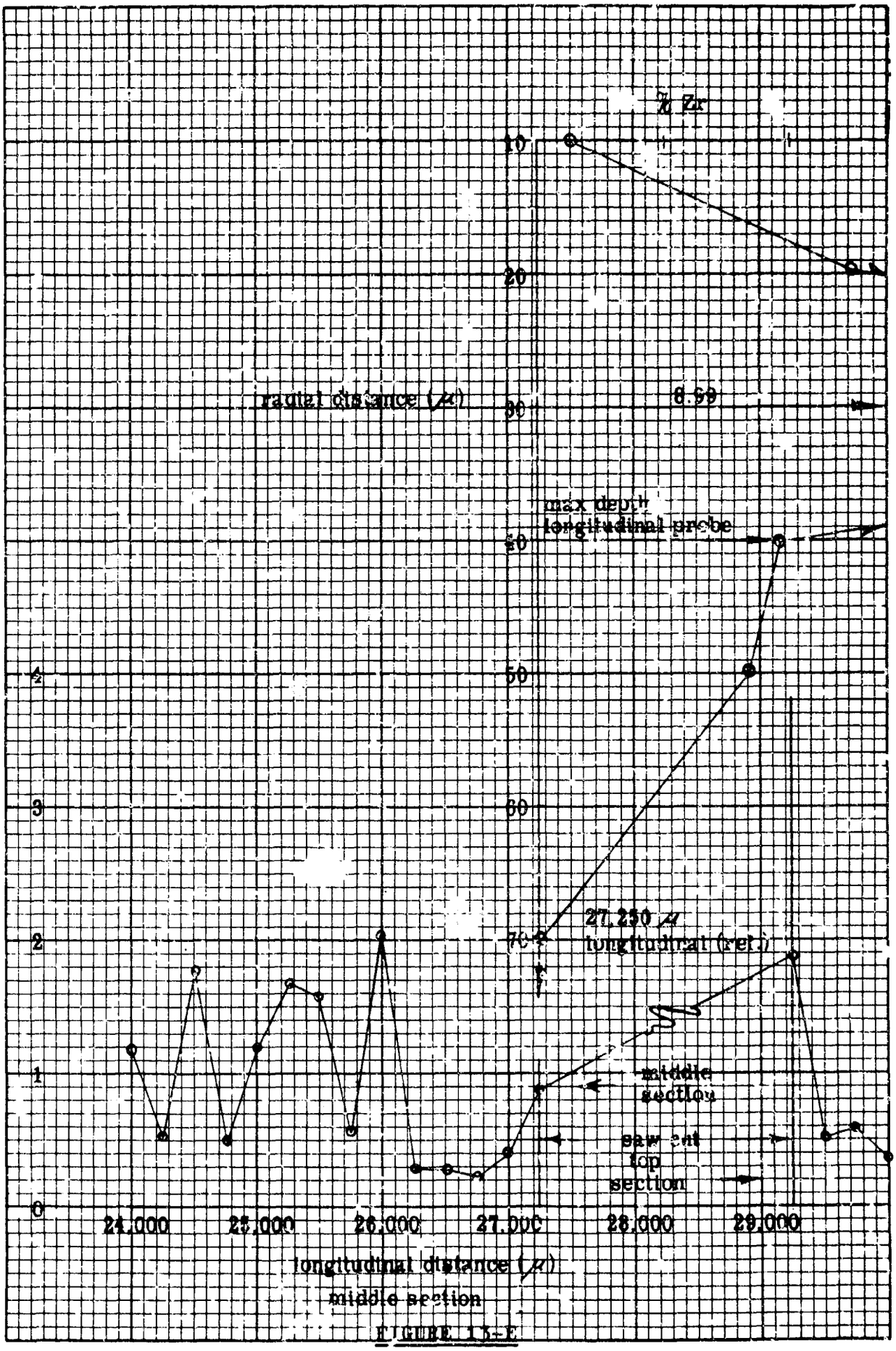

% Zr
10
20
radial distance (μ)
30
8.99
max depth
longitudinal probe
40
50
60
27.250 μ
longitudinal (ref.)
70
middle
section
saw cut
top
section
0
1
2
3
½
24.000
25.000
26.000
27.000
28.000
29.000
longitudinal distance (μ)
middle section

FIGURE 13-E

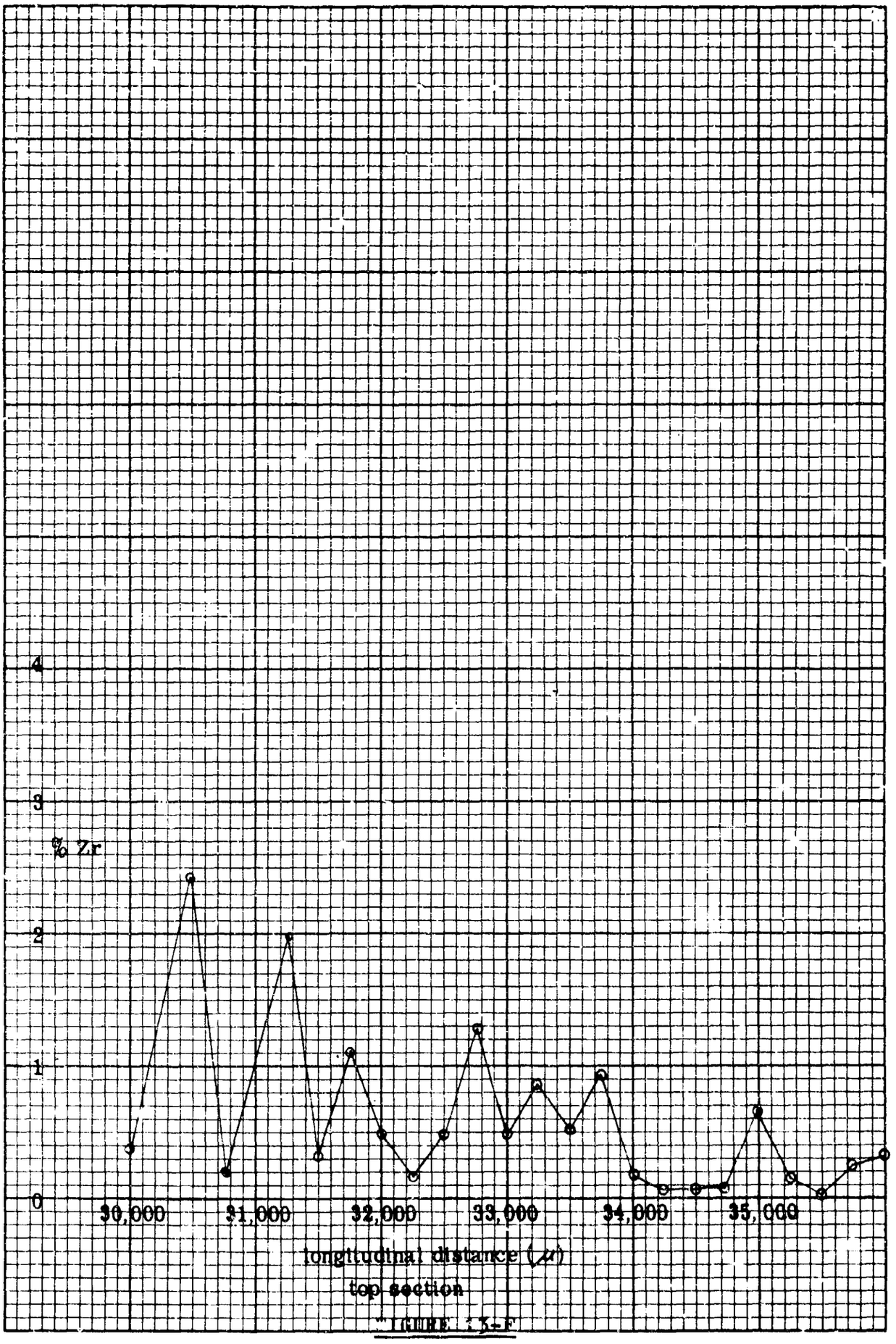

4
3
% Zr
2
1
0
30,000
31,000
32,000
33,000
34,000
35,000
longitudinal distance (μ)
top section

FIGURE 13-F

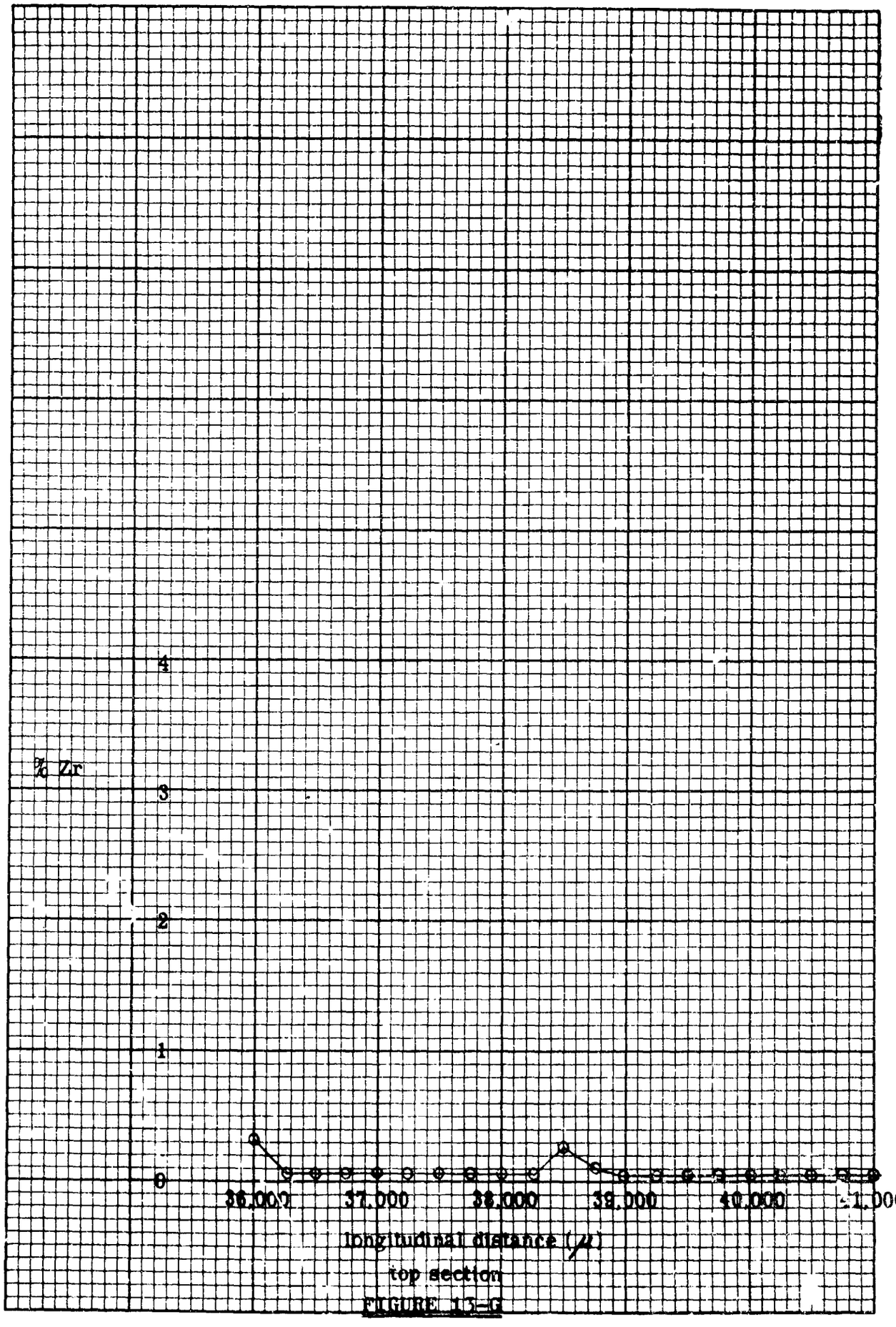

4
% Zr
3
2
1
0
36.000
37.000
38.000
39.000
40.000
41.000
longitudinal distance (μ)
top section

FIGURE 13-G

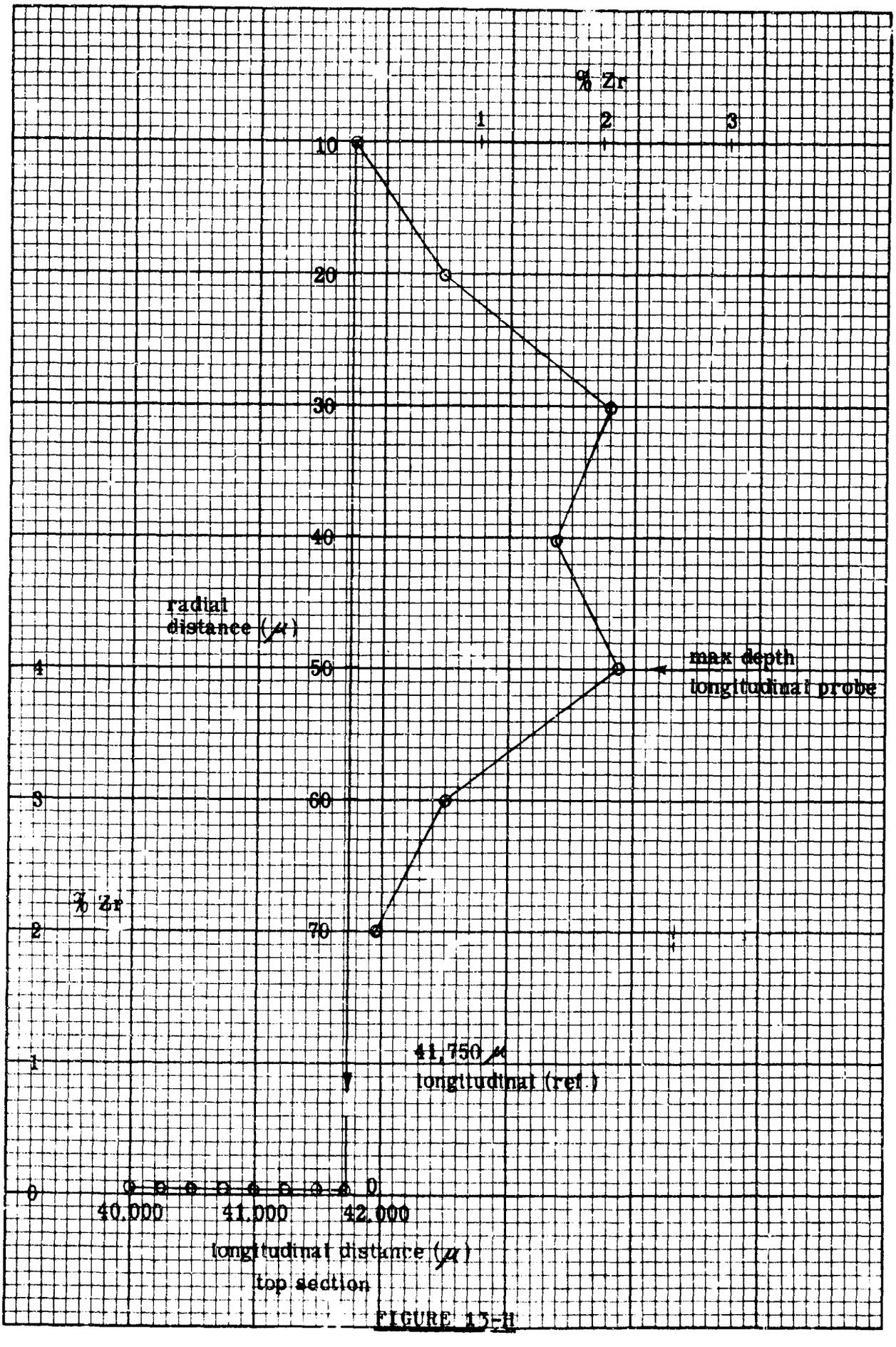
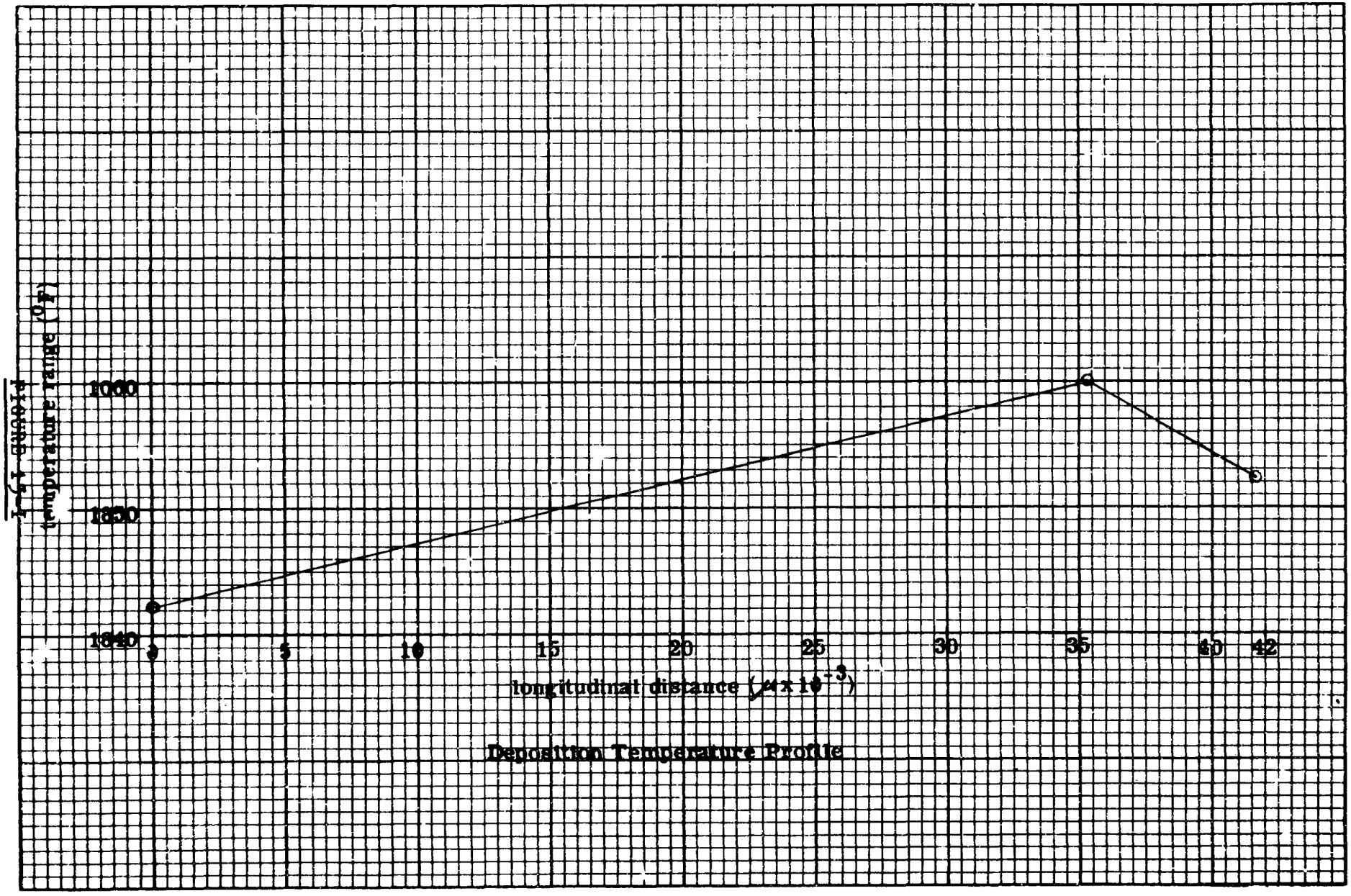

% Zr
1
2
3
10
20
30
40
radial
distance (μ)
50
max depth
longitudinal probe
60
% Zr
70
41,750 μ
longitudinal (ref.)
0
40.000
41.000
42.000
longitudinal distance (μ)
top section

FIGURE 13-H



Deposition Temperature Profile

There is an additional error to consider in the positioning of each data point. A certain amount of drifting of the probe "spot" occurred during a traverse and this varied somewhat from sample to sample. The ferromagnetic interaction of the probe with the stainless steel bends the probe toward the stainless. This interaction is not particularly serious in longitudinal section probing where the stainless remains a fixed distance from the plate and the traverse path; the entire path is merely displaced rather uniformly toward the stainless. However, magnetic deflection could be quite significant during a radial scan. In moving from the stainless outward over the deposited region the error in a 150μ indicated traverse could be as great as minus 50μ. That is, bending of the beam in a direction opposite that of the traverse could cause a fixed 10μ step between data points to become perhaps 7 to 8μ. A certain amount of interference is also possible from the sample mounting material.

The indicated axial uniformity of the deposit was encouraging; however the radial data in Figure 13 first indicated a phenomenon later observed on several occasions. The Cb/Zr deposition had a certain tendency to begin at a rather high zirconium percentage and then cease to plate zirconium entirely after the first few mils of deposit have been plated. This subject is explored in detail in Section VIII of this report.

In keeping with the indicated desirability to limit oxygen contamination in the zirconium metal feed material, and because preparation of feed material by machining zirconium bar stock proved to be time consuming, sources of high purity zirconium pellets were explored. The largest possible pellets (up to 1/4 inch diameter) were sought to limit the surface-to-volume ratio and therby limit surface contamination. Zirconium pellets, -10 +20 mesh, and 710 ppm oxygen content, were finally purchased. This mesh size was the largest available in high purity material.

The zirconium pellets were used in three calibration runs, employing flow ratios of $ZrCl_4$ to $CbCl_5$ of 50:50, 60:40, and 70:30. Figure 14 shows the data for the 70:30 run presented similarly to the data of Figure 13. The tendency for the zirconium content to suddenly drop to zero or near zero midway through the plate is again apparent from the radial data.

FIGURE 14

COLUMBIUM/ZIRCONIUM ALLOY SPECIMEN
PREPARED WITH 70:30 $ZrCl_4$:$CbCl_5$ RATIO

Radial and Longitudinal Composition Profiles,

Microprobe Data ---------- A through F

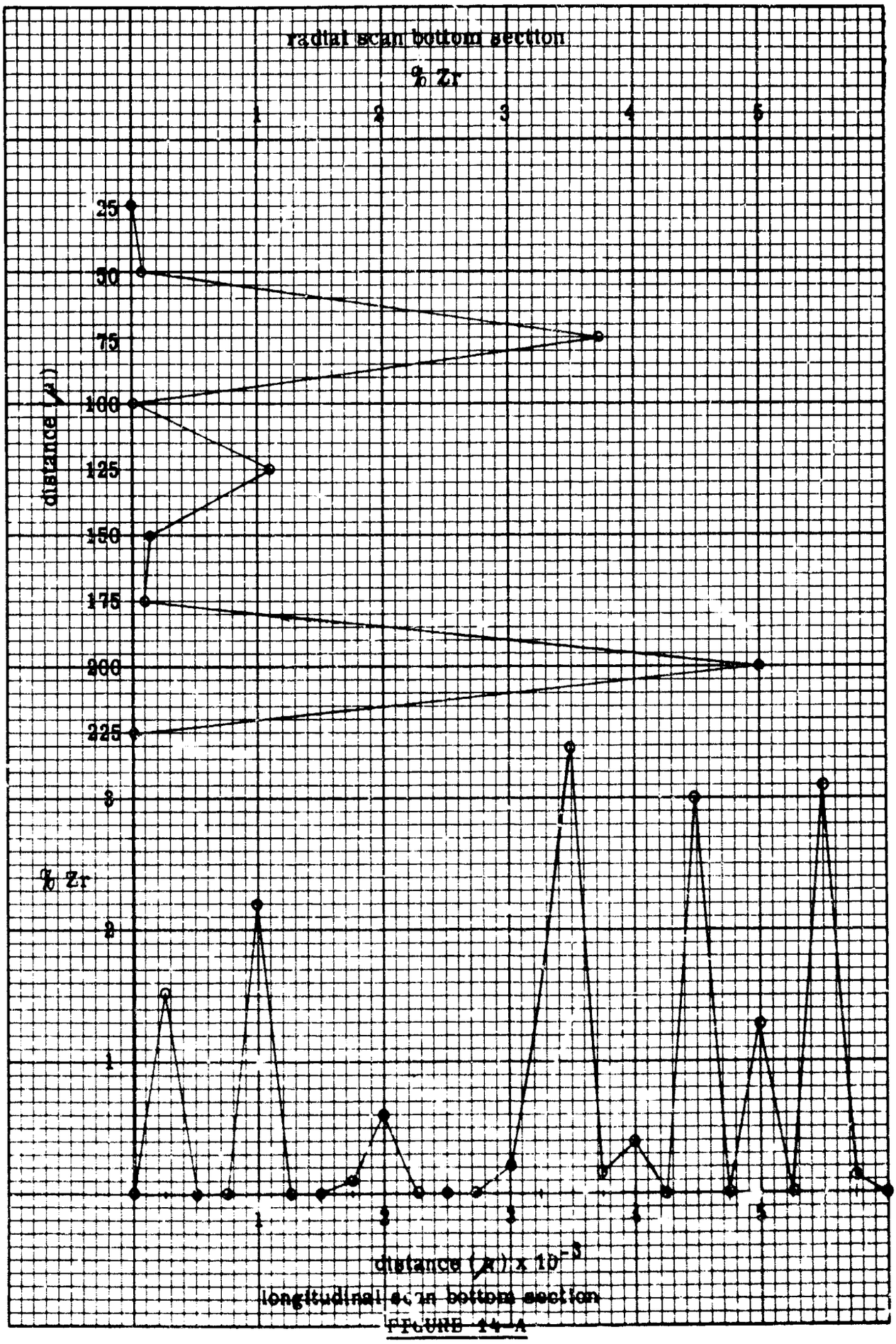

radial scan bottom section
% Zr
1
2
3
4
5
25
50
75
100
125
150
175
200
225
distance (mil)
% Zr
3
2
1
1
2
3
4
5
distance (mil) x 10⁻³
longitudinal scan bottom section

FIGURE 14-A

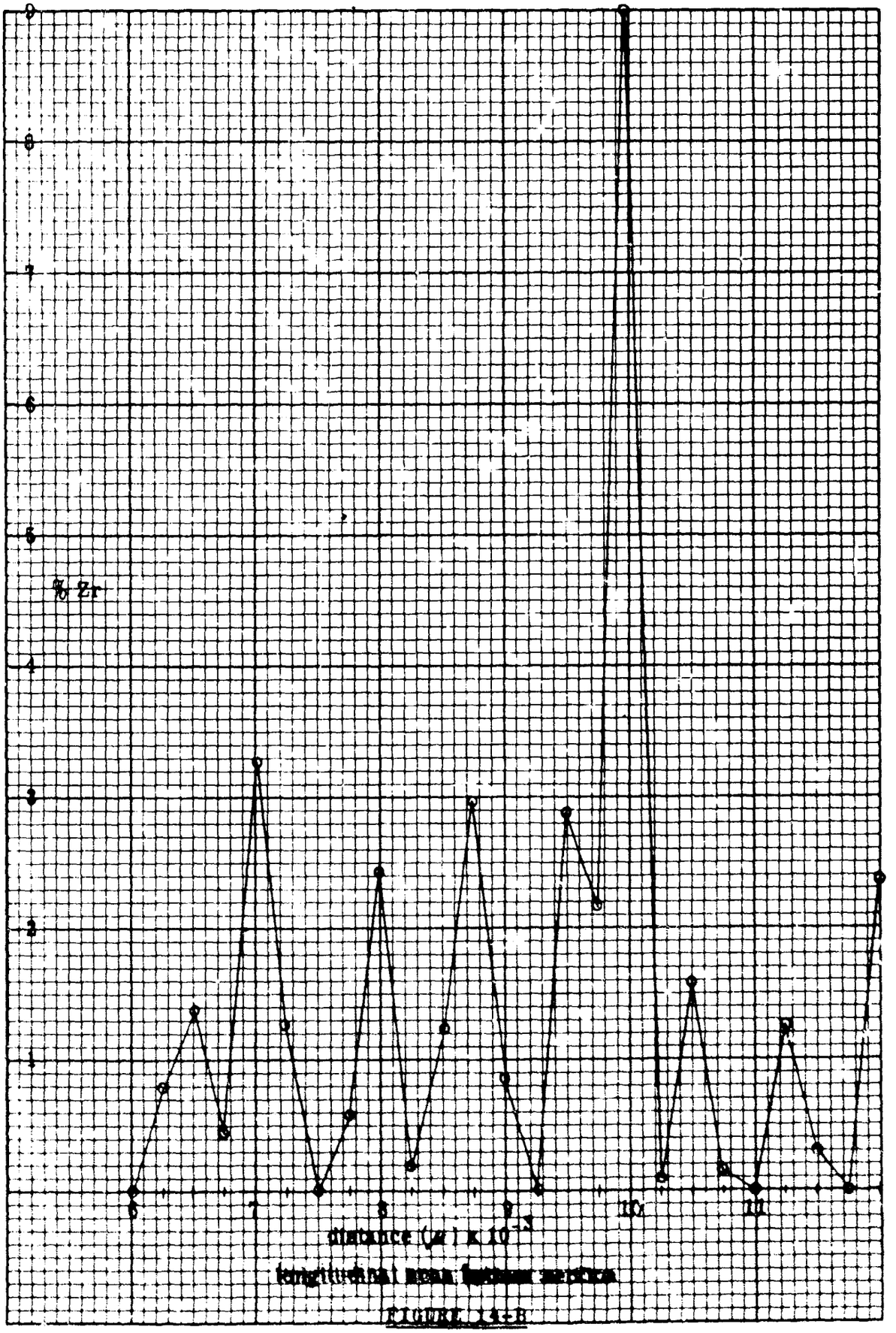


FIGURE 14-B

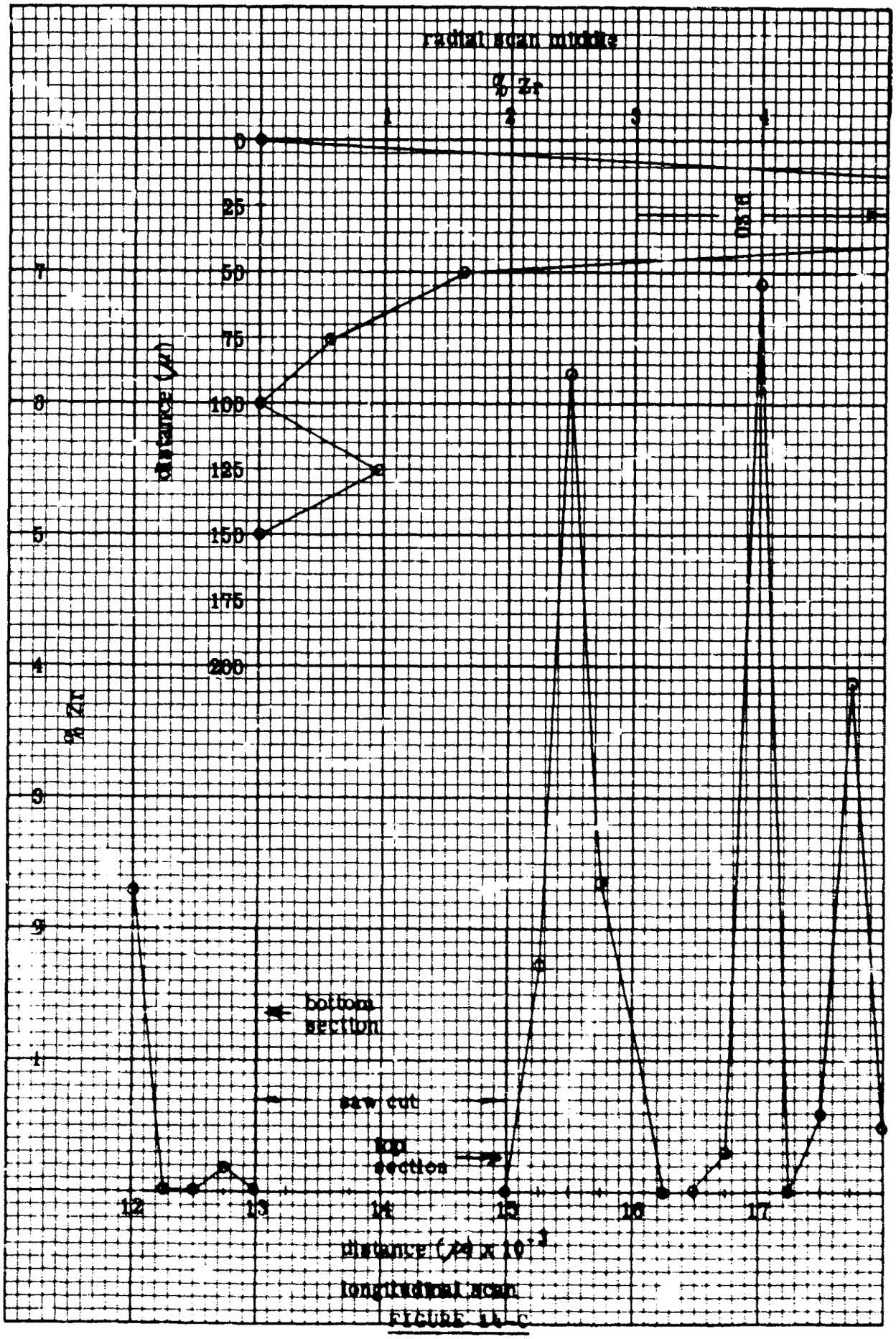
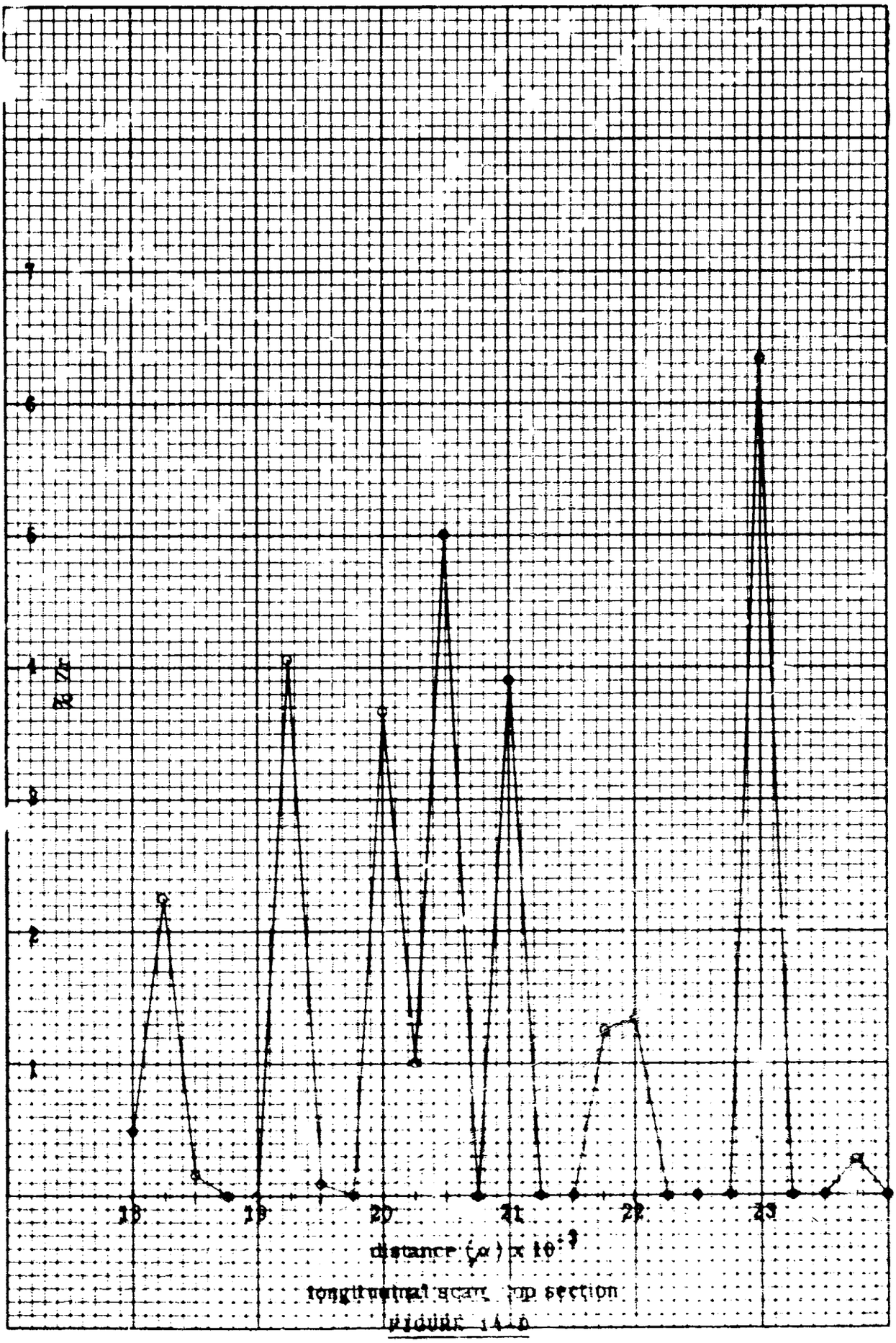
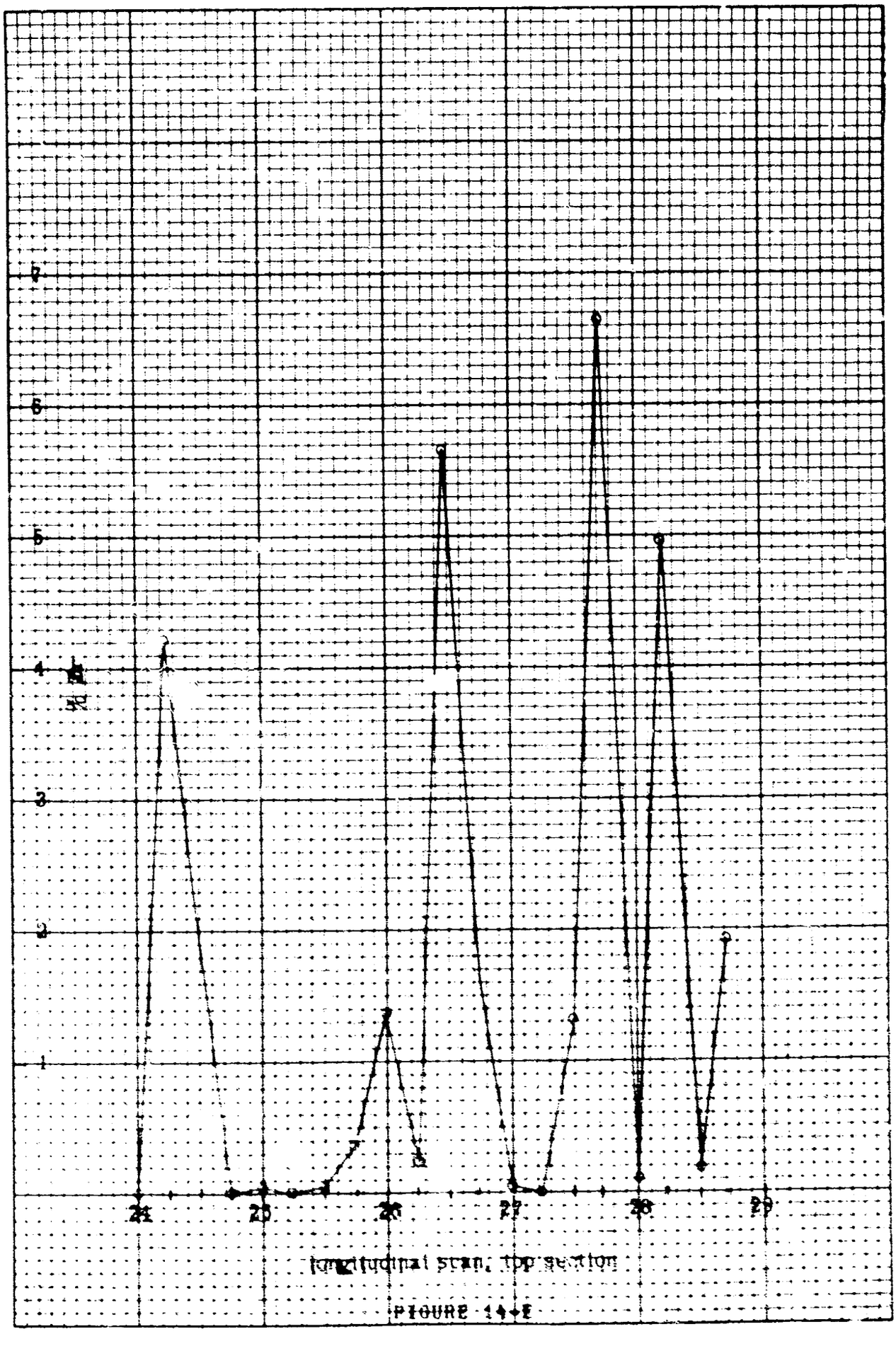

radial scan middle
% Zr
distance (μ)
bottom section
saw cut
top section
distance (μ) x 10⁻³
longitudinal scan

FIGURE 14-c



longitudinal scan, top section

FIGURE 14-D



Longitudinal strain, top section

FIGURE 14-E

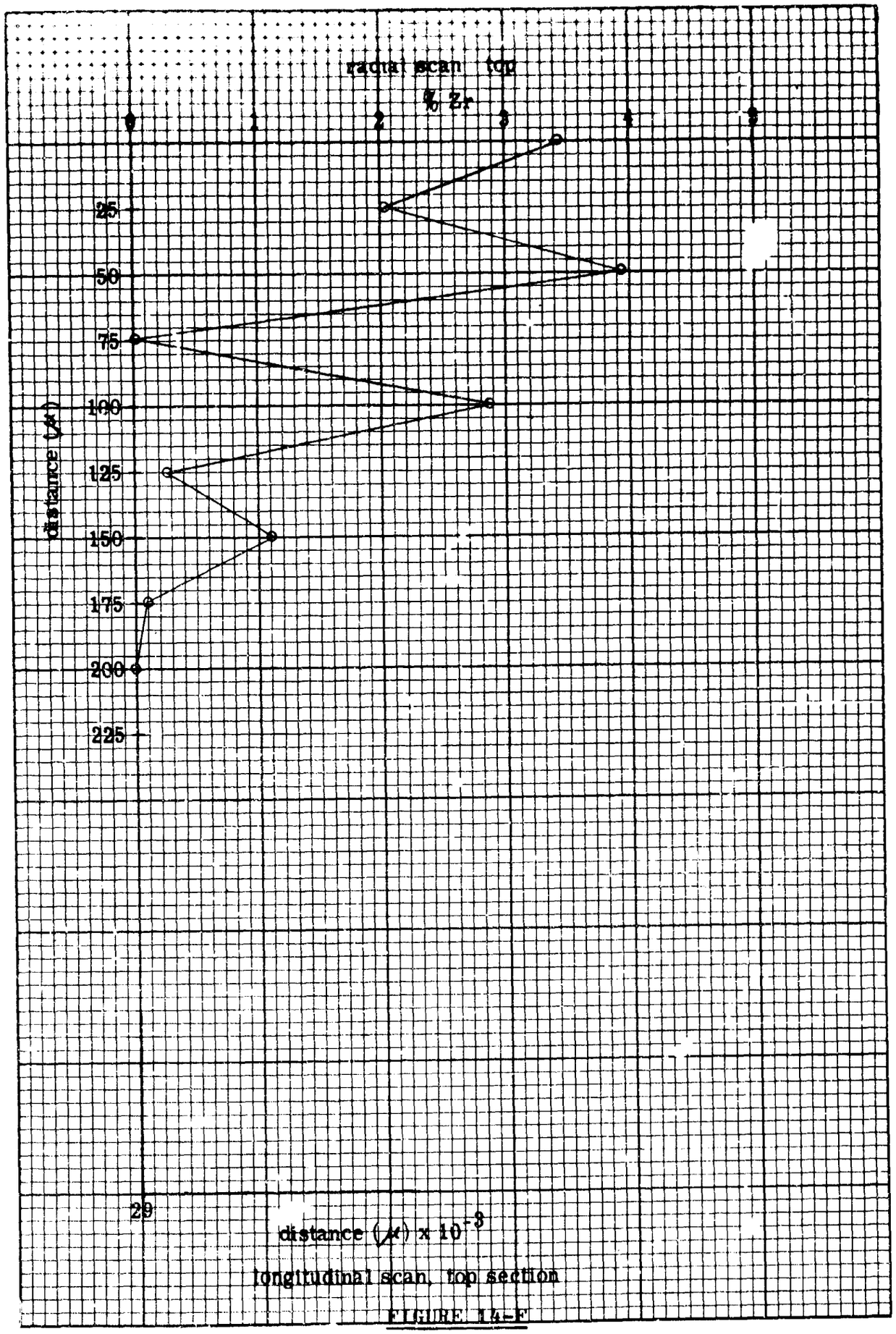

radial scan top
% Zr
0
1
2
3
4
5
25
50
75
100
125
150
175
200
225
distance (μ)
29
distance (μ) x 10⁻³
longitudinal scan, top section

FIGURE 14-F

Only the radial data for the 60:40 run is shown in Figures 15, 16, and 17. The zirconium depletion phenomena is more apparent for this run (the $ZrCl_4$:$CbCl_5$ ratio is lower) so it is not surprising that only trace quantities of zirconium were detected in the corresponding longitudinal sections as these samples were not polished sufficiently to cut into the Cb/Zr region.

The 50:50 samples showed only trace amounts of zirconium, both longitudinally and radially, which corresponds to the 30:70 run using the zirconium bar stock feed material. There is an interesting observation to be made here. The first point next to the 316 SS substrate for each of the three radial samples showed a zirconium content of 0.7 percent, 0.1 percent, and 3.2 percent at the specimen top, middle, and bottom, respectively. The initial high value followed by a sudden drop in zirconium content further substantiated the existence of a zirconium depletion phenomena.

Table I is a summary of data which compares the measured overall deposit thickness of various specimens with the thickness of the Cb/Zr alloy layer as found by microprobe analyses. All numbers are in microns.

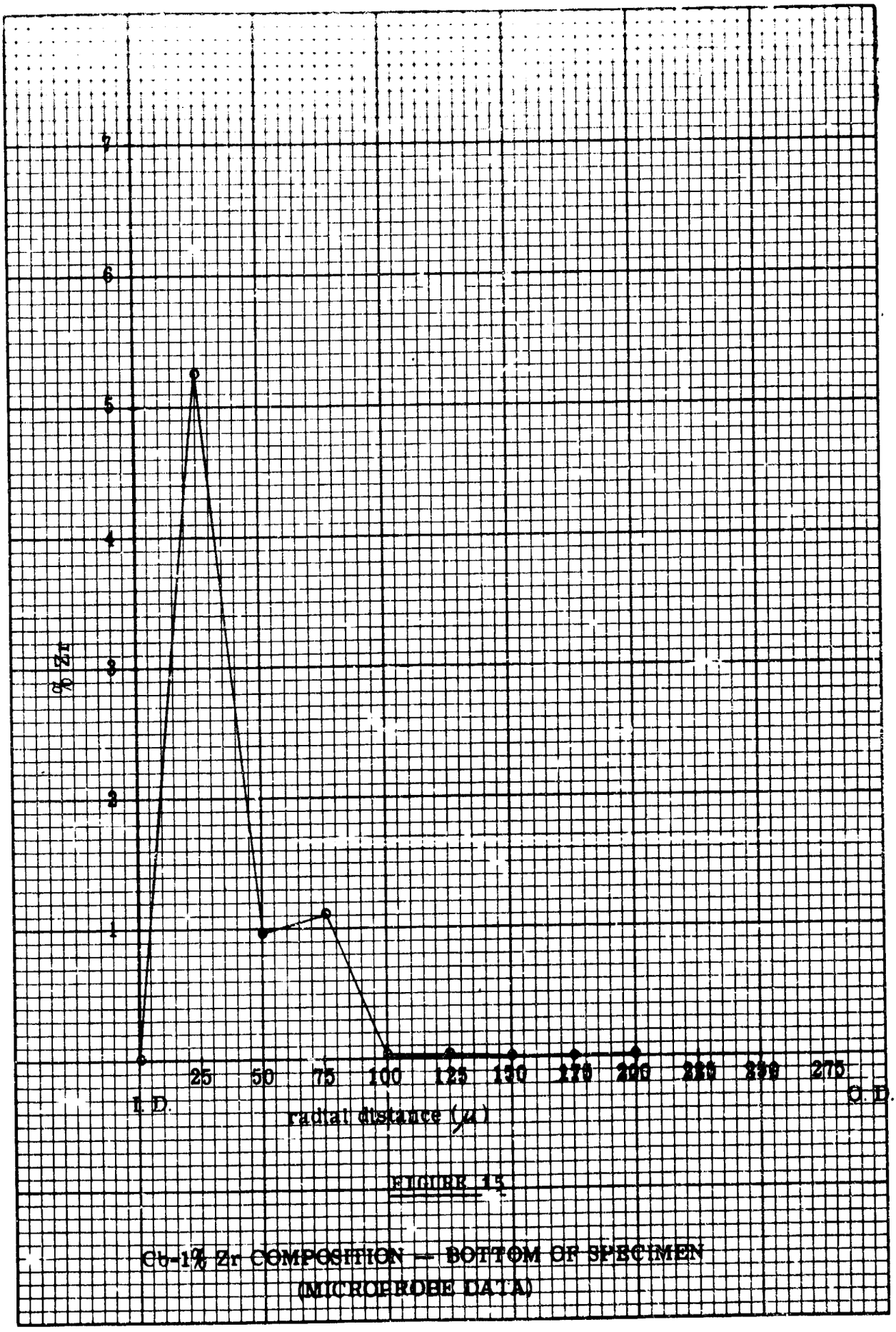


FIGURE 15

Cu-1% Zr COMPOSITION -- BOTTOM OF SPECIMEN
(MICROPROBE DATA)

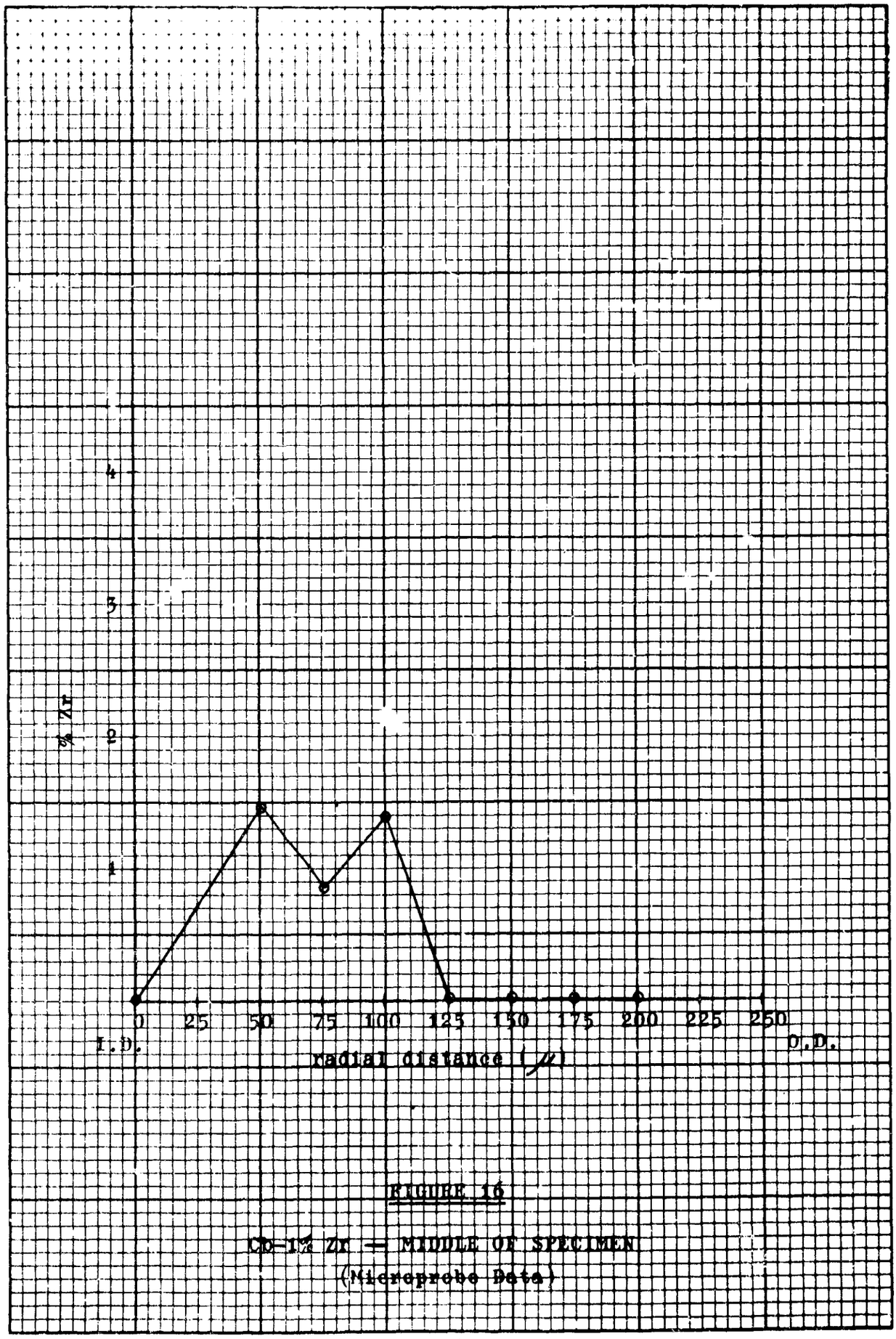


FIGURE 16

Cb-1% Zr — MIDDLE OF SPECIMEN

(Microprobe Data)

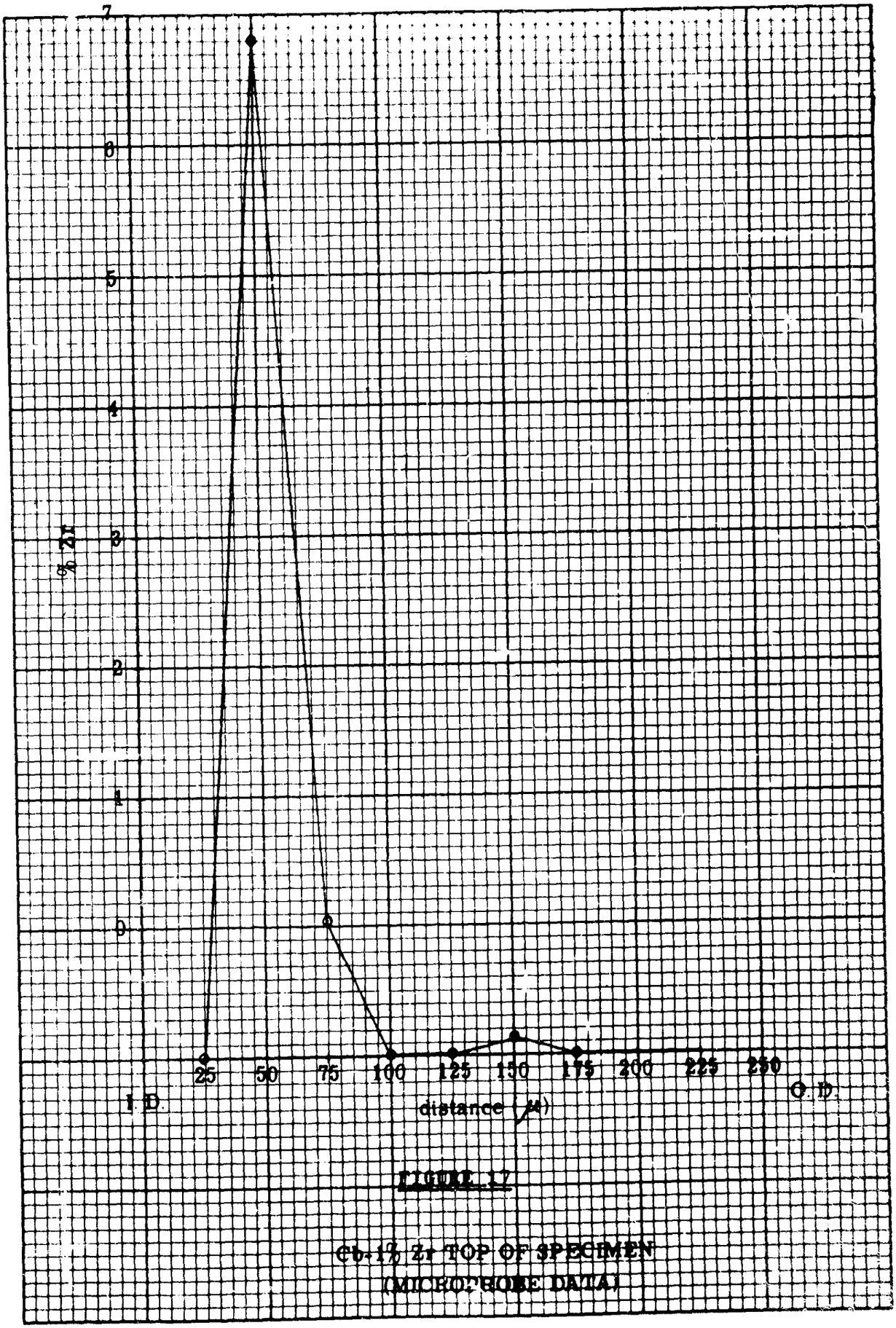


FIGURE 17

Cb-1% Zr TOP OF SPECIMEN
(MICROPROBE DATA)

TABLE I

COMPARISON OF Cb-Zr THICKNESS VIA MEASUREMENT AND MICROPROBE

Sample #24 - Zirconium Bar Stock Feed Material (70:30 $ZrCl_4$:$CbCl_5$ Ratio)

Radial Section	Measured Deposit Thickness		Microprobe Analysis Thickness	
	Cb	Cb-Zr	Cb	Cb-Zr*
Lowest	12.5	37.5	-	30
#24 Bottom	10.0	32.5	-	40
#24 Middle	17.5	50	-	50
#24 Top	20.0	55	-	50
Sample #34 - Zirconium Pellet Feed Material (70:30 $ZrCl_4$:$CbCl_5$ Ratio)				
#34 Bottom	12.5	110	-	125
#34 Middle	12.5	115	-	100
#34 Top	15.0	117.5	-	175
Sample #33 - Zirconium Pellet Feed Material (60:40 $ZrCl_4$:$CbCl_5$ Ratio)				
#33 Bottom	15.0	187	-	75
#33 Middle	20.0	220	-	75
#35 Top	6.25	71	-	75

*Note that the microprobe data generally peaks within the first 10-20 microns and then falls off rapidly to a much lower number or to zero. The thicknesses of Cb-Zr deposits given here from microprobe data are maximums measured to the point of complete zirconium extinction. Also, the indicated thickness is accurate to 0 - 50 μ in a 150 μ traverse, due to magnetic drift of the probe.

SECTION VII

BONDING OF Cb-1% Zr ALLOY TO A 316 SS SURFACE

When a specimen was prepared by depositing a few microns of pure columbium and then depositing the Cb-Zr alloy, an adherent bond was obtained with the 316 SS substrate. No bonding was achieved when Cb/Zr was deposited directly upon 316 SS. This difference between Cb-1% Zr/316 SS and Cb/316 SS bonding has also been observed in bimetal co-extrusion tubing operations. (See Reference 2.) The diffusion bond between Cb and 316 SS was a hard, brittle intermetallic (refer to Section XI, Part 7, and to Reference 2). However, its integrity was proven in 170° bend tests and tensile tests (refer to Section XI).

Columbium-zirconium alloy specimens were prepared in various ways to determine the best way to establish a bond with the 316 SS substrate. Figure 18 shows a plate which shattered away from the substrate upon cool-down. The plate was deposited from a constant $CbCl_5/ZrCl_4$ mixture from time zero to run termination. The same shattering phenomena was encountered when either a $CbCl_5/ZrCl_4$ mixture or pure $ZrCl_4$ was employed at the beginning of the plating run. Figure 19 is a photomicrograph of a specimen prepared in this manner; complete absence of bond to the stainless is apparent.

The feasibility of affecting a diffusion bond between a thin deposited layer of pure columbium prior to depositing the Cb-1% Zr alloy was explored and positively established. Figures 20, 22 and 24 are photomicrographs of the bond area taken longitudinally along adjacent sections of the same sample. Figures 21, 23 and 25 are photomicrographs taken radially across the top ends of the mirror halves of the longitudinal sections. (See Figure 26 for the sample configurations.) The sections of the specimen which appear in Figures 20 through 25 are the same sections, polished and etched to expose the 316 SS-plate bond area. The microprobe analyses are reported in Figure 13.

In Figures 20, 22 and 24 several layers are apparent. They include the 316 SS substrate, the diffusion bonds in the stainless steel and the columbium, the initially plated columbium layer, and the outer Cb-1% Zr plate.

The width of each of these layers appears greater than actual in the longitudinal samples because they were prepared to expose surfaces parallel to a chord rather than the

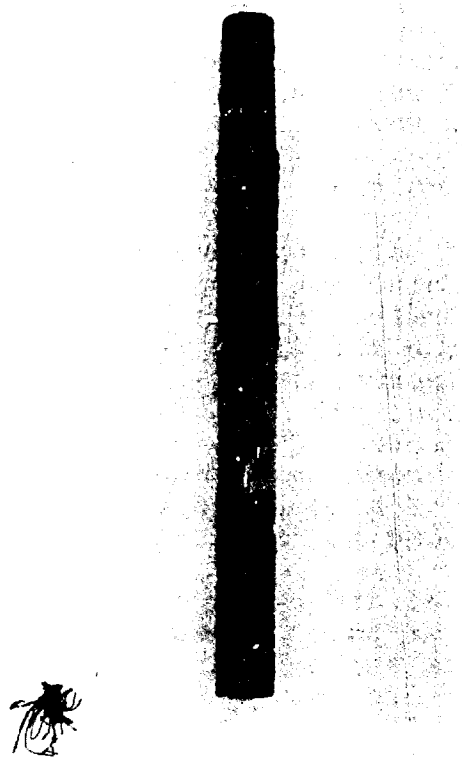


FIGURE 18

NON ADHERENT Cb-1% Zr PLATE ON 316 SS

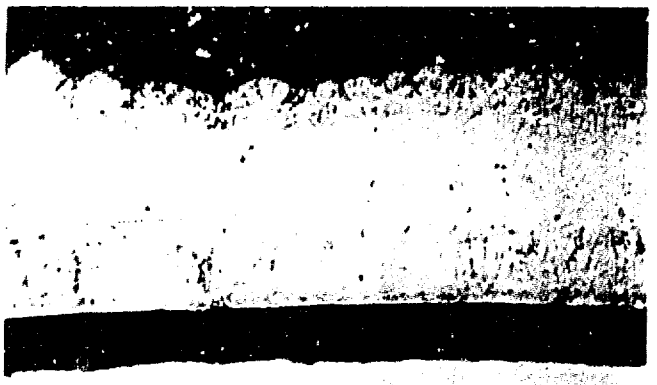


FIGURE 19

Cb-Zr PLATE SEPARATED FROM 316 SS
RADIAL SECTION (200X)

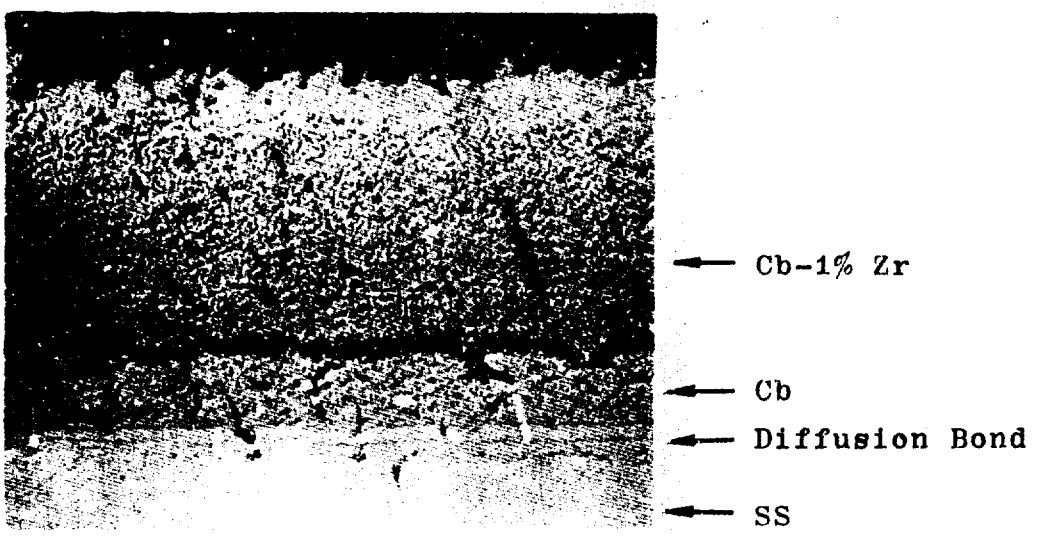


FIGURE 20

Cb-1% Zr BOTTOM
LONGITUDINAL SECTION (200X)

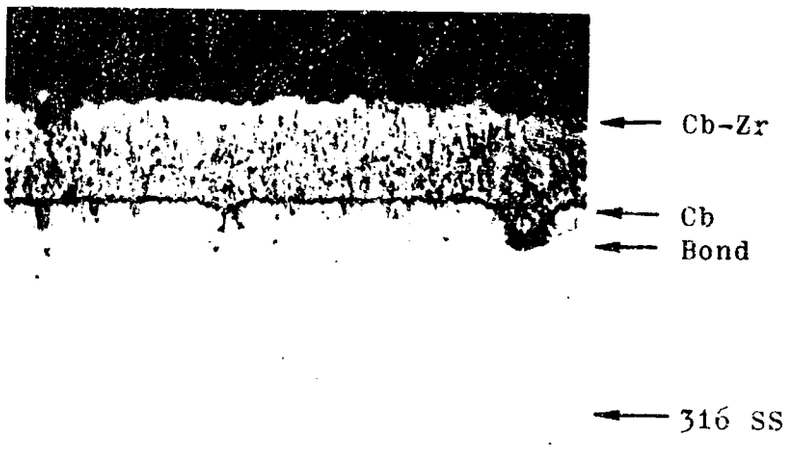


FIGURE 21

Cb-1% Zr BOTTOM
RADIAL SECTION (400X)

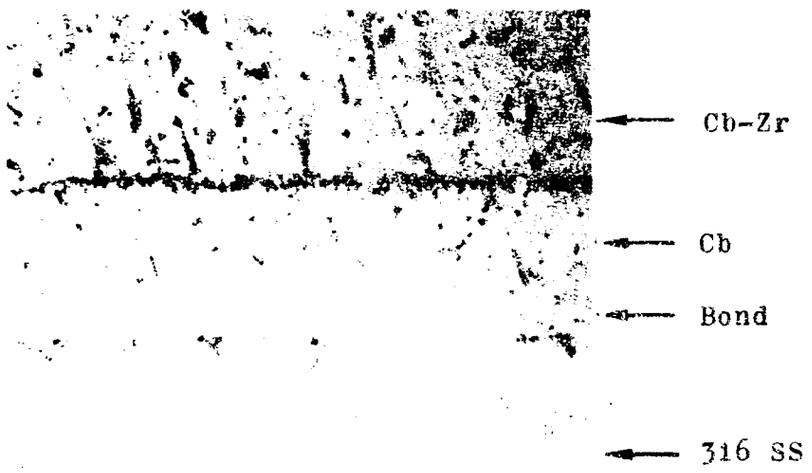


FIGURE 22

Cb-1% Zr MIDDLE
LONGITUDINAL SECTION (250X)

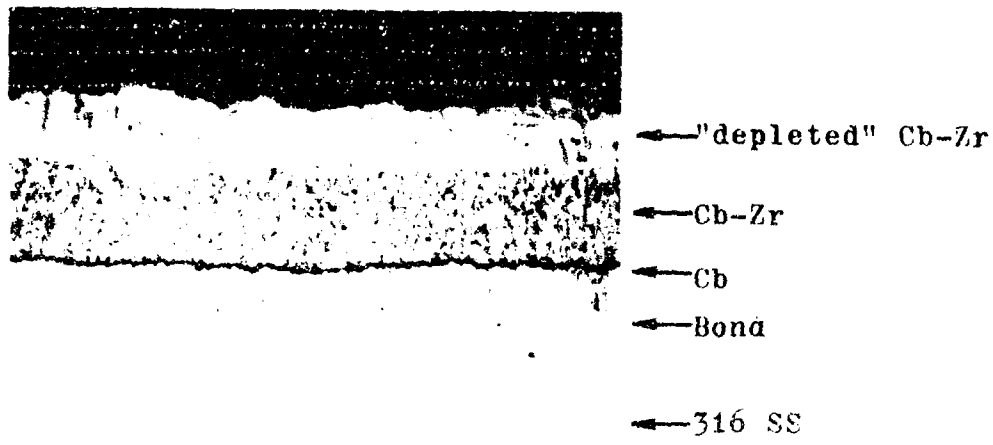


FIGURE 23

Cb-1% Zr MIDDLE
RADIAL SECTION (400X)

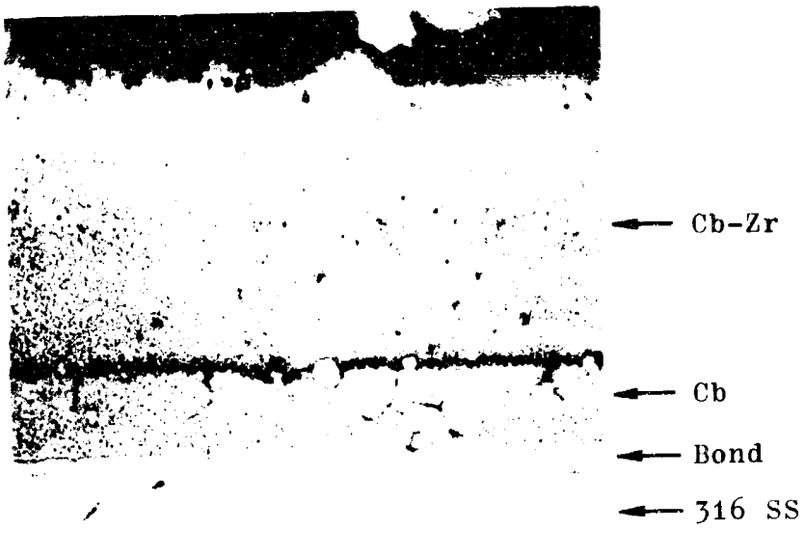


FIGURE 24

Cb-1% Zr TOP
LONGITUDINAL SECTION (200X)

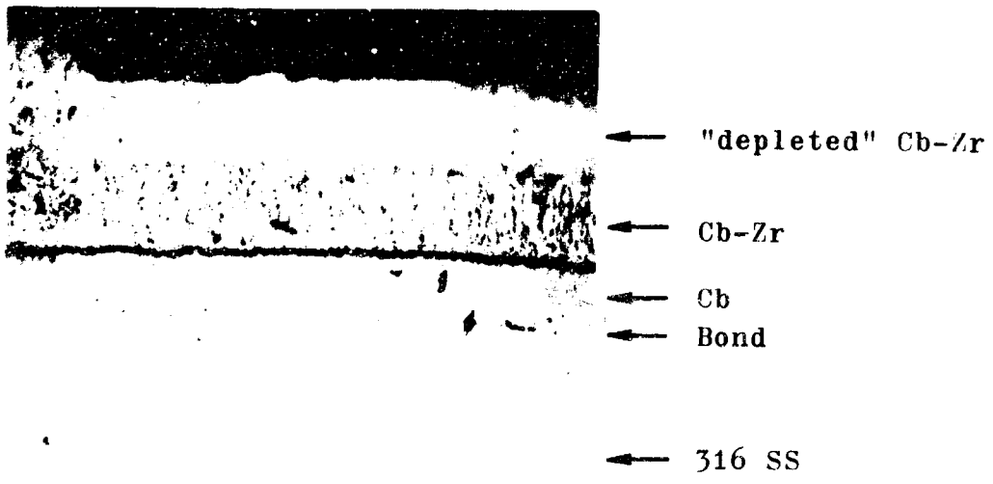


FIGURE 25

Cb-1% Zr TOP
RADIAL SECTION (400X)

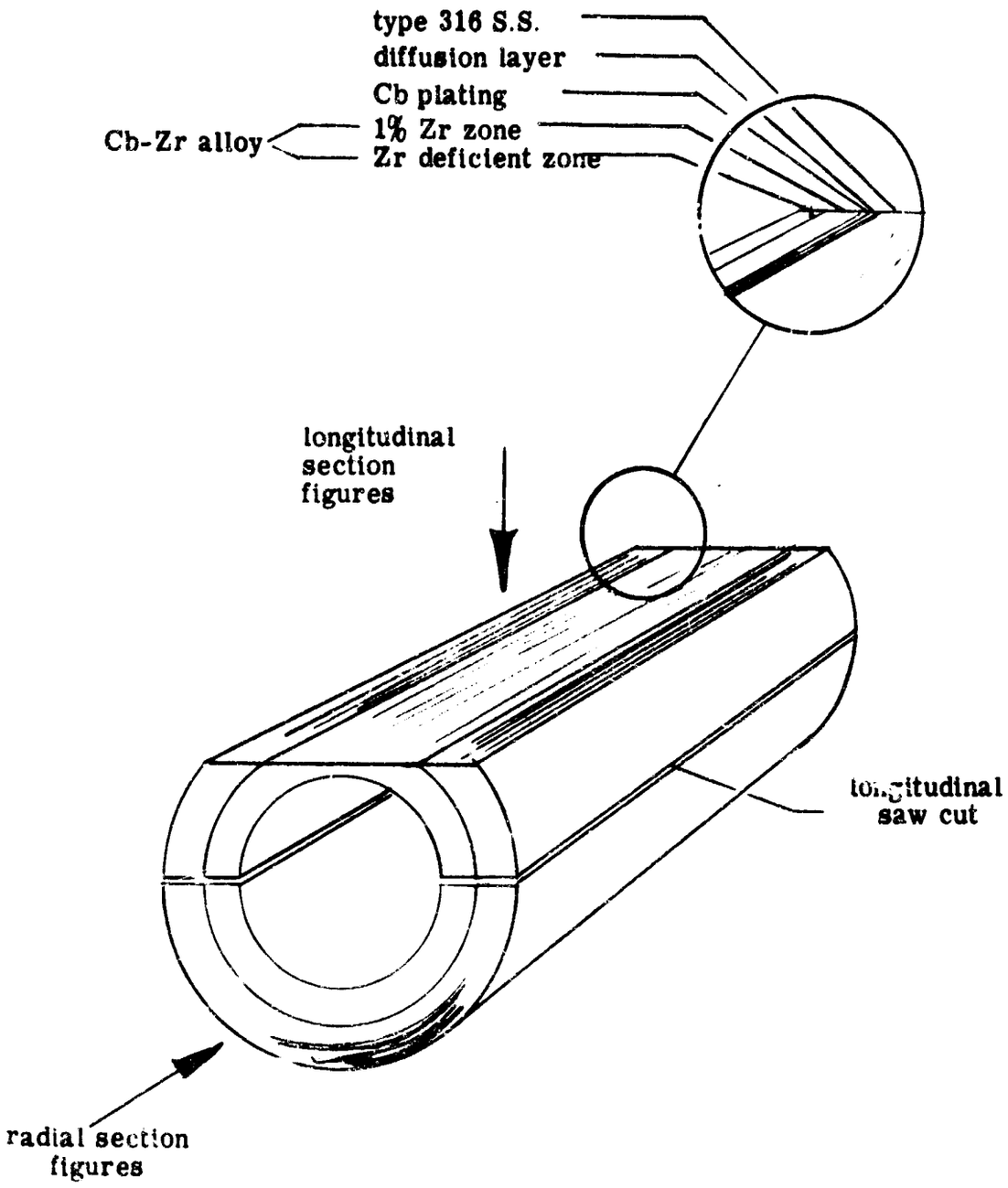


FIGURE 26

Cb-Zr SAMPLE AS PREPARED FOR PHOTOMICROGRAPHY (SKETCH)

radius. The radial views in Figures 21, 23 and 25 depict the layers in more accurate proportion to one another.

The boundary between the Cb and Cb-Zr layers appears as a dark region in these photographs. However, when these layers are examined at higher magnification (800X) it becomes apparent that this boundary is not a gap but an alloy deposit quite similar to the bulk Cb-Zr zone but with a much finer grain structure. Figure 27 is a radial photomicrograph of a typical Specimen #33, top, taken at 800X, and is unetched to show the Cb/Cb-Zr boundary. Figure 28 is a photomicrograph of the same sample, etched. The boundary is deceptively pronounced when etched.

The region of Cb-Zr deposit can be readily differentiated from an apparent Zr-depleted region (see Section VIII) in Figures 22 and 24 as well; the two regions become more distinct toward the top (hottest) end of the sample. The Zr-depleted region bears a close resemblance to the pure columbium inner bonding layer.

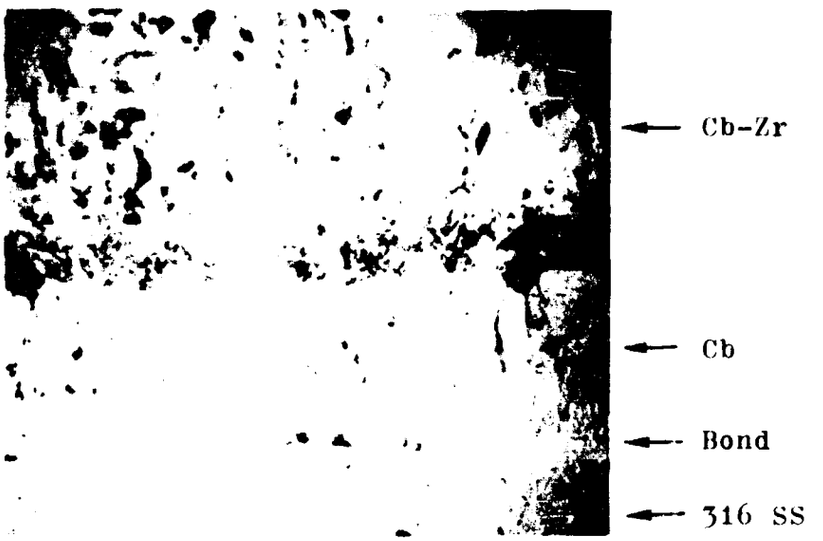


FIGURE 27

Cb-Zr SPECIMEN
RADIAL SECTION (800X), UNETCHED

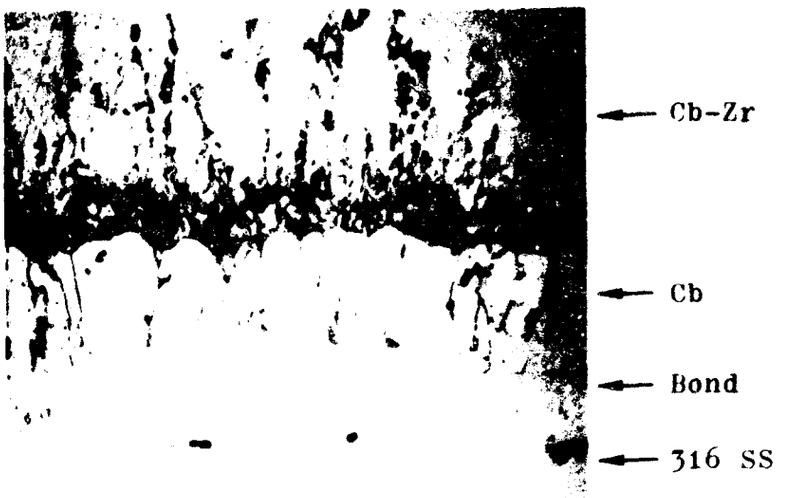


FIGURE 25

Cb-Zr SPECIMEN
RADIAL SECTION (500X), ETCHED

SECTION VIII

ZIRCONIUM DEPLETION

Channeling of chlorine through the chlorinator metal bed was eliminated by doubling the mass and length of the bed and mixing small diameter zirconium rod stock and zirconium sponge with the usual granular zirconium feed.

The zirconium depletion phenomena indicated by the behavior of Cb-Zr composition data and the pseudo-laminations in Figures 23 and 25 could logically be attributed to two causes — first the formation of a passivating layer on the surface of the zirconium pellets in the chlorinator, second, the channeling of chlorine through the metal bed in the chlorinator. An oversupply (100% excess) of zirconium metal in the chlorinator was therefore used to increase the amount of fresh metal surface area available for chlorination. This also increased the length of the bed over which a channel would have to develop before unreacted chlorine could fully penetrate the bed.

Experience from many test runs employing the extended metal bed indicated that chlorination of fresh metal surface did tend to produce more of the proper zirconium chloride plating species than did chlorination of the remainder of the metal. However, channeling was proved to be the more formidable problem. This was proved especially in the long duration internal plating runs discussed elsewhere in this report.

A trial deposition was made to determine the relative contributions of channeling and surface passivation of the chlorinating zirconium metal. This run employed only used zirconium pellets that had been reclaimed from the 100% excess runs. The specimen was microprobed at various locations along its length. Although serious probe spot drifting was encountered it can be generally concluded that some zirconium was deposited, rather sporadically, from this reclaimed feed material. Surface passivation of the zirconium, while not totally discounted, was therefore determined to be not primarily responsible for the "depletion phenomena". On subsequent runs employing a fresh 100% excess zirconium metal charge, examination of the zirconium chlorinator confirmed that extensive gas channeling had taken place in the chlorinator during the run.

Two of the flat specimens prepared for tensile tests and retained by SFL (refer to Section XI of this report) from Run No's. 38 and 39 were microprobed and these data are presented in Figures 29 and 30. A 200% excess zirconium chlorinator metal charge was used to prepare these samples. Composition peaks were still apparent in these runs but zirconium appeared to have been successfully deposited throughout the deposit. The measured thickness of the Cb-Zr layer of Sample #38, for example, was 75 microns; the microprobe data of Figure 29 show that zirconium was found to be present over a 75 micron portion of the thickness of this sample.

A photomicrograph of Specimen No. 38 was also prepared and it is included as Figure 31. Note the uniformity of the Cb-Zr layer from the pure columbium under-layer out to the exterior surface of the deposit. No abrupt change to a Zr-depleted region was apparent as was the case in Figures 23 and 25 and no darkened boundary was apparent between the Cb and Cb-Zr deposited regions.

Two remedies were attempted since channeling did not stop chlorination completely but only retarded it below that point necessary to deposit zirconium. The first was to increase the $ZrCl_4$:$CbCl_5$ ratio to 80:20. The second was to mix large zirconium metal shavings, rod, or sponge with the fine pellet feed to disperse the channels.

The 80:20 run produced over 10% Zr in the deposit. This sudden increase in Zr will be explored further during the coming year. The use of sponge material and high purity small diameter rod was evaluated in long duration internal plating runs. These materials were found to be very effective in greatly reducing gas channeling in the zirconium chlorinator.

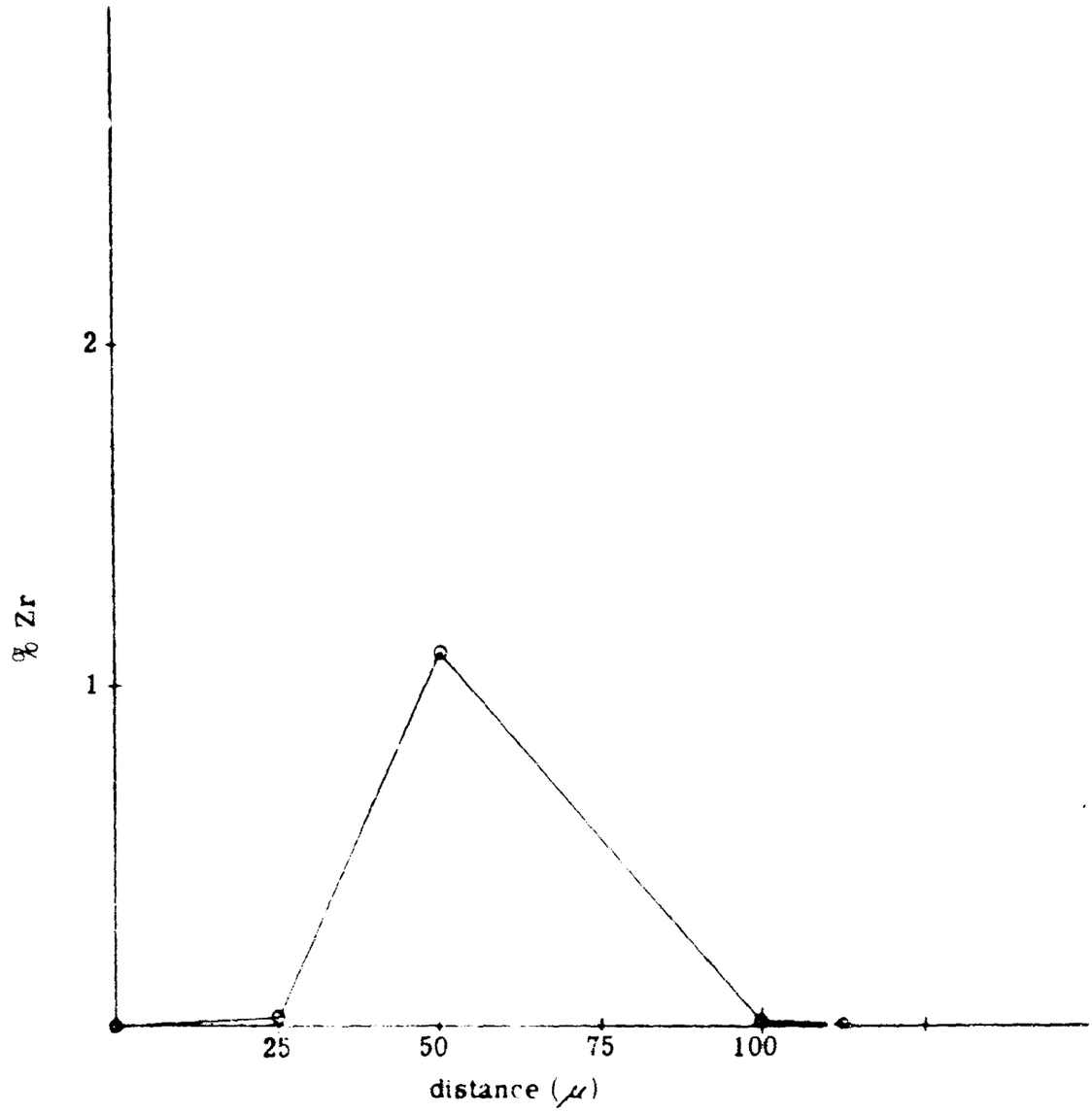


FIGURE 29

Cb-Zr ALLOY, SAMPLE 38
(MICROPROBE DATA)

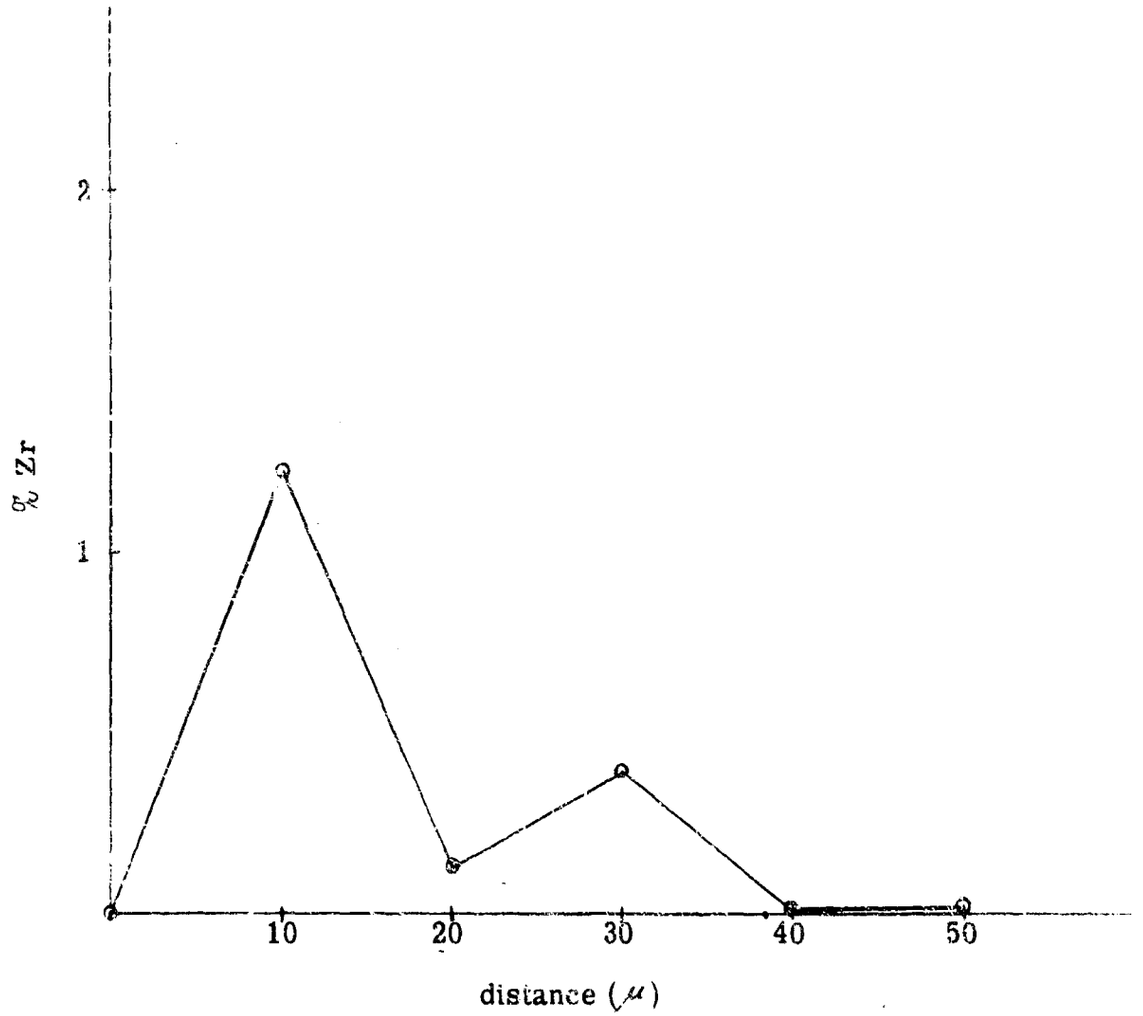


FIGURE 30

Cb-Zr ALLOY, SAMPLE 39
(MICROPROBE DATA)

FIGURE 31

Cb-1% Zr SPECIMEN
SECTION OF TENSILE SPECIMEN (400X)

SECTION IX

ACCURACY OF MICROPROBE DATA

A number of references have been made about the drifting of the probe spot during its traverse across a specimen. This was remedied by mounting flat specimens in a stainless steel sandwich. This mounting adequately equalized the magnetic deflection interference on either side of the specimen. The method was proved by periodically burning a mark into the specimen with a probe spot and subsequently determining the position of the burn marks through microscopic examination. These positions were then compared with the calculated positions of the data points. Excellent agreement was obtained.

Probe spot drifting could not be eliminated for circular samples as it was for flat samples. Alternate current conducting mounting compounds were tried. Graphitic epoxys were also tried but were found to be inconvenient because of long setting times. Dispersed copper compounds were found to be very promising, however, care was required in exposing the copper mount to etching acids.

SECTION X

EFFECT OF TEMPERATURE ON ZIRCONIUM DEPOSITION

The zirconium content of Cb-Zr plate was found to increase with deposition temperature. Negligible zirconium was deposited at 1700°F; zirconium content was adequate at both 1800°F and 1900°F. The data were gathered from a specimen cycled through the 1700°-1900°F temperature range.

Figure 14 shows microprobe data which cycled rather uniformly in zirconium composition because difficulty was encountered with the RF heating unit during the run causing moderate temperature cycling about the desired 1850°F brightness operating temperature. Subsequently a trial deposition was made while purposely cycling the specimen temperature. First $CbCl_5$ was deposited for 10 minutes at 1700°F-1800°F to affect a diffusion bond. A 30% $CbCl_5$-70% $ZrCl_4$ mixture was then introduced to the specimen. During the run the first 20 minutes were at 1800°F, the next 20 minutes were at 1700°F, and the last 20 minutes were at 1900°F. Six samples were cut at 1/2" intervals and examined for zirconium content by microprobe analysis.

The data are shown in Figures 32 through 37. The points shown as large circles represent points that were burned into the sample by the probe. These burn spots were employed to accurately index the probe position at various points over the probe traverse. The calculated intervals between data points were then adjusted relative to these reference burn spots via microscopic examination of the probed sample.

Figures 32 through 37 shows exactly what was expected, a minimum zirconium concentration during the middle one-third (1700°F) portion of the deposit, over the entire length of the sample. This data and previous related data confirm the desirability of maintaining a minimum specimen temperature of 1800°F in the Cb-Zr system.

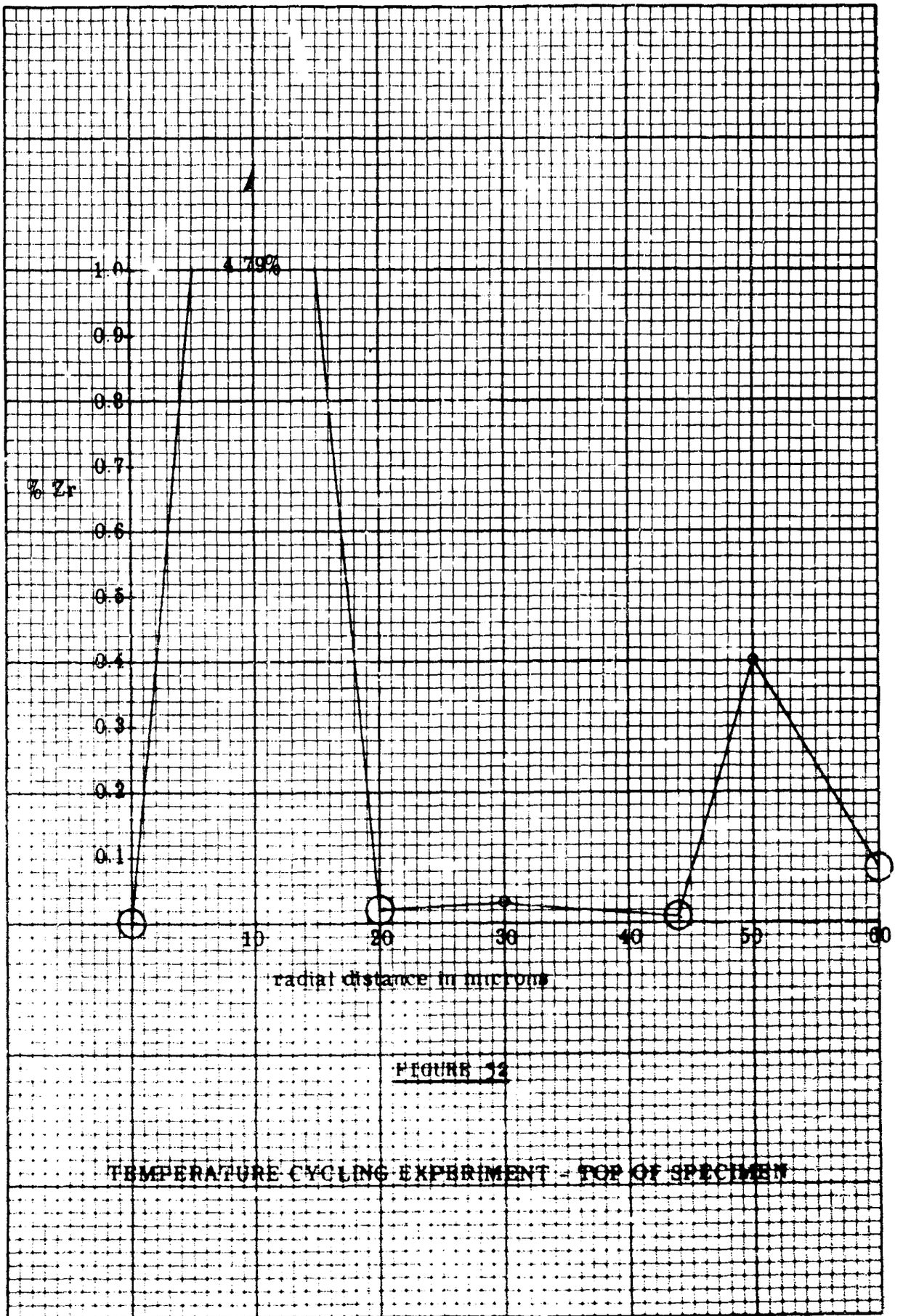


FIGURE 12

TEMPERATURE CYCLING EXPERIMENT - TOP OF SPECIMEN

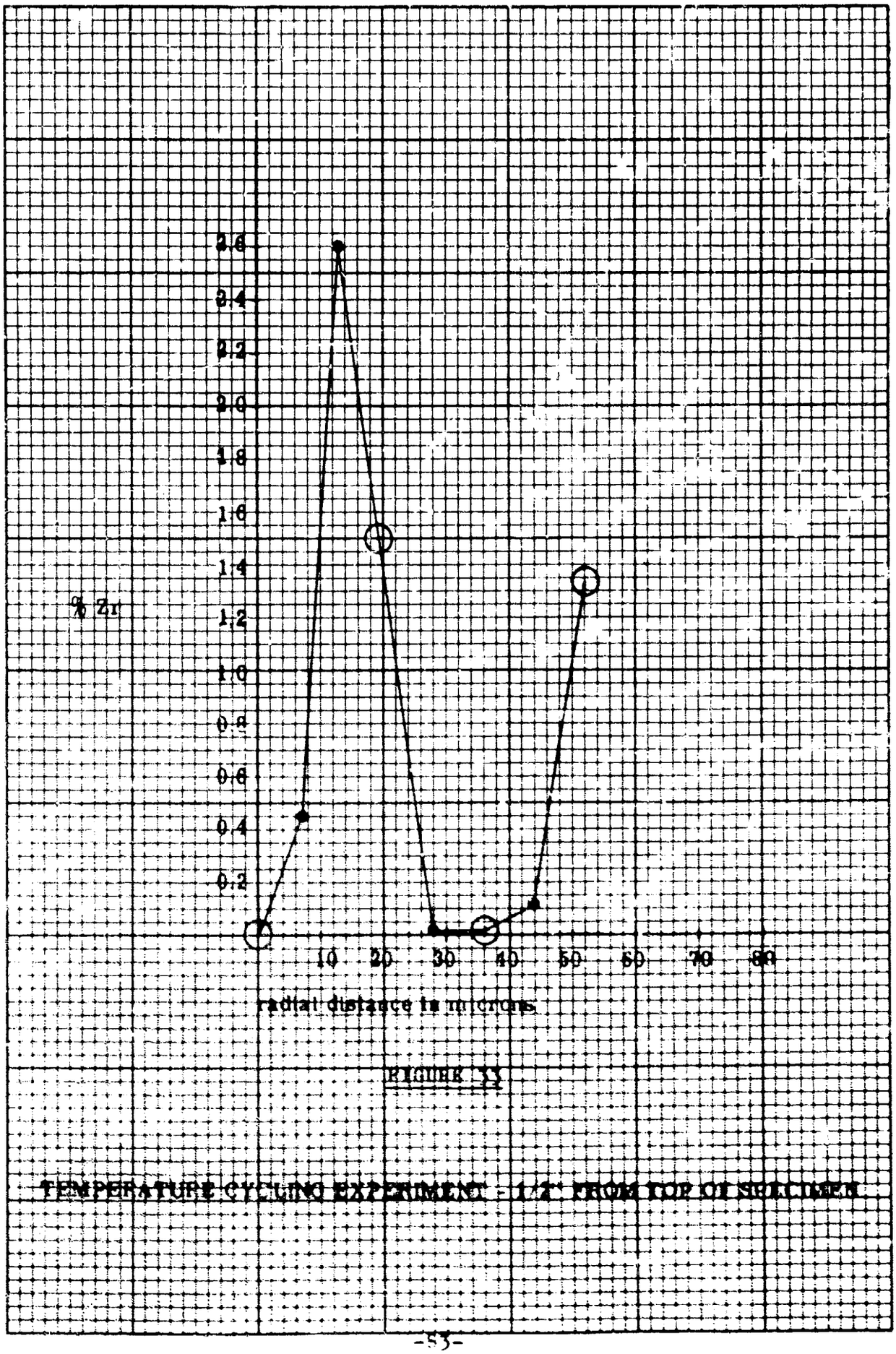


FIGURE XX

TEMPERATURE CYCLING EXPERIMENT - 1/2" FROM TOP OF SPECIMEN

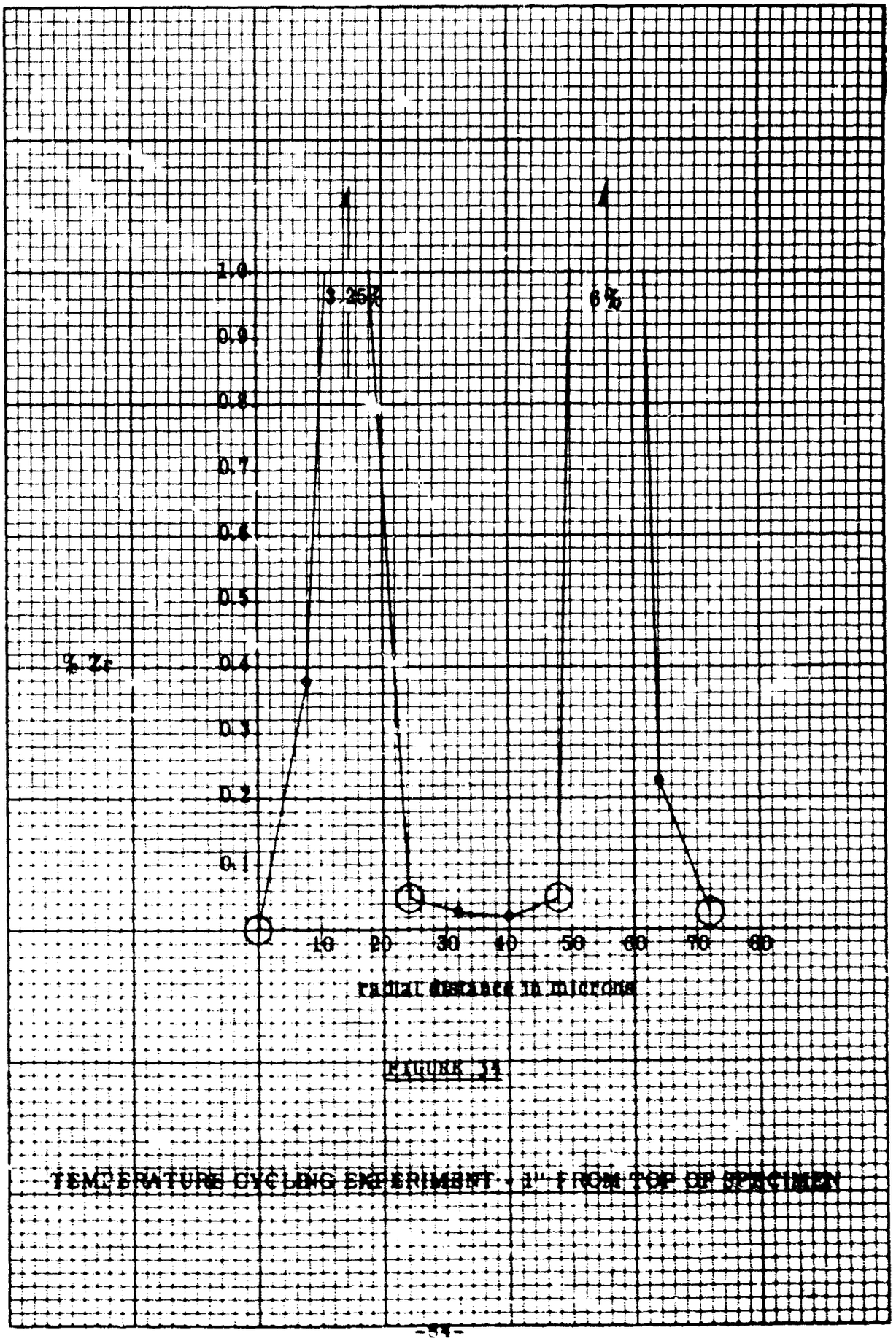


FIGURE 34

TEMPERATURE CYCLING EXPERIMENT - 3" FROM TOP OF SPECIMEN

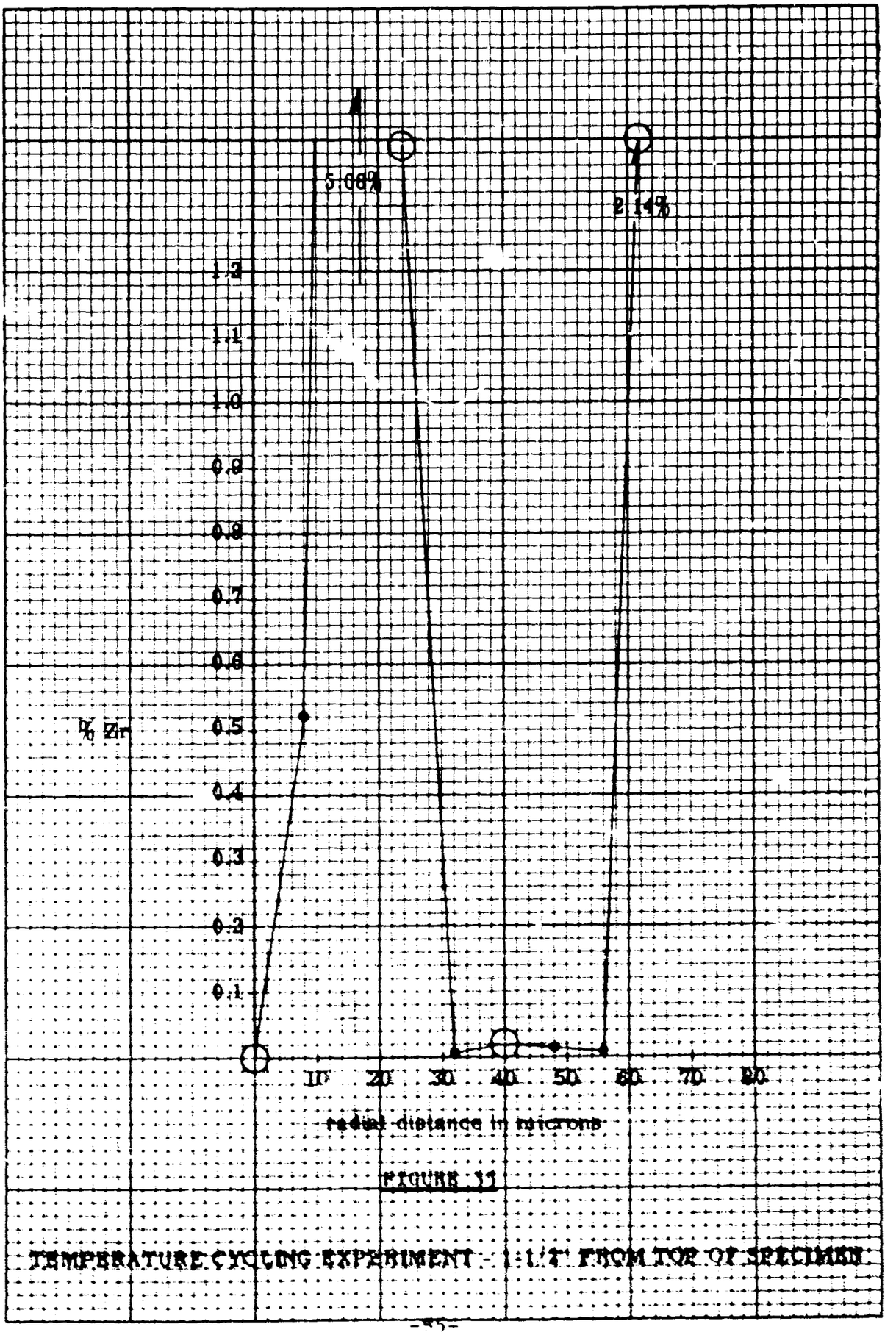


FIGURE 11

TEMPERATURE CYCLING EXPERIMENT - % Zr FROM TOP OF SPECIMEN

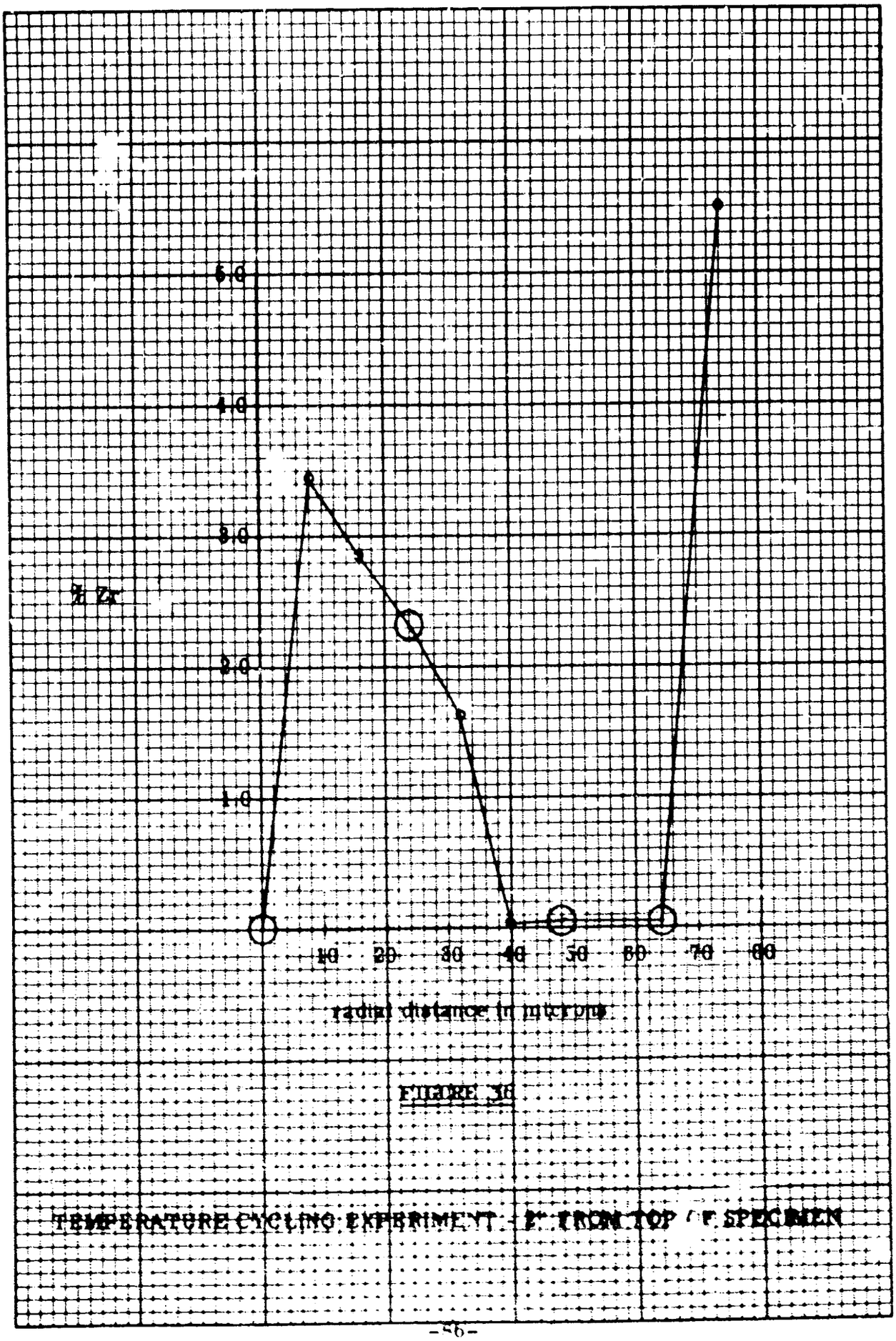


FIGURE 36

TEMPERATURE CYCLING EXPERIMENT - 1" FROM TOP OF SPECIMEN

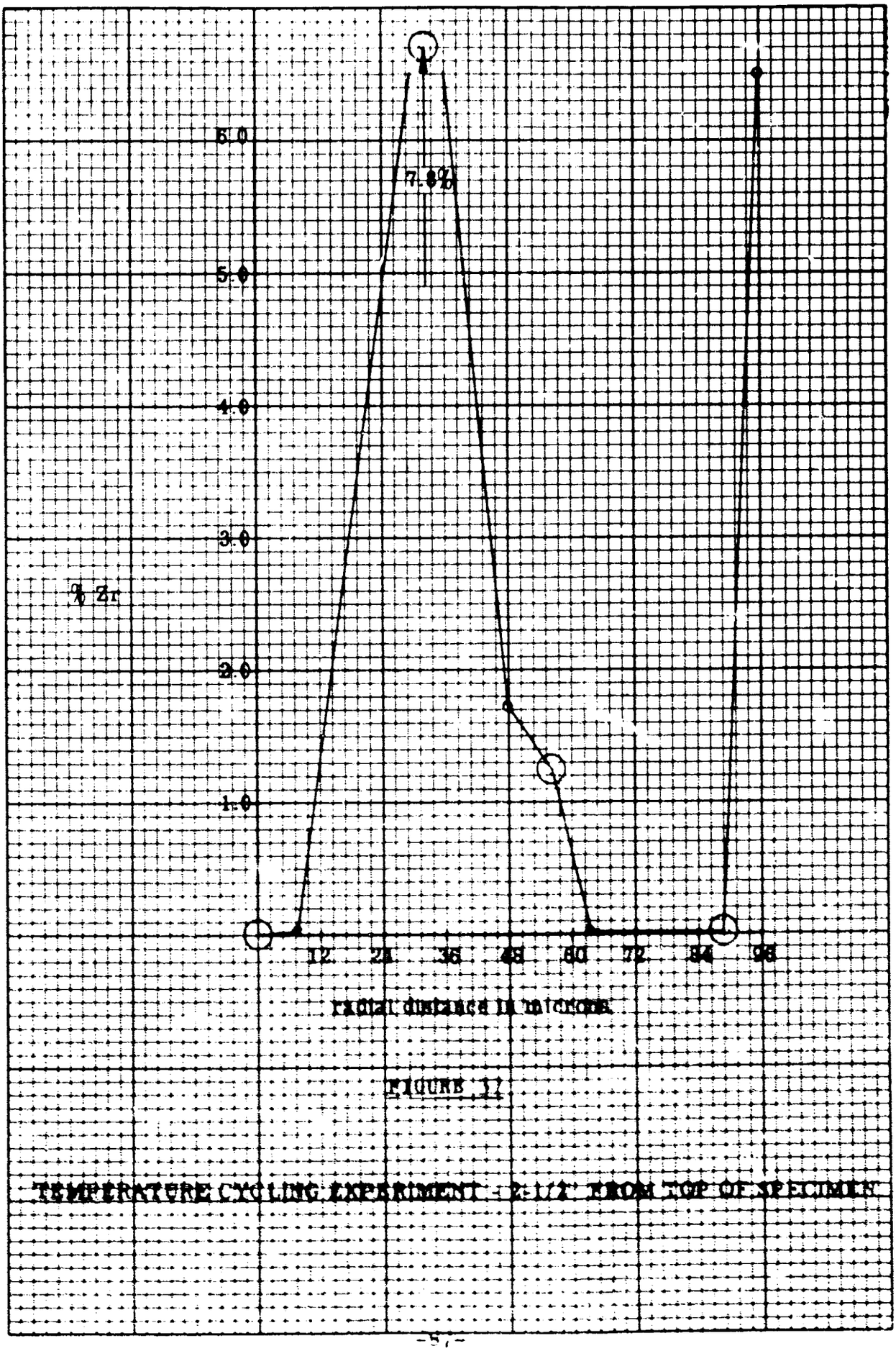


FIGURE 11

TEMPERATURE CYCLING EXPERIMENT - 2-1/2" FROM TOP OF SPECIMEN

SECTION XI

MECHANICAL TESTING OF Cb-1% Zr SPECIMENS

Bend and tensile tests of flat Cb-1% Zr/316 SS coupons and tensile tests of 316 SS tubes internally plated with Cb-1% Zr were conducted before and after a 200 hour heat treatment at 800°F which included excursions to 1200°F every six hours. Although Vickers hardnesses of 1000 DPH were measured for the plate/316 SS diffusion bond, these mechanical tests proved the integrity of the bond especially after heat treatment. For example, none of the heat treated coupons failed when given a 170° bend against a "twice thickness" radius with either plate or 316 SS against the radius. Additionally all of the as-deposited specimens survived a 90° bend. No discernible increase in the diffusion zone width accompanied the heat treatment. Some elongation of the deposit occurred prior to failure in the tensile tests; in many instances failure took place as discreet cracks at regular intervals along the length of the plate. The bond remained intact between these cracks.

The mechanical properties of columbium deposits and Cb-1% Zr deposits were studied. Both flat tensile and bend specimens and tubular specimens were prepared. Alloy composition, ultimate and yield tensile strength, plate hardness and plate/substrate bond integrity were studied in the as-deposited condition as well as after a long term heat treatment and temperature cycling treatment.

1. PREPARATION OF PLAIN TENSILE AND BEND TEST SPECIMENS

316 SS sheet stock, 0.023 inch thick, was bent into a square channel and the channel was seam welded shut. A few specimens were also prepared from 316 SS "U" channels but these plated somewhat unevenly due to non-uniform susceptibility to RF heating. The channels were cleaned by sanding with particular attention to weld areas, then outgassed and plated. Pure columbium was deposited first to affect a diffusion bond and then Cb-Zr was deposited. The 2" x 0.5" tensile specimens were cut from the sides of the channels. Some pure columbium deposits were also prepared and analyzed as control samples. Twenty-one tensile coupons plated with Cb-1% Zr were delivered to Research and Technology Division for evaluation. The remainder were evaluated by SFL.

2. PREPARATION OF WELDED TENSILE AND BEND TEST SPECIMENS

316 SS sheet stock, 0.023 inch thick, was cut into 2"x 2-1/2" pieces. The pieces were then welded, side by side, to form a long 2-1/2" wide strip. The strip was finally bent into a square channel and seam welded shut. (See Figure 38.) The channels were cleaned by sanding, then outgassed and plated. As before, pure columbium was deposited first to affect a diffusion bond and then Cb-Zr alloy was deposited. Tensile and bend specimens 2" x 0.5" were cut from the sides so that a transverse weld would be in the center of the specimen. Ten of these specimens were delivered to RTD for evaluation. The remainder were evaluated by SFL.

Four to eight specimens were prepared from each of the plated channels. Table II summarizes the allotment of specimens between RTD and SFL for each of the deposition runs. Table II also designates which specimens were plain or welded, which were tested in the as-deposited or heat treated conditions, and the specific test each specimen underwent.

3. TYPES OF MECHANICAL TESTS

SFL conducted four types of tests on the specimens of Table II. (See Figure 39.) A number of the specimens were machined into tensile coupons. Those designated in Table II for "Test No. 1" were tensile tested to determine the failure point of the plate/substrate combination. Those designated for "Test No. 2" were first etched in aqua regia to remove the central portion of the 316 SS substrate. 316 SS was retained at the ends of these specimens to facilitate gripping during the test. These latter specimens were then tensile tested to determine the failure point of the plate alone.

A number of the specimens were kept in their original rectangular shape and bent over a "2 x thickness" radius with either the 316 SS surface (Test No. 3) or the plated surface (Test No. 4) against the bend radius.

The four types of mechanical tests were conducted on specimens in either the as-deposited condition or after a heat treatment for 200 hours at 800°F with periodic 5 minute excursions to 1200°F, followed by a 5 minute dwell at 1200°F, and a 5 minute cooling period to 800°F. This excursion was

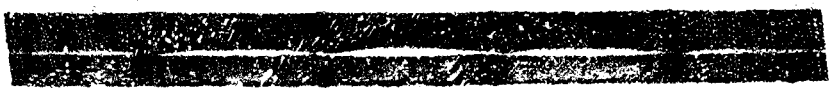


FIGURE 38

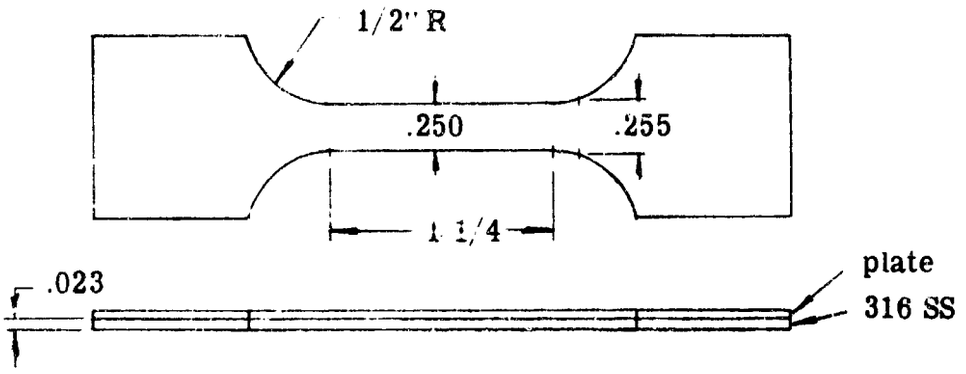
316 SS SQUARE CHANNEL FOR
BUTT WELDED TENSILE SPECIMENS

TABLE II

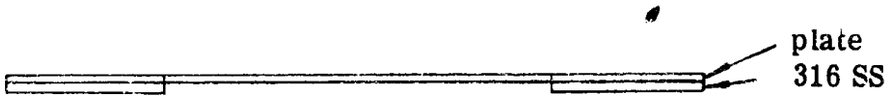
TENSILE AND BEND TEST SPECIMEN FORMAT*

RUN NO.	TENSILE TEST (Test No. 1)		TENSILE TEST (Test No. 2)		BEND TEST (Test No. 3)		BEND TEST (Test No. 4)	
	A	B	A	B	A	B	A	B
			Plain 316 SS, Cb Plated					
35	X	-	-	-	-	-	-	-
35	-	-	X	-	-	-	-	-
36	-	X	-	-	-	-	-	-
36	-	-	-	-	-	-	X	-
			Plain 316 SS, Cb-Zr Plated					
40	X	X	X	-	X	X	X	X
41	X	-	X	X	X	X	X	X
42	-	-	X	X	X	X	X	X
37	X	-	-	-	-	-	-	-
37	-	X	-	-	-	-	-	-
38	-	-	-	-	X	-	-	-
38	-	-	-	-	-	X	-	-
39	-	-	-	-	-	-	X	-
39	-	-	-	-	-	-	-	X
			Welded 316 SS, Cb-Zr Plated					
45	X	X	-	-	X	X	-	-
46	-	-	X	X	-	-	X	X
47	X	X	-	-	-	-	X	X
48	-	-	X	X	X	X	-	-

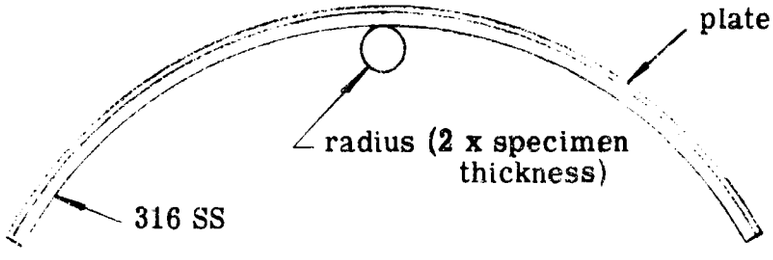
A - Heat Treated
B - As-Deposited
X - One Sample From Run
* - 21 Plain Cb and Cb-Zr Specimens were sent to RTD
10 Welded Specimens were sent to RTD



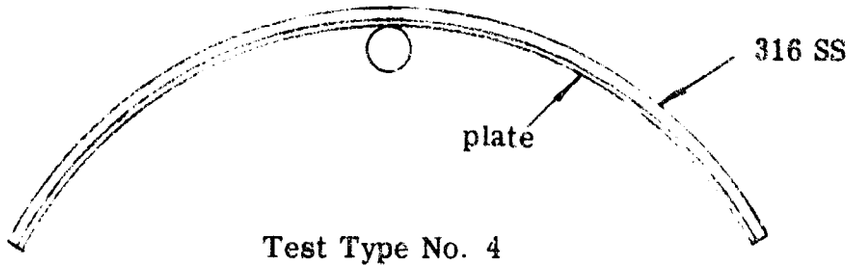
Test Type No. 1
Pull With Substrate



Test Type No. 2
Pull Without Substrate



Test Type No. 3
Bend



Test Type No. 4
Bend

FIGURE 39

TENSILE AND BEND SPECIMEN CONFIGURATIONS

imposed upon the heat treated specimens every six hours over the 200 hour period. Heat treatment was conducted in an ABAR Series 90 vacuum furnace at 10^{-6} torr pressure.

The tensile tests were performed with an Instron Model TTC 10,000 pound Universal Testing Machine at a strain rate of 0.005 in/in/min to yield and 0.050 in/in/min thereafter to failure. The test machine had been calibrated with National Bureau of Standards proving rings. The vacuum heat treatments and the mechanical tests were contracted by SFL to outside test laboratories.

4. BEND TESTS

Figure 40 shows two as-deposited specimens. The one on the left was given Test No. 3 and the one on the right Test No. 4. Microscopic examination of the specimens after bend testing indicated no separation between plate and substrate in most cases. The specimens were visually examined at the 90° bend point and microscopically examined at the 170° bend point. Table III summarizes the state of each of the specimens at each of these check points.

Four of the five failures that did take place involved the four specimens with welded substrates. The cracking in all cases took place at the edge of the weld. Figure 41 shows the most extensive failure of the four.

The heat treated specimens fared considerably better than did the as-deposited specimens. None of the specimens whether plain or welded, pure Cb or Cb-Zr, failed at the 90° bend point in either Test No. 3 or Test No. 4. Both of the welded specimens given Test No. 4 survived to the 170° bend point. However, both of the welded specimens bent in Test No. 3 failed in the final bend to 170°. Table IV summarizes comments on these tests.

Photomicrographs of two as-deposited specimens are shown in Figure 42. The photographs were taken at the apex of the bend on each specimen midway through the 1/2" width of the specimens. In the photograph of the specimen subjected to Test No. 3, lines of cleavage perpendicular to the bond are apparent along the diffusion bond but no separation has taken place. The photograph of the specimen subjected to Test No. 4 confirms that the bond zone of the specimen was placed under considerably greater stress than would be the case in Test No. 3. Since no visual sign of plate separation was evident for this specimen it is probable that

Test No. 3 Test No. 4

FIGURE 40

BEND TEST SPECIMENS

TABLE III

AS-DEPOSITED BEND TEST SPECIMENS

Sample No.	Remarks (90° Bend)	Final Bend	Plate Thickness
316 SS Against Radius			
38	No Cracks	Bent to 170° No Failure	0.0043"
40	No Cracks	Bent to 170° No Failure	0.0027"
41	No Cracks	Bent to 170° No Failure	0.0020"
42	No Cracks	Bent to 170° No Failure	0.0015"
45	Plate Cracked at 90°	Plate cracked & peeled	0.0035"
48	Plate cracked and split away at 90°	Further splitting of Cb/Zr Plate	0.0047"
Plate Against Radius			
39	No Cracks	Bent to 170° No Failure	0.0010"
40	Plate split at 90°	Continued splitting of Cb/Zr Plate	0.0039"
41	No Cracks	Bent to 170° No Failure	0.0024"
42	No Cracks	Bent to 170° No Failure	0.0031"
46	Plate peeled	Plate peeled	0.0024"
47	Plate peeled	Plate peeled	0.0035"

Bend Requirements: 2T Radius to 90°, Continue to Failure

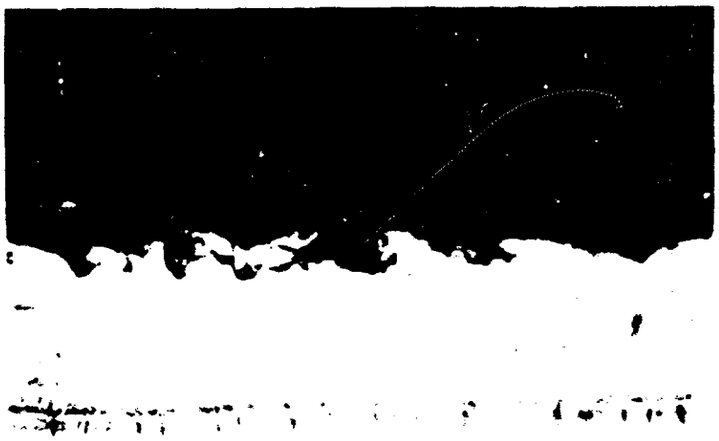
FIGURE 41

BEND SPECIMEN FAILURE AT WELD

TABLE IV

HEAT TREATED BEND TEST SPECIMENS

Sample No.	Remarks (90° Bend)	Final Bend	Plate Thickness
316 SS Against Radius			
38	No Cracks	Bend to 170° No Failure	0.0043"
40	No Cracks	Bend to 170° No Failure	0.0012"
41	No Cracks	Bend to 170° No Failure	0.0015"
42	No Cracks	Bend to 170° No Failure	0.0008"
43	No Cracks	Plate Cracked	0.0024"
48	No Cracks	Bend to 170° No Failure	0.0035"
Plate Against Radius			
36	No Cracks	Bend to 170° No Failure	0.0036"
38	No Cracks	Bend to 170° No Failure	0.0015"
41	No Cracks	Bend to 170° No Failure	0.0024"
42	No Cracks	Bend to 170° No Failure	0.0008"
46	No Cracks	Bend to 170° No Failure	0.0039"
47	No Cracks	Bend to 170° No Failure	0.0039"



Sample from Run 40, Bend Test No. 3

Sample from Run 47, Bend Test No. 4

FIGURE 42

AS-DEPOSITED BEND SPECIMENS (100X)

the bend area was weakened in Test No. 4 and separated in the cutting operation employed to prepare the sample for metallographic mounting and examination. All of the Test No. 4 specimens demonstrated bond cleavages but the example shown in Figure 42 was the most pronounced.

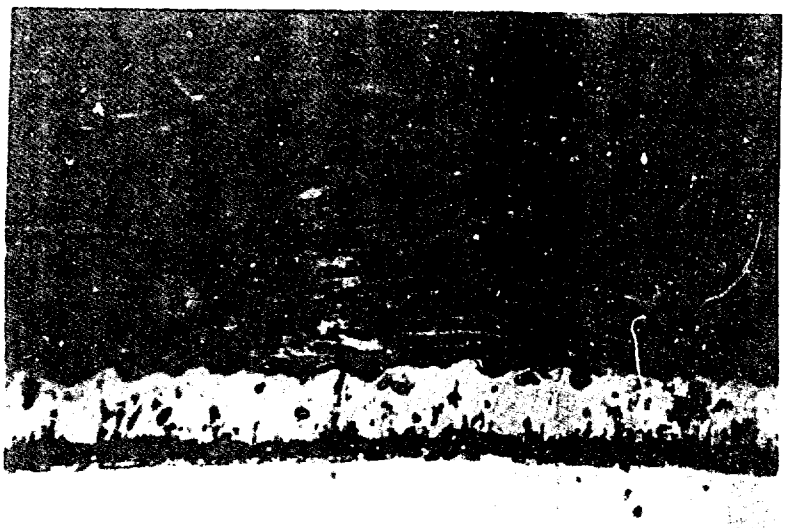
Photomicrographs of typical heat treated Test No. 3 and Test No. 4 specimens, taken at the apex of the bend in each case, appear in Figure 43. The bond cleavages are not as extensive as those found in the as-deposited specimens.

5. TENSILE TESTS

The tensile tests employed a 0.5" extensometer. This size was the largest permitted by the size of the test coupons. This imposed a certain limit upon the accuracy of the tests. Figure 44 shows the tested as-deposited specimens. The top photograph shows the specimens that were tested with their 316 SS substrates intact and the bottom photograph shows the specimens that were tested with their 316 SS substrates removed. Note that in the top photograph the pure columbium deposit of Run No. 36 elongated nearly as far as did its 316 SS substrate before failure took place. The other specimens in this photograph are of less ductile Cb-Zr alloy deposits which failed before their substrates failed.

All of the plate/substrate bonds were sheared in the tensile tests of the specimens shown at the top of Figure 44. However, the bond proved to be very tenacious in spite of the inherent mismatch in ductility between the basic materials involved. Note particularly samples 45 and 47 in the upper photograph of Figure 44. Portions of the plate cracked in "rattlesnaking" fashion to relieve the strain of the tensile test but the plate has remained bonded to the 316 SS substrate. Failure was manifested as discreet cracks at regular intervals along the length of the plate with the bond remaining intact between these cracks. This is in contrast with the results reported in reference 2; in this latter work, complete shearing at the bond apparently always took place.

Table V summarizes the tensile test data for the as-deposited specimens. Figures 45, 46 and 47 are representative strain rate curves for Cb-Zr plate/no substrate, Cb plate/316 SS substrate, and Cb/Zr plate/316 SS substrate specimens in Table V.

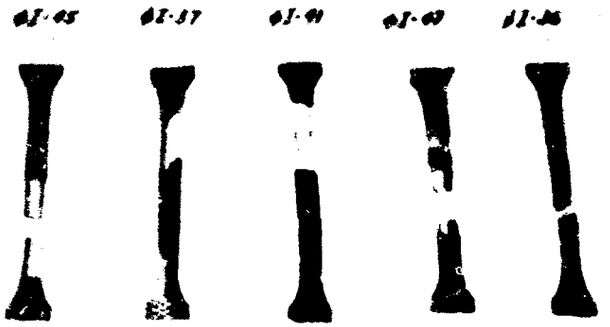


Sample from Run 41, Bend Test No. 3

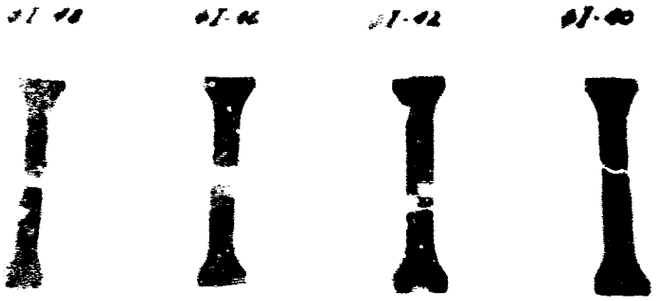
Sample from Run 41, Bend Test No. 4

FIGURE 43

HEAT TREATED BEND SPECIMENS (100X)



Tensile Test No. 1 with 316 SS Substrate



Tensile Test No. 2 without 316 SS Substrate

FIGURE 44

AS-DEPOSITED TENSILE SPECIMENS

TABLE V

AS-DEPOSITED TENSILE SPECIMENS

Sample No	Thickness		Yield Load, Pounds	Yield Strength PSI*	Ultimate Load, Pounds	Ultimate Strength PSI	% Elongation in 0.5"
	Plate	316SS					
40	0.003	-	42.6	67,600	44.0	70,000	1
42	0.004	-	49.7	57,000	53.4	49,700	2
46	0.005	-	Sample broken in handling, no test				
48	0.004	-	15.5	17,600	16.5	18,750	-
36	0.008	0.023	280	41,700	600	89,500	58**
37	0.003	0.023	257	39,800	484	74,900	74**
41	0.007	0.023	258	35,000	455	61,700	63**
45	0.003	0.023	250	38,700	546	84,500	50**
47	0.007	0.023	250	33,600	449	60,200	28**

* - Yield Strength by Extensometer at 0.2% in 0.5"

** - Plate failed first, typically, after 1-4% elongation

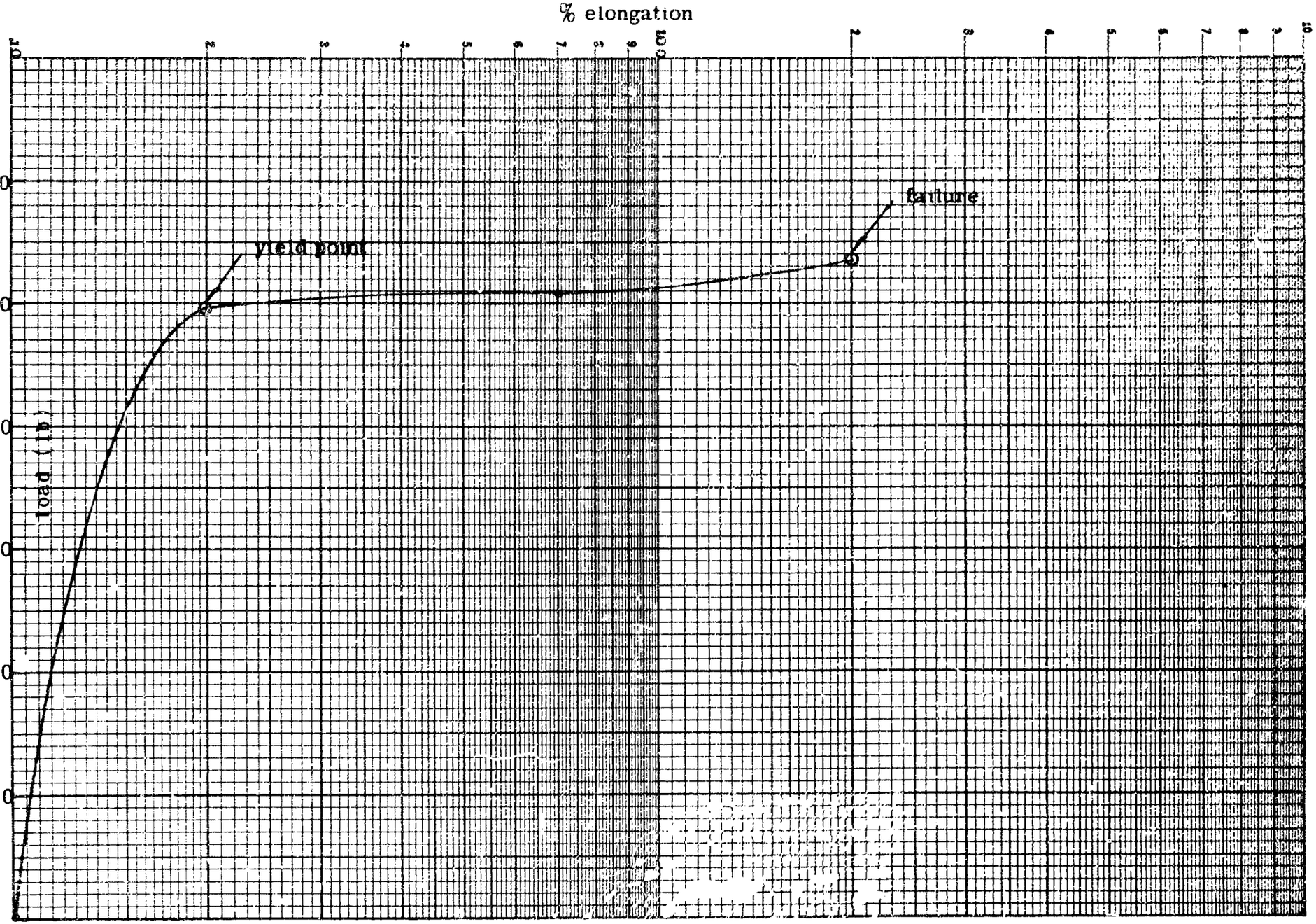


FIGURE 45 - TENSILE TEST Cb-1% Zr ONLY, SPECIMEN NO. 42, AS-DEPOSITED

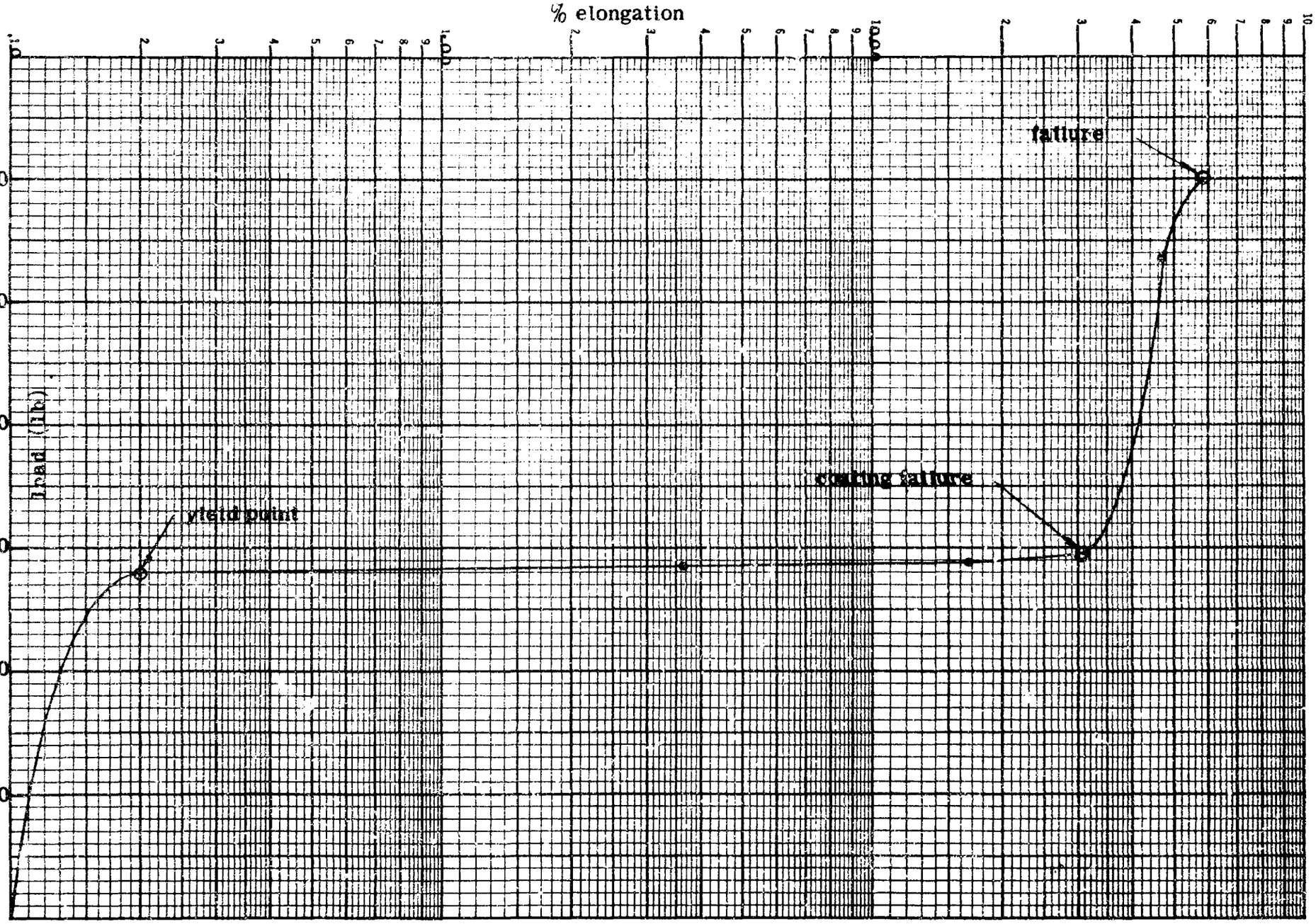


FIGURE 46 - TENSILE TEST Cb ON 316 SS, SPECIMEN NO. 36, AS-DEPOSITED

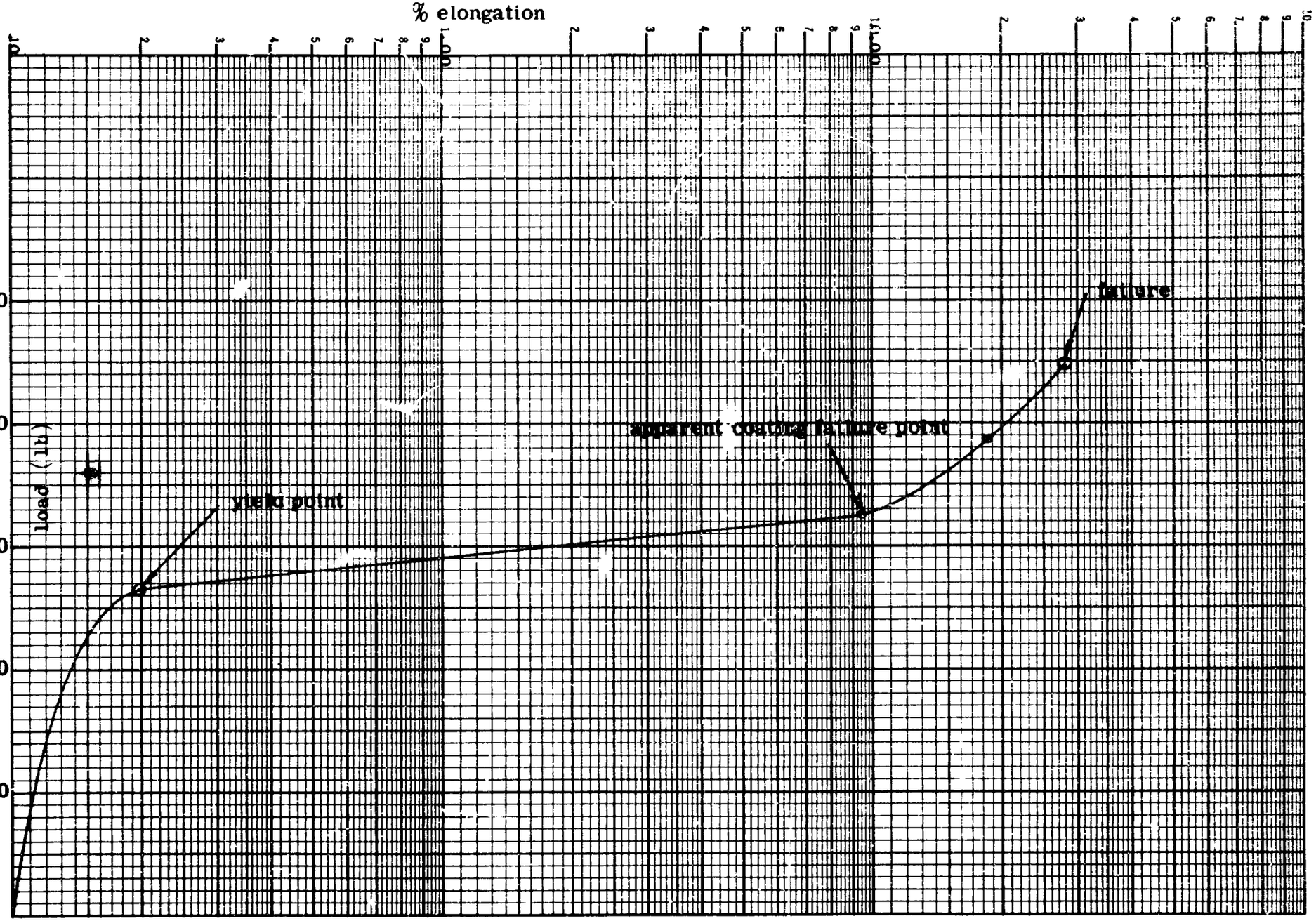


FIGURE 47 - TENSILE TEST Cb-1% Zr ON 316 SS, SPECIMEN NO. 47, AS-DEPOSITED

The specimens tensile tested after heat treatment appeared very similar to those shown in Figure 44. Table VI summarizes the data for the specimens tested after heat treatment.

Some of the strength values given in Table VI are extraordinarily high; those particular tests would appear to be suspect. However, neglecting these data, an overall trend of higher strengths for the heat treated specimens over the as-deposited specimens is still clearly indicated. Discussions with the test laboratory personnel who conducted these tests have not yielded a clear explanation for these high strength values.

The microprobe data for the flat tensile and bend test coupons generally fell in the 0-2% Zr range, typically 0.75% Zr. One or two points above 5% Zr were also found in a typical compositional plot of these specimens.

6. TUBULAR SPECIMENS

A number of 6" x 3/4" dia x 0.035" wall lengths of 316 SS tubing were plated internally with Cb-Zr alloy for both RTD and SFL evaluation (refer to Section XII of this report). Some of the tubing specimens were butt welded together at the center prior to depositing Cb-Zr alloy. A microprobe scan of composition of one of the higher zirconium alloy specimens is given in Figure 48. Figure 49 is a photomicrograph of this specimen.

Some of the tubular specimens were heat treated under conditions previously described for flat test coupons. Figure 50 is a photomicrograph of a Cb-Zr tubular specimen after the heat treatment. Figure 51 is a photomicrograph taken in the vicinity of the weld of a heat treated welded tubular specimen. The photographs show no discernible ill effects attributable to the heat treatment.

A summary of the tensile data for the tubular specimens appears in Table VII. These tests were conducted on a 120,000 lb Tinius Olsen Super L Testing Machine. All of the welded specimens, except No. 30, failed in the vicinity of the weld. Only the plate failed at the weld in Specimen No. 30; the 316 SS substrate failed one inch from the weld.

The plate in the unwelded specimens remained intact in the failure zone. In all of the welded specimens, except no. 30, either delamination or "rattlesnaking" was found to have taken place in the weld region.

TABLE VI

HEAT TREATED TENSILE SPECIMENS

Sample No.	Thickness Plate	Thickness 316SS	Yield Load, Pounds	Yield Strength PSI*	Ultimate Load, Pounds	Ultimate Strength PSI	% Elongation in 0.5"
35	0.007	-	98	59,500	118	71,700	>5
40	0.002	-	Sample broken in handling, no test				
41	0.005	-	51	50,000	525	420,000	>3
46	0.004	-	270	270,000	340	340,000	>30
48	0.009	-	Sample broken in handling, no test				
35	0.007	0.023	400	52,600	730	96,000	>40**
37	0.007	0.023	318	41,900	560	73,700	>35**
40	0.004	0.023	280	40,200	560	80,200	>40**
41	0.007	0.023	300	39,600	560	73,900	>40**
45	0.004	0.023	295	43,000	535	78,000	>23**
47	0.006	0.023	325	33,000	522	53,000	>20**

* - Yield Strength by extensometer at 0.2% in 0.5"

** - Point of plate failure, prior to substrate failure, not distinguishable from strain curve readout as was the case for the as-deposited tests.

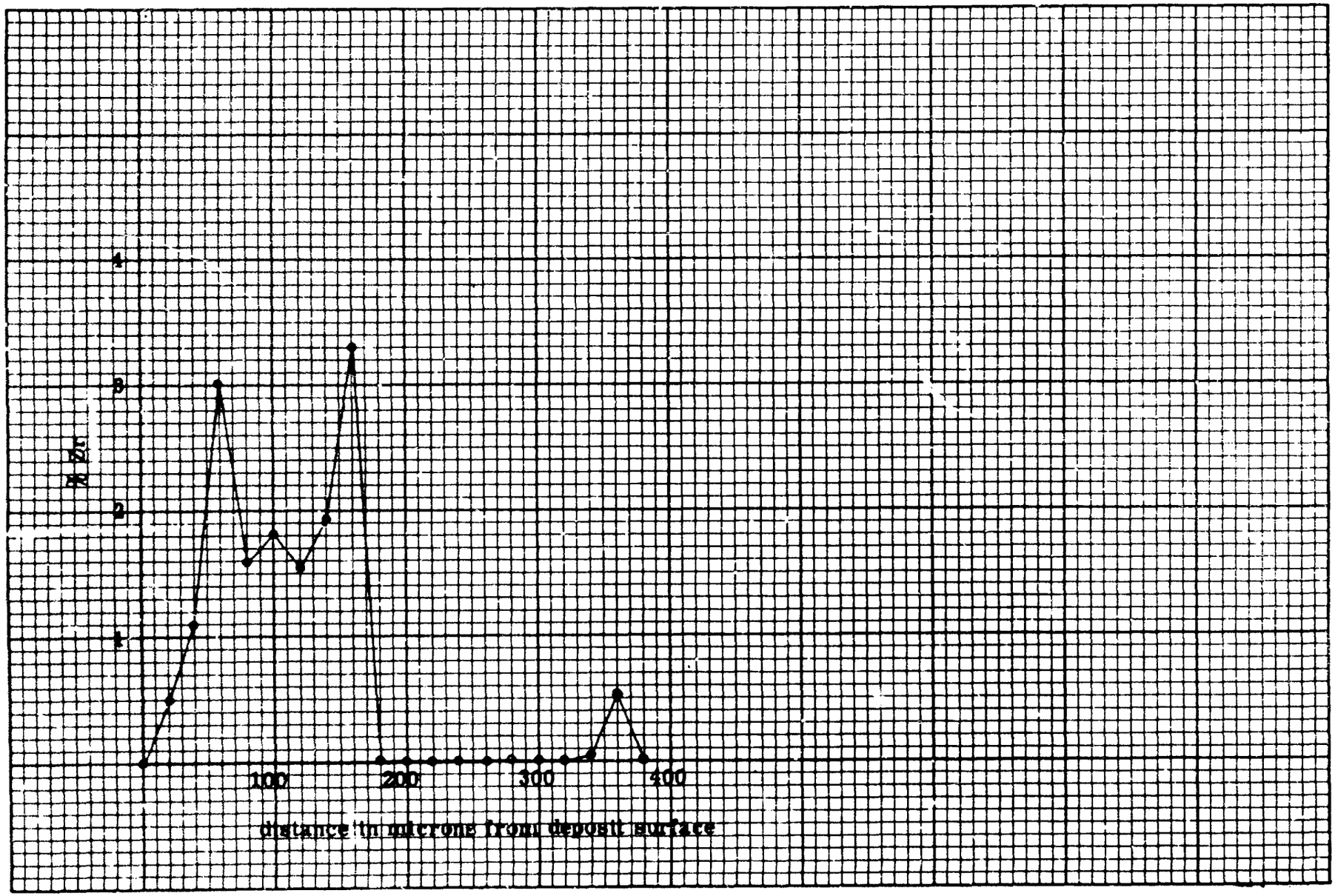


FIGURE 48 - MICROPROBE DATA OF INTERNAL DEPOSIT, TUBULAR SPECIMEN NO. 34, 3-1/2" FROM INLET

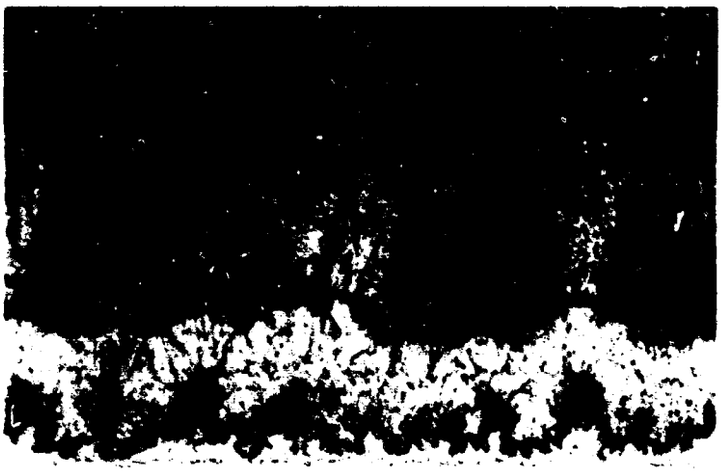


FIGURE 49

INTERNAL DEPOSIT, TUBULAR SPECIMEN
NO. 34, 3 1/2" FROM INLET (200X)

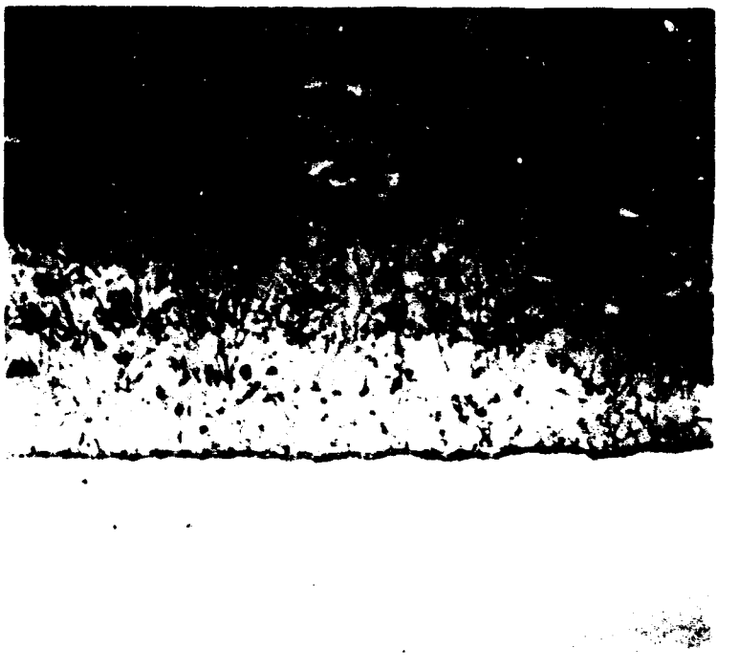


FIGURE 50

HEAT TREATED Cb-Zr INTERNAL DEPOSIT (200X)

FIGURE 51

HEAT TREATED Cb-Zr INTERNAL DEPOSIT,
VICINITY OF SUBSTRATE WELD, 100X

TABLE VII

TUBULAR TENSILE SPECIMENS

Sample No.	As-Deposited	Heat Treated	Plain	Welded	Yield Strength PSI	Ultimate Strength PSI	% Elongation in 0.5"
16	X		X		39,800	83,800	30
19		X	X		34,800	88,600	33
20	X		X		38,100	88,600	35
21		X	X		33,600	85,200	35
30	X			X	39,800	65,000	33
31		X		X	19,600	63,600	32
33		X		X	19,600	62,800	33
37	X			X	19,600	56,600	29

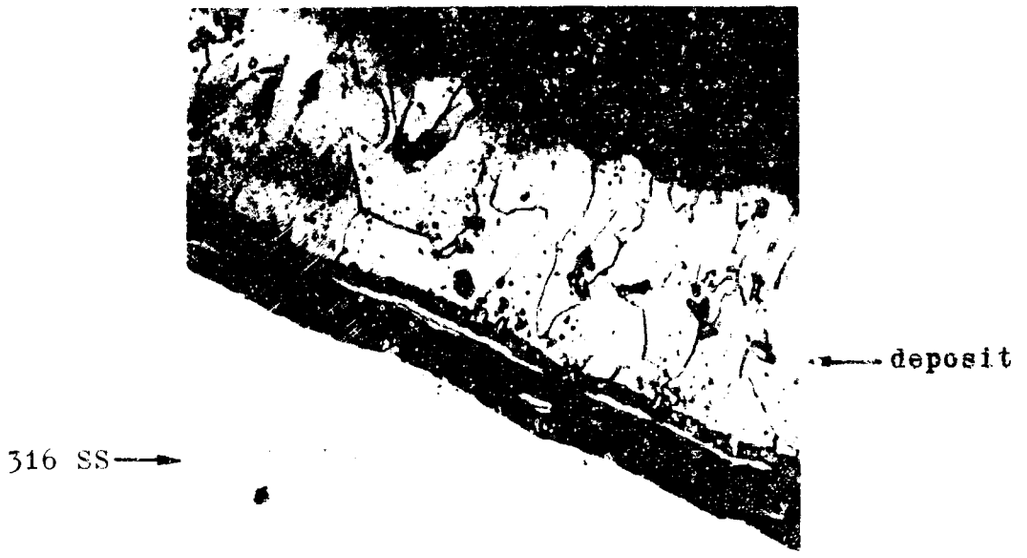
There was no discernible difference in tensile strength between the as-deposited and heat treated specimens. The major observation made from the data in Table VII was that the yield point for the welded specimens was approximately 50% lower than for the unwelded specimens.

7. PLATE HARDNESS

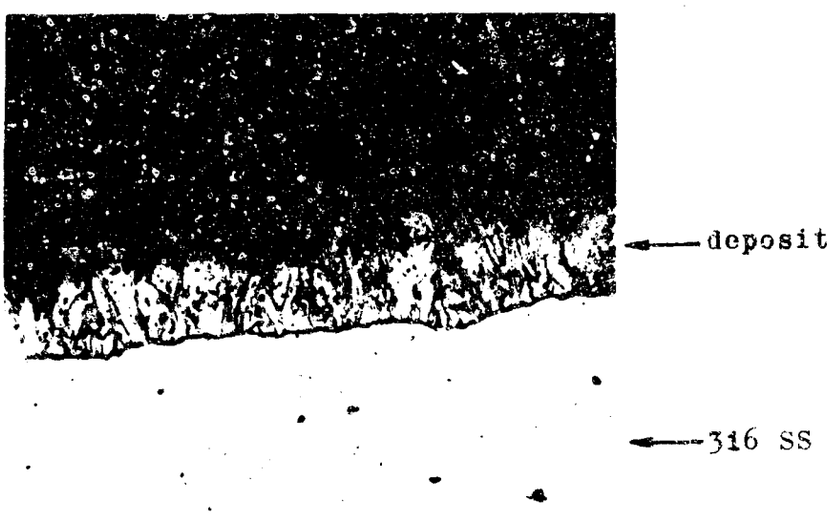
A number of specimens were tested for Vickers diamond point hardness, using a 300 gm weight. Hardness readings as high as 180 kg/mm^2 were found to be typical near the bond area. Readings ranged between 135 kg/mm^2 and 165 kg/mm^2 in the bulk of the plate. Twenty-five specimens from external and internal depositions were evaluated.

Using a 25 gm weight the hardness of the substrate-plate bond was determined for four external deposits. All hardnesses ranged between 700 kg/mm^2 and 1300 kg/mm^2. Most of the readings were 1000 kg/mm^2 or above.

These results do not necessarily mean that the bond area must be considered to be a brittle weak point in the substrate-plate structure. The bend tests of these deposited structures did not reveal any strong tendency toward catastrophic failure of the bond. Figure 52 is an interesting example of the apparent strength of the plate and the bond area. The top photomicrograph shows a plate and bond that has been pulled from its 316 SS substrate by a mechanical cutting operation. The cut was taken 7" from the internally plated specimen inlet. Note that the bond has pulled some of the stainless steel away from the substrate. Figure 52, bottom, shows the bond at 1" from the inlet of the same specimen.



Deposit at Outlet End (400X)
316 SS pulled away with bond



Deposit at Inlet End (400X)
Plate Intact

FIGURE 52

BONDS OF INTERNALLY PLATED TUBULAR SPECIMEN

SECTION XII

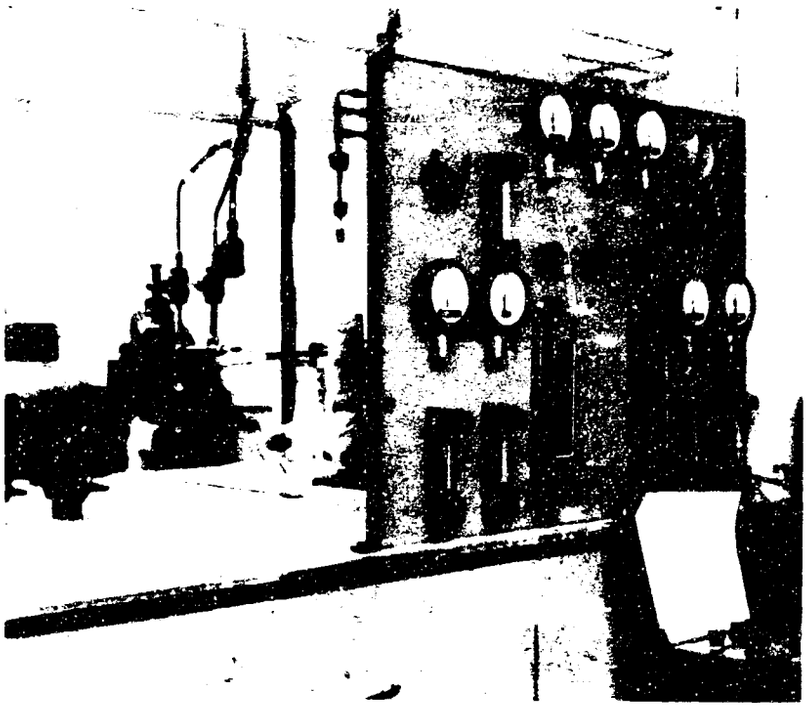
DESIGN AND FABRICATION OF INTERNAL PLATING SYSTEM

Deposition apparatus was initially designed and built for depositing Cb-Zr alloys on the inside of 316 SS tubular specimens. Various modifications and improvements were made during the course of trial depositions. The system was refined to permit the plating of large tubing loops early in the second contract year.

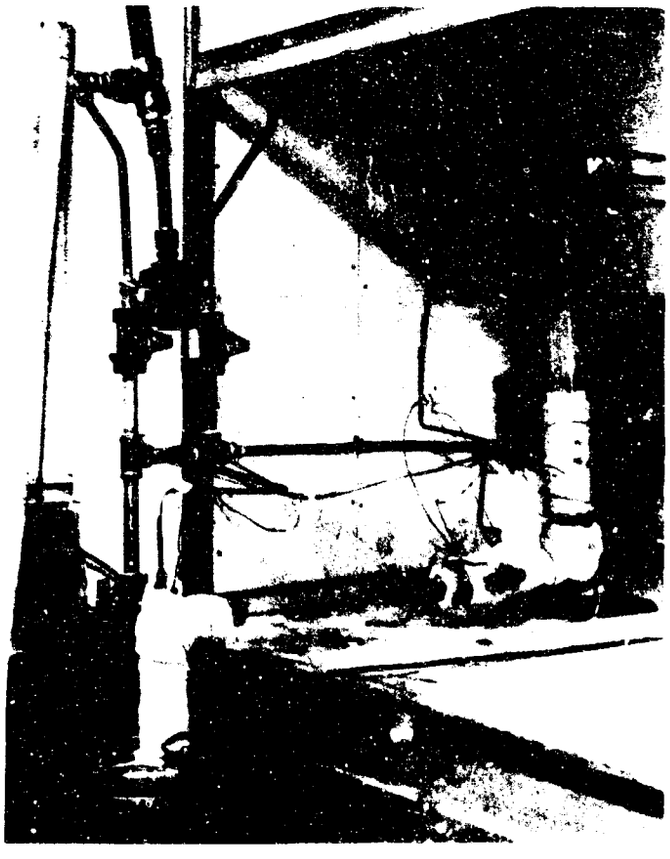
A preliminary plating system was designed to permit deposition of columbium and Cb-Zr alloys on the inside of 316 SS tubular specimens. A schematic of the system is shown in Figure 53. Photographs appear in Figure 54. The photos show the system with the test section removed. One of the primary differences between this design and the external plating apparatus design was a provision to maintain all gas lines above a predetermined minimum temperature. This was to prevent sub-chloride condensation and subsequent plugging within the tubular specimen. A water cooled sub-chloride "knockout" chamber was also placed in the exhaust line to trap sub-chloride condensibles before they could enter the vacuum pumping system.

Initial runs were made with $CbCl_5$ or $CbCl_5 + ZrCl_4$ utilizing a nine inch long stainless steel "reactor" specimen and a six inch long external heater around the specimen (see Figure 55). The reactor inlet and outlet lines were insulated to prevent condensation of $CbCl_5$, $ZrCl_4$ and lower chlorides. The hydrogen inlet line was externally heated with heater cord. Temperatures of the reactor, the hydrogen inlet line, and the reactor inlet and outlet lines were monitored using chromel/alumel thermocouples fastened to the outside of these units. Temperature corrections were made manually. However, once the system was brought to equilibrium plating temperature, changes occurred slowly and did not require immediate accurate correction. Based upon data obtained in the outside depositions, the internal plating system was first operated at slightly above atmospheric pressure to maximize plating rate. The system was vented to the atmosphere. Gas flows were based upon successful outside deposition data.

A number of difficulties were encountered with this arrangement. The initial deposits were found to be non-uniform in various ways.



Control Panel



Chlorinator, Hydrogen Inlet Line and Exhaust System (Reaction Section Removed)

FIGURE 54

INTERNAL PLATING SYSTEM

(a) Peeled plate and coarse non-adherent plate was produced. This was attributed to a specimen temperature cycle which occurred when the cooler plating gases first entered the reaction zone, followed by a rise in temperature as warm reaction products began to form. This initial depression lowered the temperature to a point where plating but no bonding took place. The thin, non-adherent plate then peeled when the temperature rose again. Subsequent plating over the peeled plate produced bumps.

(b) Circumferentially, non-uniform plate was produced with a reasonably thick and bonded deposit on one half while the opposite half was very thin and unbonded. This was apparently due to a difference in heating capability between the two halves of the clamshell heater assembly.

(c) The three or four inch length of deposit was less than desired.

A number of modifications were made in the plating rig to eliminate or at least minimize these problem areas.

(a) The clamshell heater unit previously used was an exposed element type. Completely "potted" element heaters were therefore incorporated to increase the temperature capability of the heater and to promote more uniform heating.

(b) A stainless steel heat distributor was introduced to further smooth the heat input to the specimen. This distributor was a heavy-walled jacket which was fitted over the specimen tube.

(c) A heater was placed downstream of the reaction zone to prevent excessive heat losses from the exit end of the reactor.

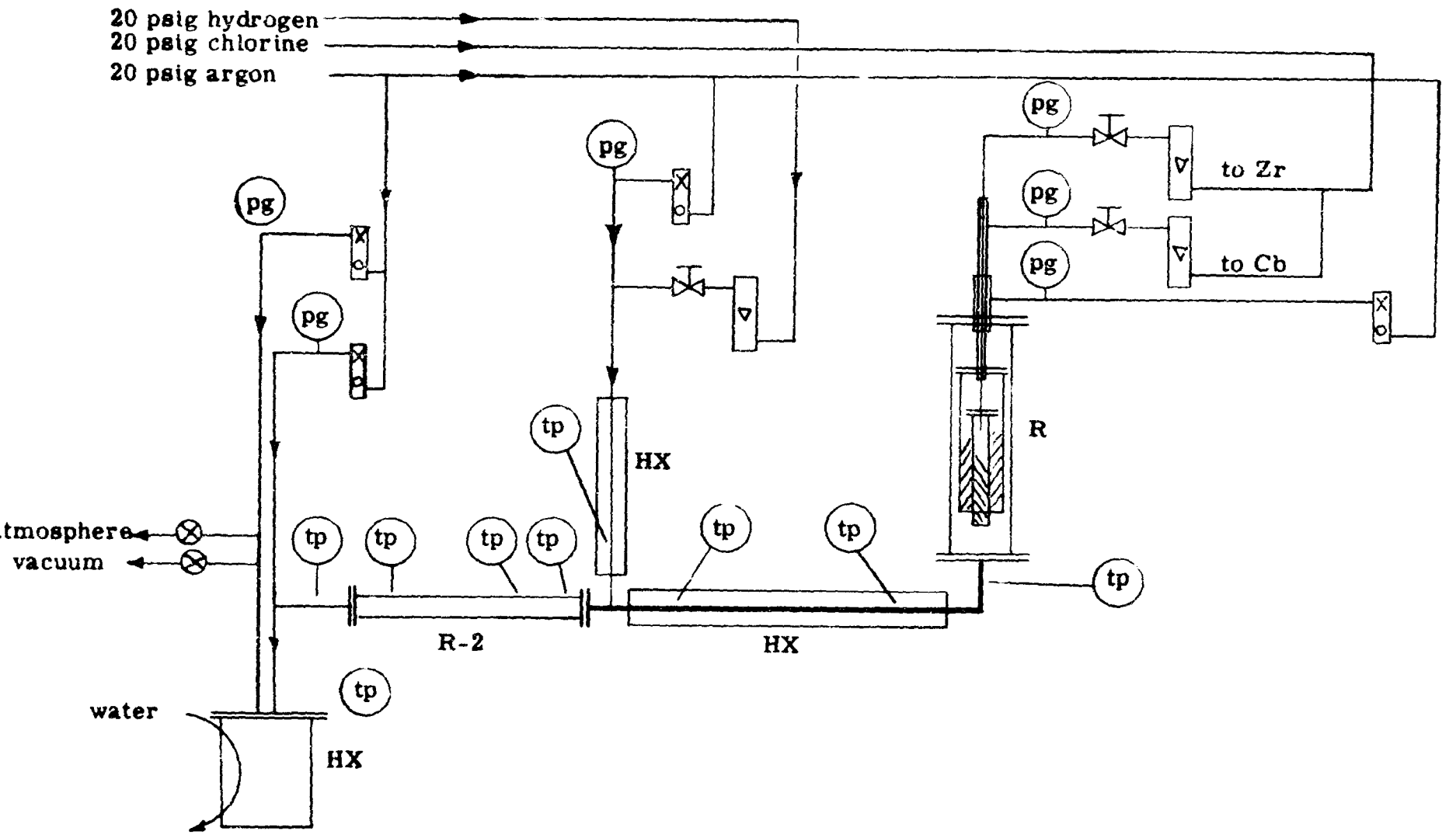
(d) A preheater was added before the reactor inlet to prevent chilling of the initial plating zone by cold reactant gases. Heretofore an externally controlled preheater was used only on the hydrogen inlet line. Chlorides from the chlorinator were, of course, produced hot. The mixing line (now the preheater) was merely insulated to minimize heat losses.

(e) The length of the reaction zone was doubled to twelve inches to minimize end effects.

(f) The plating conditions were modified to include operation below one atmosphere to increase gas velocity and to increase the penetration of plate down the tube (at some possible sacrifice to plating rate).

Figures 56, 57 and 58 show the modified system.

The chlorinator was patterned after the concentric columbium/zirconium chlorinator arrangement used in external depositions. Two concentric vycor cylinders, one filled with columbium metal chips and the other filled with zirconium metal, were placed at the entrance to the preheater section. Separate chlorine lines were run to each of the concentric chlorinators, thus enabling the generation of $CbCl_5$ and $ZrCl_4$ to be separately controlled. An argon diluent line was fed into the cavity between the outer chlorinator and the chamber wall. Hydrogen was mixed into the chloride gas stream midway through the preheater section. Near the end of the year's work this concentric chlorinator was set aside in favor of the arrangement shown in Figure 59. This allowed separate control of the heat input and temperature of the Cb and Zr chlorinators. The reasons for this final modification are covered in Section XIII of this report.



HX — heat exchanger
R — reactor
pg — pressure gage
tp — temperature measurement point

FIGURE 56

REVISED INTERNAL PLATING SYSTEM SCHEMATIC

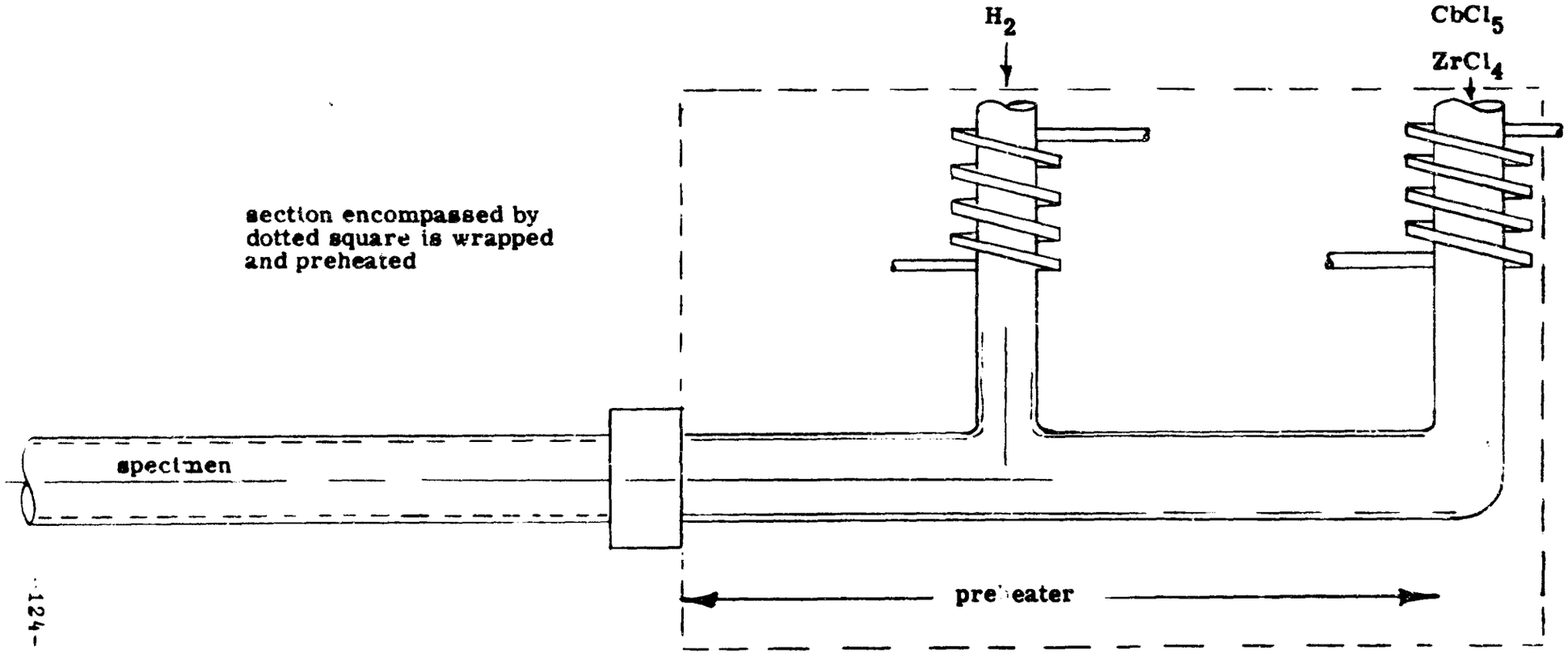


FIGURE 57

PREHEATER TO PLATING REACTOR ZONE

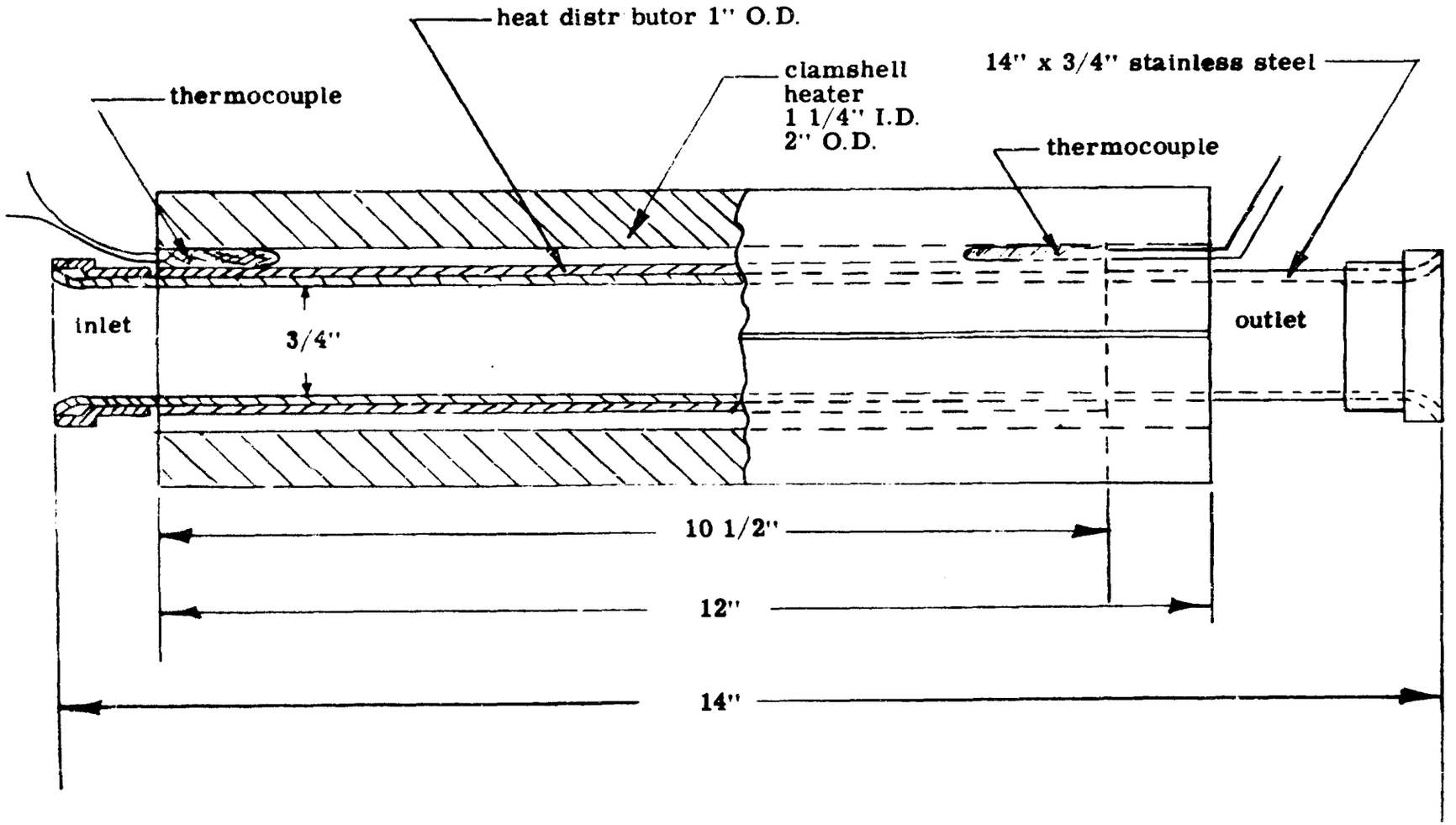


FIGURE 58

EXTENDED PLATING REACTOR ZONE

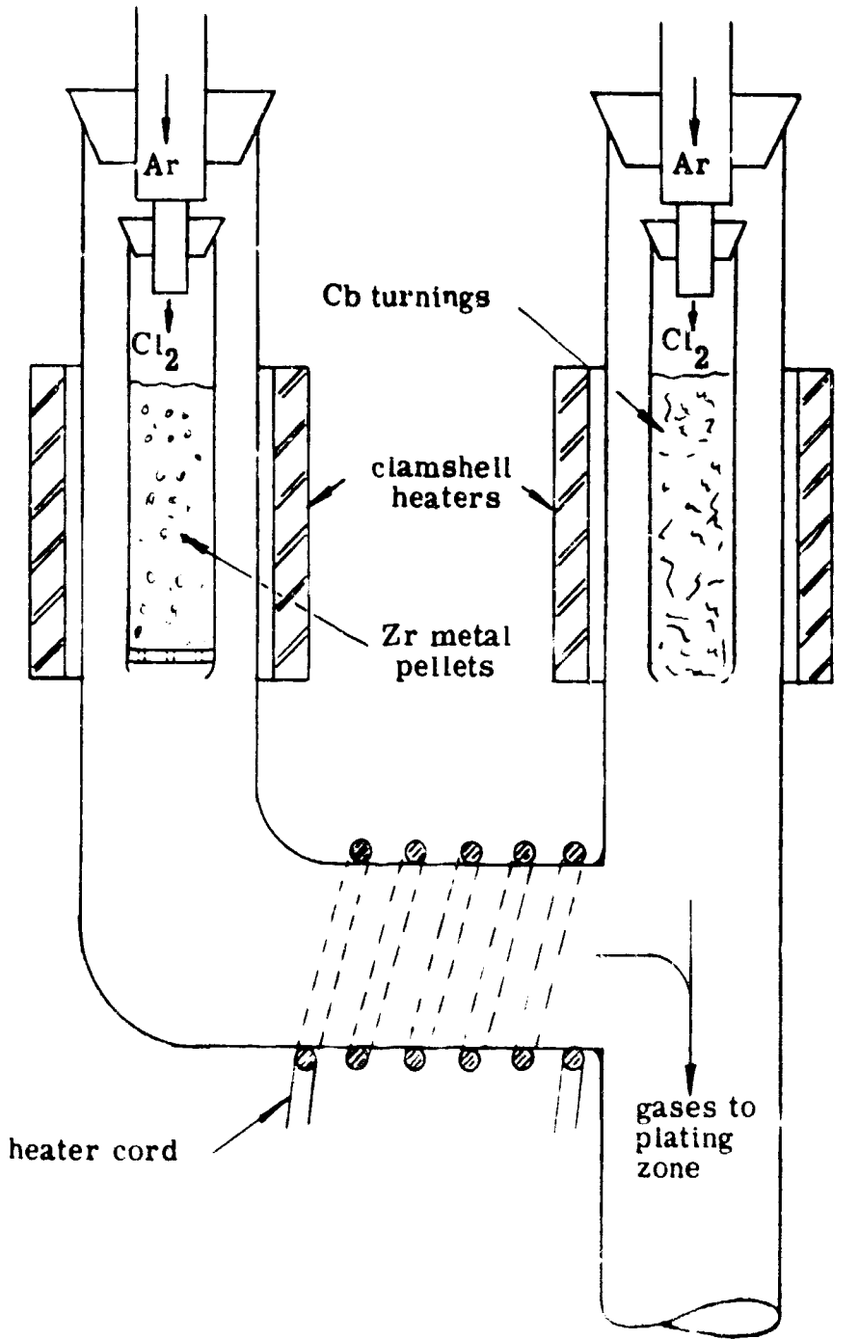


FIGURE 59

SEPARATED COLUMBIUM & ZIRCONIUM CHLORINATORS

SECTION XIII

DETERMINATION OF THE OPTIMUM RUN CONDITIONS FOR THE DEPOSITION OF COLUMBIUM-1% ZIRCONIUM ON THE INTERNAL SURFACE OF 316 SS TUBING

Functional parameters were optimized for internal depositions. This included reaction zone temperature, reactant gas preheater temperature, exhaust temperature and reactant gas flow ratios. The apparent quality of the Cb and the Cb-1% Zr plate and the diffusion bond for the internal deposits prepared under the optimized plating conditions were comparable to that obtained in external depositions.

The variables associated with internal deposition were explored extensively first with pure columbium runs and then with columbium-zirconium runs. Initial runs were conducted with gas flows which had previously been established in successful external depositions and at atmospheric pressure to maximize plating rate. Section IV describes preliminary external deposition data which indicated substantially higher plating rates at higher pressures. This was later disproved. A most difficult problem was found to be associated with the high melting and boiling points of the various chlorides generated in the plating process. The temperature of the chlorinators, hydrogen inlet line, reactant gas preheater, and reaction zone exit line were adjusted from run to run to refine these parameters.

Under normal internal plating operating conditions it was found that a preheater temperature of 300°C was sufficient to maintain the gaseous state of both $CbCl_5$ and $ZrCl_4$. It has previously been noted that chlorination temperature must be carefully controlled to insure the formation of fully chlorinated Cb without producing subchlorides or allowing free chlorine to pass through the chlorinator unreacted. It was found that subchlorides condensed in the preheater and reaction zone portions of the system. Accumulation of subchlorides in the preheater would result in a pluggage at that point (300°C is not sufficient to maintain the volatility of subchlorides). Subchloride particles that reached the reaction zone would form nucleation sites on the bottom of the reaction tube and columbium would deposit over these particles resulting in coarse, porous deposits. A temperature of approximately 700°C was required to maintain subchloride reaction products as gases in the exit line from the reaction zone.

The chlorination reaction is exothermic. After the various sections of the system are brought to the proper equilibrium temperatures, the chlorination reaction is started and the resultant hot gas reduces the heating demand upon the preheater section. Typically a 10 to 25°C temperature excursion occurs at this point.

The initial design of the plating system included a hydrogen inlet line to the preheater midway between the chlorinators and the reaction zone. Considerable evidence was gathered to indicate that the temperature excursion just described was sufficient to bring the mixed chlorides to a temperature sufficient for partial hydrogen reduction to occur. When it occasionally affected the inlet portion of the reaction zone this excursion and the consequent cooling resulted in peeling of the thin initial plate. This is described more completely in Section XII of this report.

Lower hydrogen inlet line preheater temperatures were tried in attempts to compensate for the temperature surge that resulted in partial reduction at the junction of the mixed chloride and hydrogen lines. It was found to be rather difficult to maintain the hydrogen supply at a temperature that would be low enough to eliminate the partial reduction reaction yet high enough not to cool the unreacted chlorides below their condensation temperature. The problem was finally resolved by changing the location of the hydrogen inlet line to a point immediately preceding the reaction chamber. Using this configuration a plating run was begun by bringing the system to temperature while flowing hydrogen through the reaction zone at the plating operation flow rate. The hydrogen inlet line was maintained at approximately 700°C at this time and throughout the deposition run. No reoccurrence of the partial reduction problem at the hydrogen inlet was encountered with this arrangement.

Higher gas flows were employed at atmospheric pressure to extend the length of the plating zone from the 2 to 3" obtained in initial runs. The plating length was doubled. However, a point was reached where the heat capacity of the greater gas mass flows made temperature control of the preheater and reaction zone inlet sections very difficult. It was then decided to extend the plating zone length by increasing the gas velocity through reducing system pressure rather than through increasing gas mass flow rates. A plating length of 6" to 7" was achieved without significantly effecting the control of system temperatures at a system pressure of 10" Hg below atmospheric. Most of the meaningful internal depositions conducted under the program were conducted at 10" Hg below atmospheric pressure with the exception of a few trials that were conducted near the end of the

contract year at minus 20" Hg. The lower pressure yielded longer but thinner plate. Further evaluation of low pressure deposition is anticipated with long length tubing during the second contract year.

Figures 60 and 61 are photomicrographs of the bond area of an internally plated specimen prepared near the conclusion of the plating parameter studies outlined above. The specimens shown in these figures include inlet and outlet sections of the same plated sample, 7" apart. The apparent quality of the plate and the diffusion bond for these specimens prepared under the proper plating conditions is comparable to that obtained in O.D. depositions. Figure 62 is a photomicrograph of another specimen similarly prepared. It shows the reproducibility of the bonding method.

The optimum system parameters presently include the following:

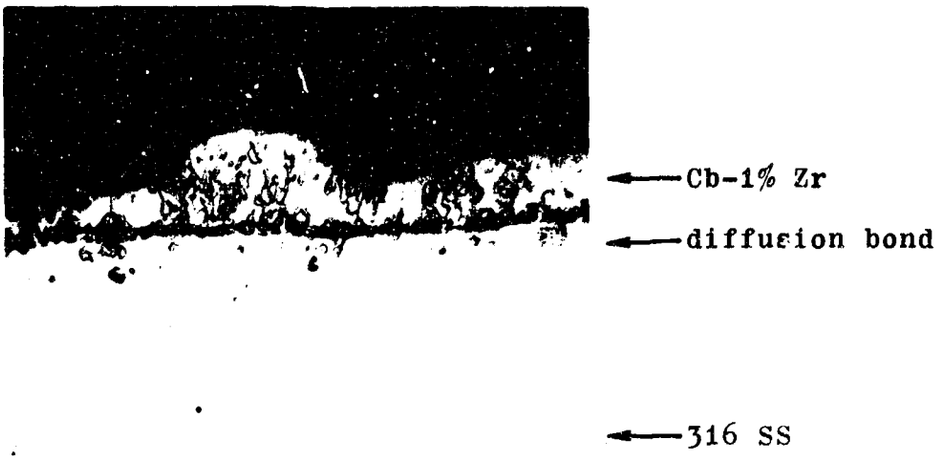
System Pressure	Minus 10" Hg or less
$CbCl_5$ flow for bond	250 cc/min
$ZrCl_4$+$CbCl_5$ flow	250 cc/min($ZrCl_4$:$CbCl_5$=70:30)
H_2 flow	1600 cc/min
Reactor Temperature	1050°C - 1075°C
Chloride Preheater Temperature	300°C - 310°C
H_2 Preheater Temperature	300°C - 310°C
Exit Line	720°C - 740°C
Cb Chlorinator Temperature Below Ignition Zone	300°C - 400°C
Zr Chlorinator Temperature Below Ignition Zone	350°C - 450°C

Most of the internal depositions conducted under the program were made with concentric vycor chlorinators as described in Section III. Independent control of the temperature of each chlorinator was rather gross with this arrangement. Initially accurate independent control was not considered to be critical. However accumulation of subchlorides occurred at the exit of the columbium chlorinator or $ZrCl_4$ condensate occurred at the exit of the zirconium chlorinator. This was due to either a decomposition of $CbCl_5$ to a less volatile species through overheating the concentric chlorinator assembly or condensation of $ZrCl_4$ through underheating the assembly. Figure 59 shows a chlorinator designed to allow independent temperature control of each chlorinator. The design was very successful in eliminating chlorinator pluggages due to chloride condensation.

Specimen 1, Inlet (400X)

FIGURE 60

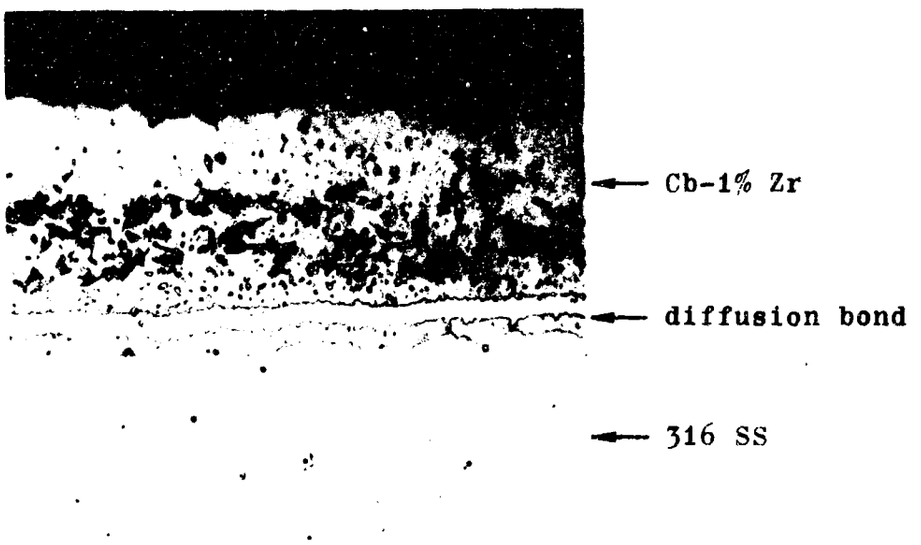
ILLUSTRATION OF DIFFUSION BOND



Specimen 1, Outlet (400X)

FIGURE 61

ILLUSTRATION OF DIFFUSION BOND



Specimen 2 (400X)

FIGURE 62

ILLUSTRATION OF DIFFUSION BOND

SECTION XIV

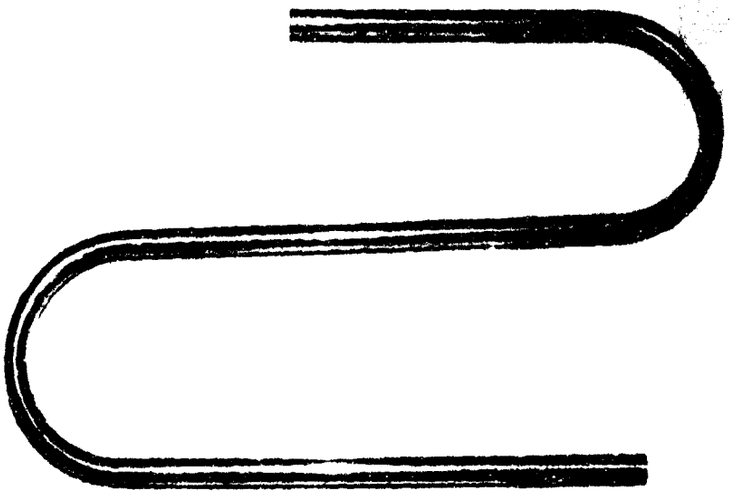
INTERNAL PLATING OF TRIAL LOOP CONFIGURATION

Two 3/4" diameter x 5' long 316 SS tubing loops as shown in Figure 63 were plated internally with Cb-1% Zr. Sectioning of the loops indicated that metal had been successfully deposited over the entire inner surface of the loop.

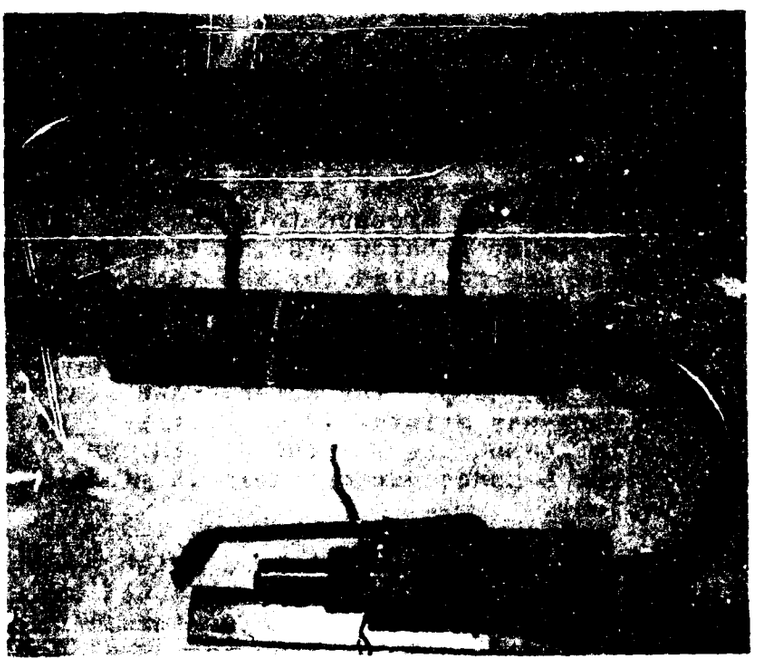
The plating system used was identical to that shown in Figure 56 except that seven separately controlled plating zones were used along the length of the loop. Thermocouple measurement of the temperature of each of the seven plating zones was maintained. Six inch long clamshell resistance heaters were used on the 5 straight sections of the loop while stainless steel sheathed nichrome heating wire was wrapped around each of the 180° bends. The entire loop was then wrapped in glass insulation. The lower view in Figure 62 shows the loop with clamshell heaters and thermocouples in place.

The plating process was begun by bringing the entire reaction length (the 7 controlled zones) to plating temperature and then introducing a $CbCl_5/H_2$ mixture into one end of the loop. The procedure to this point was identical to that previously described for short straight internal plating runs. After 15 minutes the power to the first (closest to inlet) resistance heater was dropped to allow the temperature in the first zone to drop below plating temperature. Approximately 15 minutes was required for the temperature of this zone to drop from 1050°C to 700°C. The temperature of each successive downstream zone was similarly dropped, sequentially, and the plating zone was moved from zone to zone down the length of the loop. The seventh and final (closest to exhaust) zone was maintained at plating temperature for 30 minutes to compensate for the plating that had taken place in the first 6 zones during their 15 minutes transient cooling periods.

The flow of plating gases was terminated after the Cb plate had been deposited and the seven plating zones were returned to the original 1050°C plating temperature. Cb-1% Zr was then plated throughout the tube from the usual $CbCl_5/ZrCl_4/H_2$ plating mixture in a manner identical to that just described for Cb deposition. A 30 minute plating time for each zone was employed for the Cb-1% Zr deposition.



Basic Loop Configuration



Loop with Clamshells & Thermocouples in place

FIGURE 63

316 SS LOOP FOR INTERNAL PLATING

Metal was deposited over the entire inside surface of the loop. However total success of both deposition runs was impaired by system leaks which occurred and resulted in heavy oxidation and scaling of the hot deposit surfaces. Both runs experienced the leaks midway through the Cb-1% Zr portion of the run. Only the first reaction zone (which had fully completed its term of deposition) escaped with merely a surface oxidation. The downstream plating zones which were still to be plated with Cb-1% Zr showed evidence of moderate to heavy scaling from plating that took place over the oxide layer.

The atmospheric leakage to the plating system was found to have taken place at a vycor-to-stainless viton seal immediately below the glass chlorinator assembly. The duration of these runs, by far the longest made to date, allowed excessive thermal deterioration of the seal to take place which eventually resulted in the failure of the seal. The temperature was 360°C at a point 2" away from the seal on the stainless side. The temperature at the seal was probably excessive for long times.

The seal just described was moved 2" farther from the preheater and a temperature probe was placed within 1" of the seal. This arrangement was employed for the manifold depositions, which are described in Section XV.

SECTION XV

INTERNAL PLATING OF TRIAL MANIFOLD CONFIGURATION

Two manifolds of the configuration shown in Figure 64 were plated internally with Cb-1% Zr. The major leg of each manifold was made of 1 inch dia 316 SS tubing and the two perpendicular branch legs were made of 3/4 inch dia 316 SS tubing. The 1 inch diameter leg was 24 inches long and the 3/4 inch dia legs were each 9 inches long. The initial objective of the depositions was to investigate the problem of plating a right angle joint of changing diameter. Such an assembly would ideally be plated by selectively plating one leg at a time by valving shut the remaining two gas flow paths. However the 700°C temperature requirement of all lines downstream of a plating zone prohibited the use of conventional valves. The type of high temperature corrosionless gate valve that would be required for this purpose was not made available by any supplier in time to be used for these trial depositions.

In lieu of high temperature valves an alternate means was attempted to selectively control the plating gas paths. A condensate chamber design is described in Section IV of this report for use on the downstream side of the reaction zone. Similar chambers were installed downstream of each of the 3/4 inch dia. legs as well as at the exit of the 1" dia. tube. Conventional low temperature valves were used on the vacuum side of each condensate chamber (the cold side) to control the gas flow path. To prevent thermal diffusion of hot reactant gases into the cool condensate chambers a hydrogen bleed stream was maintained from each of the two valved-off condensate chambers into the reaction zone. The major reactant gases were carried through the lone open exit. A flowsheet for the manifold deposition system appears as Figure 65. The assembled system is shown in Figure 66.

Both manifold plating runs were conducted in the same fashion. The entire manifold assembly was first brought to plating temperature. Five separately controlled plating zones were involved. The various zones were first plated sequentially with Cb in the manner described for the loop plating operation. Cb-1% Zr was then deposited in like manner. No oxidation problem was encountered. However, both runs were terminated before completion of the Cb-1% Zr deposition due to the development of a pressure differential across the manifold. Sectioning of the manifolds revealed a

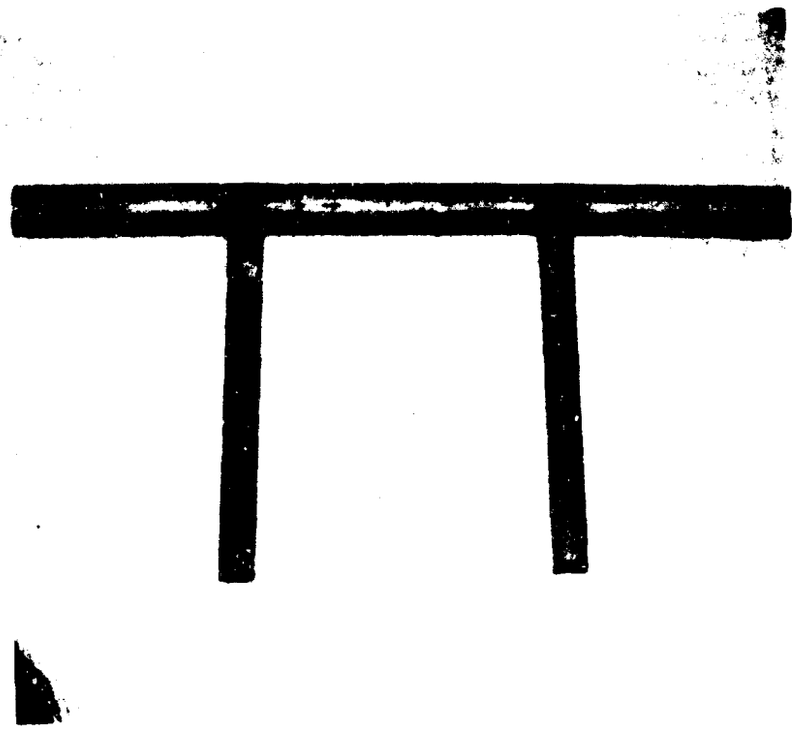


FIGURE 6.

316 SS MANIFOLD FOR INTERNAL PLATING

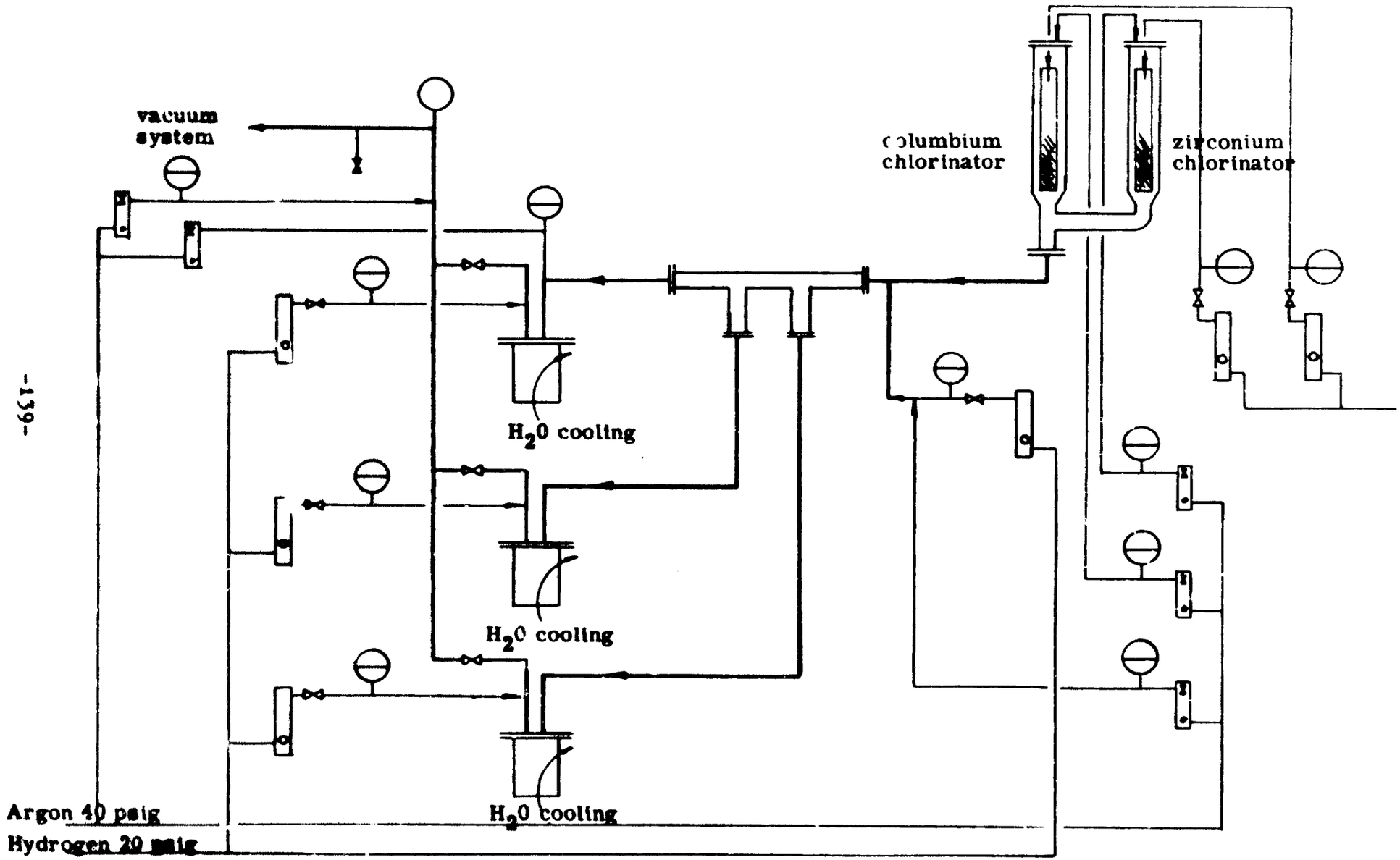


FIGURE 65 - MANIFOLD DEPOSITION FLOWSHEET

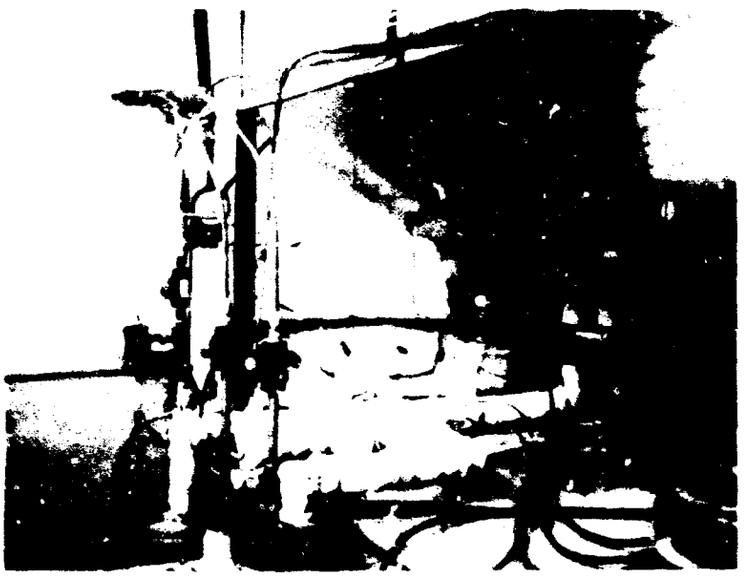


FIGURE 66

ASSEMBLED MANIFOLD DEPOSITION SYSTEM

deposited metal web extending from the upstream edge of each 3/4 inch dia. leg at the right angle junction across the 1 inch tube. This tended to seal the latter shut. Refer to Figures 67 and 68. It is believed that use of the hydrogen bleed flows, necessary in the absence of high temperature valving, was primarily responsible for this phenomenon. The geometry of the metal web seems to follow a contour of the two merging gas streams; the stream containing reactant chlorides plating along the pure hydrogen "wall".

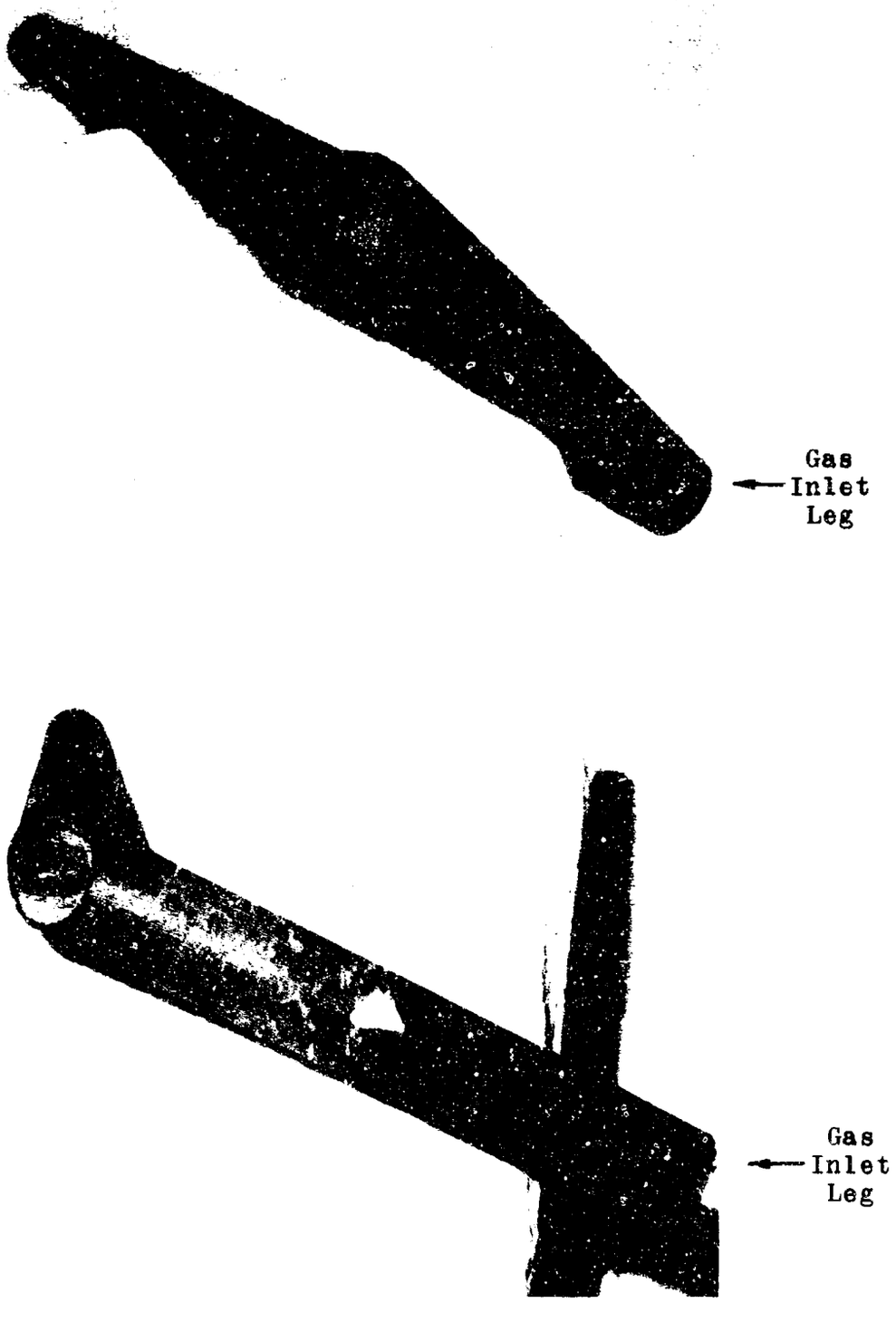


FIGURE 67

MANIFOLD NO. 1, SECTIONED

FIGURE 68

MANIFOLD NO. 2, SECTIONED

SECTION XVI

MISCELLANEOUS

1. CHEMICAL ANALYSIS OF Cb-Zr ALLOY

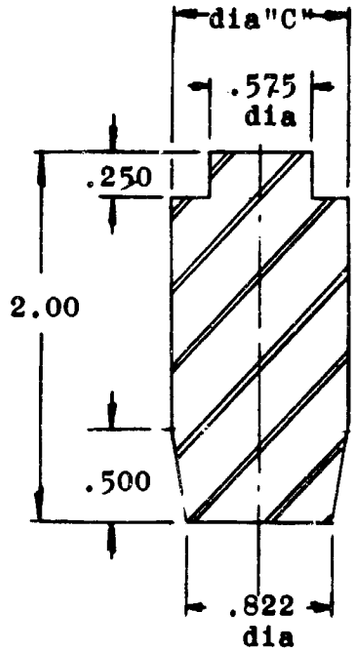
Preliminary efforts were made to develop a fast chemical determination of zirconium in Cb-Zr alloy specimens. Initial consideration of colormetric methods indicated that these methods were generally more sensitive to Cb than to Zr and were therefore probably not suitable. A method whereby diphosphatozirconic acid crystals are precipitated from a controlled acid media was found to be encouraging for, at least, a qualitative determination. However, the method was found to be somewhat inaccurate in the Zr concentration range of interest. During the same period when these wet chemical procedures were being developed, an outside source was found to be suitable for microprobe analytical service. Refinement of the chemical procedure was therefore deferred in favor of microprobe determinations.

2. STATIC TEST CAPSULES

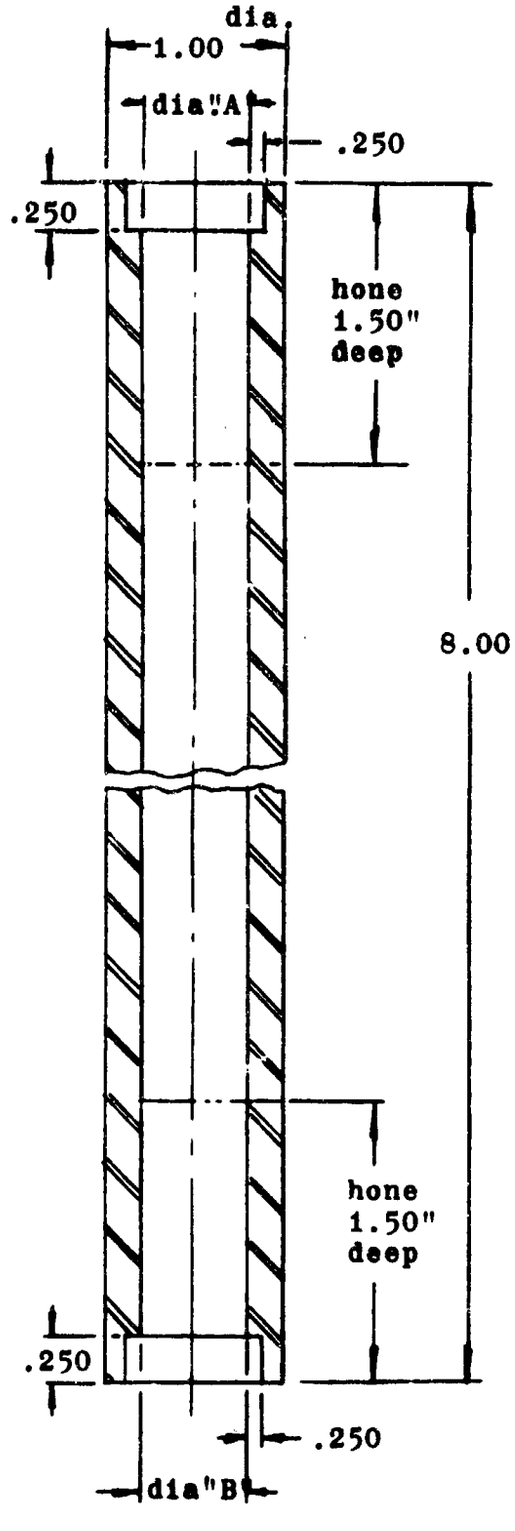
The components necessary for nine static test capsules were fabricated for time/temperative corrosion resistance testing in potassium. The capsule design was for a 1" dia x 8" long 316 SS tube plated internally with Cb-1% Zr with two solid 2" long 316 SS end plugs plated with Cb-1% Zr. The tubes and plugs were sent to a subcontractor for honing to the final dimensions shown in Figure 69 and Table VIII. The finished components will be delivered to RTD for assembly and testing with potassium.

Figure 70 shows two finished end plugs and a tube. The outside of the tube appears rough due to a slight amount of plating. Perhaps 1% of the plating gases see the outside of the tube while the inside is being plated. This is because the procedure used to plate the capsule tubes is similar to that described for external plating except that the plating gases are drawn through the tube rather than around it. The external plating system was employed using induction heating.

The stainless steel holder used to support the end plugs during deposition is shown on one of the plugs in Figure 70.



PLUG



TUBE

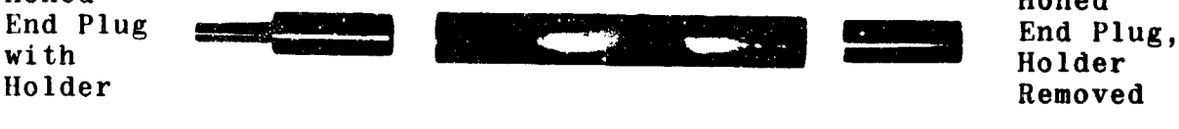
FIGURE 69

STATIC TEST CAPSULE

TABLE VIII

STATIC TEST CAPSULE DATA

Tube No.	A	B	C (Top)	C (Bottom)
4A	.834	.826	.836	.828
5A	.826	.830	.828	.832
6A	.826	.829	.828	.831
7A	.826	.829	.828	.831
8A	.830	.829	.832	.832
10A	.827	.827	.829	.829
11A	.826	.830	.828	.832
12A	.830	.828	.832	.830
13A	.833	.829	.835	.831



Internally Plated
and Honed Tube

FIGURE 70

STATIC TEST CAPSULE

3. ETCHING

Specimens mounted for metallographic and microprobe analyses were polished flat by rough grinding followed by fine Al_2O_3 and diamond dust polishing. One of two chemical etches was then used prior to examining the specimens. The first was employed to emphasize the Cb/316 SS diffusion bond zone. It consisted of:

5% Hydrofluoric acid
10% Nitric acid
30% Lactic acid
55% Water

A 5-10 second exposure time was generally found to be sufficient.

The second etchant consisted of:

5% Hydrofluoric acid
10% Sulfuric acid
30% Lactic acid
55% Water

A 10-15 second exposure time was used with this etchant.

4. PLATING OF SPECIAL ASSEMBLY

A special assembly was plated in anticipation of plating the interior surfaces of 4' x 6' 316 SS loop assemblies for alkali metal corrosion tests by RTD. A 1/4" dia Cb-1% Zr tube was suspended in a 6" long 3/4" dia 316 SS tube and the internals of this assembly were plated with columbium. This assembly was designed to roughly approximate a configuration being used in the loops for a Cb-1% Zr insert in the 316 SS boiler section. A sketch of the mock-up is given in Figure 71.

Microscopic analysis of the plated assembly indicated that adequate penetration of plate down the interior and exterior surfaces of the Cb-1% Zr tube was attained but penetration down the entire length 316 SS was not achieved. A photomicrograph of the plated Cb-1% Zr (inner) tube appears in Figure 72. This tube had previously been plated

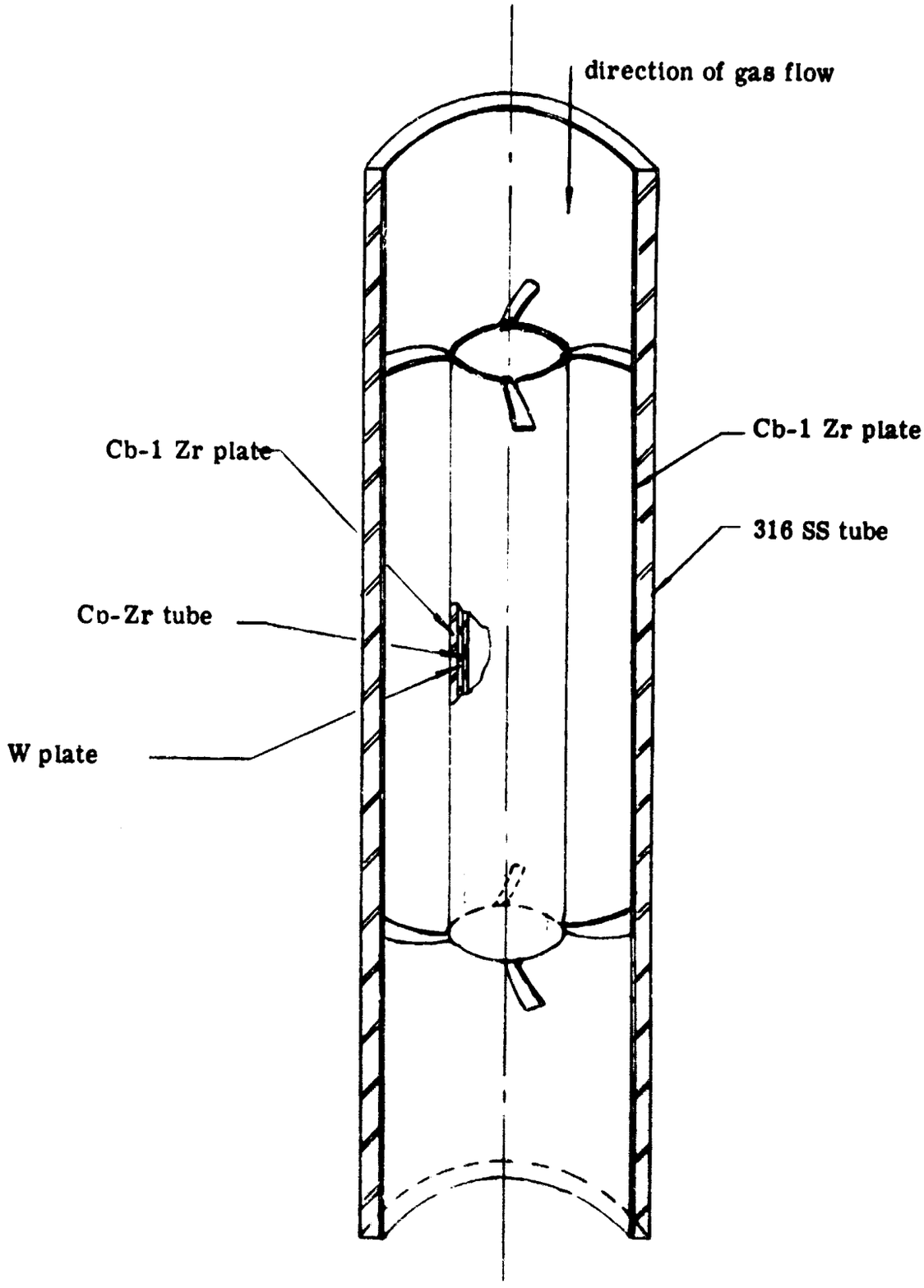


FIGURE 71

SPECIAL TUBING ASSEMBLY

FIGURE 72

INNER TUBE OF
SPECIAL TUBING ASSEMBLY (150X)

on the inside with WF_6/H_2 reduced tungsten. This had no bearing on the columbium deposition test discussed here. The layers in Figure 72, from left to right, are vapor deposited columbium, vapor deposited tungsten, drawn Cb-1% Zr, and vapor deposited columbium. It appears that an adjustment in gas velocity above that employed in this test would result in the successful plating of all inner surfaces of a similar assembly.

REFERENCES

1. Chemical Transport Reactions, H. Schaefer, Academic Press, New York, 1964, Page 125.

2. SNAP-8 Topical Materials Report for 1963, Volume II, Component Materials Development, (Report No. 2822 dated March 1964) Aerojet-General Corporation, Azusa, California.

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13. ABSTRACT

Techniques were developed for depositing Cb-1% Zr metal corrosion barrier coatings on the internal surfaces of type 316 SS tubing assemblies. Shapes approximating various parts of the SNAP 50/SPUR space nuclear auxiliary power generation system were coated with uniform and adherent deposits of Cb-1% Zr ranging in thickness from 0.002 to 0.006 inches. Deposition chemistry was investigated. A chemical system employing the hydrogen reduction of mixed chlorides at reduced pressure proved to be most suitable. Efforts to minimize interstitial contamination of the deposits resulted in impurity levels of 150 ppm C, 10 ppm H_2, 50 ppm O_2, and 50 ppm N_2. About 100 trial depositions were made on the inner and outer surfaces of tubular 316 SS specimens. A bond was not attained directly between Cb-1% Zr alloy and 316 SS. However, a diffusion bond was attained between columbium and 316 SS, and it was demonstrated that plating Cb-1% Zr over a 5-to-10 micron interlayer of Cb gave adherent coatings. The integrity of the bonding was demonstrated in comprehensive physical tests.

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