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FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

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Air Force Systems Command
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Project No. 7312, Task No. 731202

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by the MSA Research Corporation, Callery, Pennsylvania;
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FOREWORD

This report was prepared by the Materials Research Section of the Research Division, MSA Research Corporation under USAF Contract No. AF 33(657)-9168. This contract was initiated under Project No. 7312, "Finishes and Materials Preservation," Task No. 731202, "Corrosion and Deterioration Control." The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, with Mr. Jesse J. Crosby as the project engineer.

This report describes the results of research performed during the second year of the program covering the period from 1 July 1963 to 15 August 1964.

ABSTRACT

Mechanisms associated with the corrosive attack of refractory metal alloys and superalloys by liquid cesium have been investigated. The superalloys, Haynes-25 and TD-Nickel, were exposed at 1800°F and the refractory metal systems, Mo-1/2Ti, Cb-1Zr, Ta-10W and Cb-25Ta-12W-1/2Zr were exposed at 2100°F and 2500°F. Pure nickel and pure zirconium were employed as dissimilar metal additions in some tests.

Boiling reflux tests of each alloy candidate were performed. In the case of the refractory alloys, the boiling temperatures were 2100 and 2500°F, while 1800°F was the test temperature employed for Haynes-25 and TD-Nickel capsules. The Haynes-25 and the TD-Nickel show some dissolution in cesium, and a measurable amount was experienced by Mo-1/2Ti at 2500°F. The tantalum and columbium alloys show little in the way of cesium attack at 2100°F.

Metal solubility studies showed the solubility of the refractory metals columbium and molybdenum to be approximately 10-20 ppm at 2500°F. Synergistic effects appear to control solubility in some cases.

Dissimilar metal tests showed mass transfer of metallic elements to be experienced by all couples in the presence of pure liquid cesium except Mo-1/2Ti/Zr. Interstitial elements also undergo mass transfer and carbon and/or oxygen additions so the cesium can effect significant changes in the behavior of couples.

The solubility of carbon in cesium was determined between 600 and 1200°F and data obtained showing no effect of carbon on the freezing point of cesium.

This technical documentary report has been reviewed and is approved.



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ABSTRACT

Mechanisms associated with the corrosive attack of refractory metal alloys and superalloys by liquid cesium have been investigated. The superalloys, Haynes-25 and TD-Nickel, were exposed at 1800°F and the refractory metal systems, Mo-1/2Ti, Cb-1Zr, Ta-10W and Cb-25Ta-12W-1/2Zr were exposed at 2100°F and 2500°F. Pure nickel and pure zirconium were employed as dissimilar metal additions in some tests.

Boiling reflux tests of each alloy candidate were performed. In the case of the refractory alloys, the boiling temperatures were 2100 and 2500°F, while 1800°F was the test temperature employed for Haynes-25 and TD-Nickel capsules. The Haynes-25 and the TD-Nickel show some dissolution in cesium, and a measurable amount was experienced by Mo-1/2Ti at 2500°F. The tantalum and columbium alloys show little in the way of cesium attack at 2100°F.

Metal solubility studies showed the solubility of the refractory metals columbium and molybdenum to be approximately 10-20 ppm at 2500°F. Synergistic effects appear to control solubility in some cases.

Dissimilar metal tests showed mass transfer of metallic elements to be experienced by all couples in the presence of pure liquid cesium except Mo-1/2Ti/Zr. Interstitial elements also undergo mass transfer and carbon and/or oxygen additions so the cesium can effect significant changes in the behavior of couples.

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INTRODUCTION AND WORK SCOPE

Over the last two years a study has been made to elucidate the factors affecting the corrosion of structural metals by liquid cesium. During the first year, the study of the solubility of structural metals in liquid cesium was initiated. The study of mass transfer in dissimilar metal capsules was also pursued, the results of which were reported in detail in reference 1.

The second year effort involved continuation of solubility and dissimilar metal studies. Dissimilar metal studies were performed at 1800°F in the case of L-605 (Haynes-25) and TD-Nickel, while test temperatures for refractory metal alloys were in the range 2100-2500°F.

The solubility of carbon in cesium was determined to 1200°F and the effect of carbon on the melting point of cesium was also examined.

Cesium boiling refluxing tests were performed with a number of alloys including L-605, TD-Ni, Mo-1/2Ti, Cb-1Zr, Ta-10W and Cb-27Ta-12W-1/2Zr.

SOLUBILITY OF CARBON IN CESIUM

Introduction

Carbon can significantly affect the physical and mechanical properties of ferritic and austenitic steels, as well as refractory metals and their alloys. In general, carbon tends to increase the hardness and decrease ductility, stress to rupture and fatigue qualities of these various materials of construction. It has been demonstrated that carbon dissolved in

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sodium can lead to carburization of these materials and that carbon can be transferred from one material to another with the alkali metal as a carrier. A knowledge of the solubility of carbon in cesium can be useful with respect to predicting the degree of carburization which might occur as well as the feasibility of removing carbon from cesium by cold trapping or filtration.

Oxygen can be reduced to a low level in sodium since it has a temperature dependent solubility and a low solubility at or near the melting point. Other impurities, such as carbon, which exhibit these characteristics can also be removed from sodium by cold trapping. The solubility curve generated by Gratton² indicates that carbon has a temperature dependent solubility in sodium ranging from 35 ppm at 300°F to 75 ppm at 1200°F with 40 ppm O₂ and 110 ppm at 300°F to 185 ppm at 1200°F with 260 ppm O₂. Recent studies³ indicate that carbon can be removed from sodium by cold trapping.

No data existed on the solubility of carbon in cesium. Hence this study was undertaken. For an initial evaluation of the carbon solubility characteristics, an oxygen concentration of less than 10 ppm oxygen was chosen. Future work should include a determination of carbon solubility at some higher oxygen level, perhaps 100 ppm oxygen.

Analytical Procedures

Introduction - The procedure used for the analysis of carbon in cesium is identical to that used for the analysis of carbon in sodium.⁴ This procedure consists of:

1. Extracting a sample of the alkali metal at temperature.
2. Transfer of the complete sample to a dissolution apparatus.
3. Dissolution of the sample with distilled water at 0°C.
4. Titration of the sample with a standard acid.
5. Dehydration to a dry alkali metal salt.
6. Combustion of the salt in prepurified oxygen at 1200°F.

7. Collecting of CO₂ at liquid nitrogen temperature.

8. Measurement of the CO₂ by mass spectrometry.

This procedure has been shown to be accurate to ± 5 ppm carbon with salt-loop block standards.

Sampling Procedure - Extraction of the sample at temperature is an obvious requirement. If the sample were extracted through plumbing at some temperature lower than the test temperature, carbon could precipitate and low values would result. It was shown during this study that carbon will segregate as a sample is cooled, hence the total sample was analyzed in all cases.

Initial samples in this study were taken by dip sampling from a vessel shown schematically in Figure 1. A nickel bucket was lowered into the cesium melt, the sample was extracted into an inert gas chamber and then transferred to the appropriate analytical apparatus. Before a carbon source was added to the cesium charge, this method proved adequate. However, after a carbon source was added to the charge, it became evident that particulate carbon was present and reliable and reproducible samples could not be extracted by this method.

It was concluded that true solubility data could be derived only if the sample were filtered. This was done by welding a 5 micron micrometallic filter into the end of 3/8 in. stainless steel tubing and extracting the cesium into this device. Four major problem areas evolved as a result of this revised method:

1. Segregation of carbon in the sample.
2. Migration of carbon to the sampler walls.
3. Freezing the sample on the rod.
4. Operational safety procedures.

A discussion of each of these problems, their effects and the ultimate solution are given in the subsequent paragraphs.

Where a total of approximately 2 grams of cesium was extracted by the standard dip sampling procedure, a total of 10-15 grams was extracted by the filtration procedure. It was necessary to section the tubing into a number of lengths containing 1-3 grams of cesium and melt the cesium from each of these sections. It became evident that carbon was segregating within the tube (Table 1).

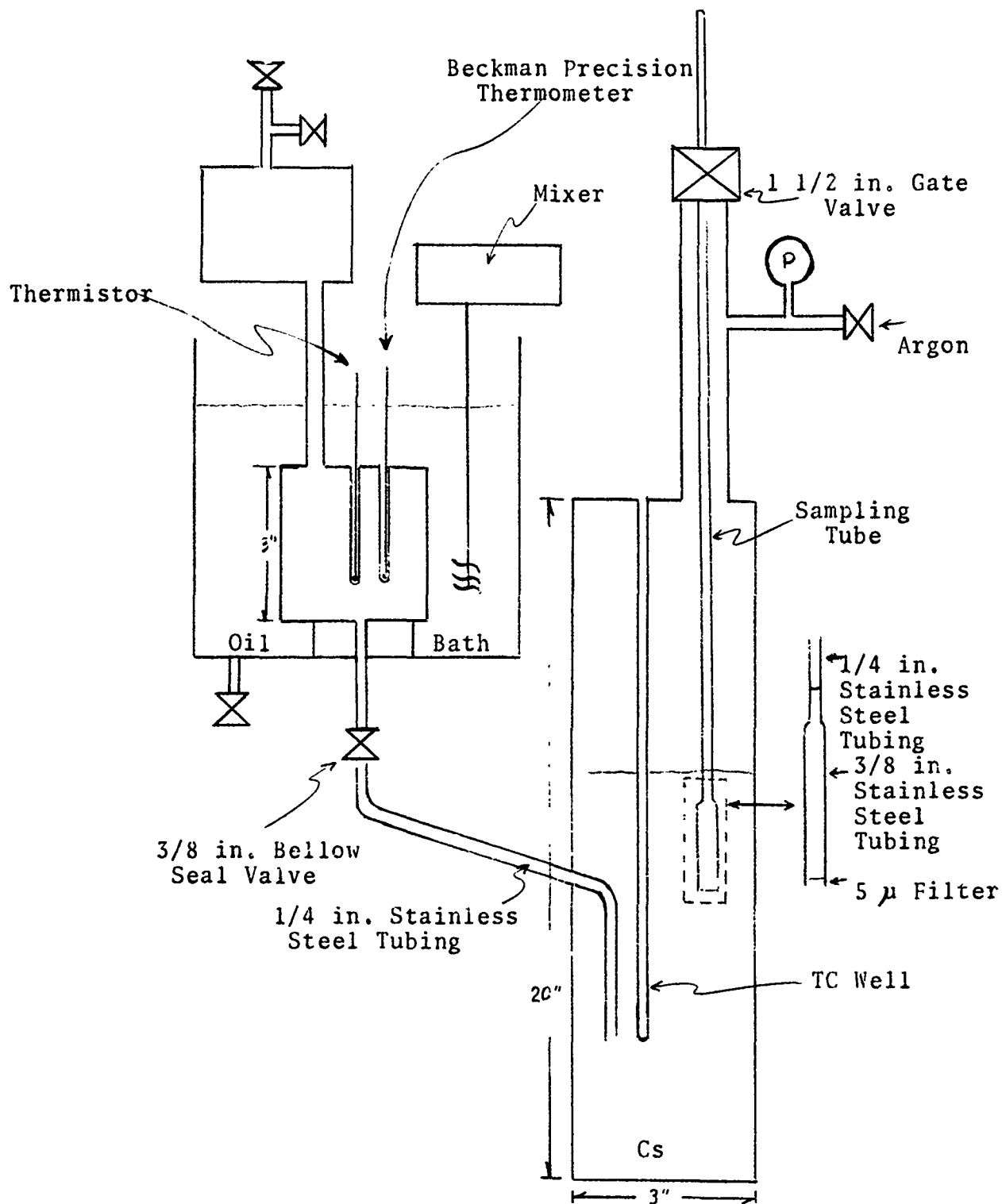


FIG 1 - SCHEMATIC DIAGRAM OF CARBON SOLUBILITY APPARATUS

TABLE 1 - CARBON CONCENTRATION IN CESIUM

Sample Temperature (°F)	Section	Wt. Cesium (gms)	Wt. Carbon (μ gm)	Carbon Concentration (ppm C)	Remarks
400	1	2.420	29.5	12.1	
	2	1.932	19.9	10.6	
	3	2.600	28.7	11.0	
	4	3.880	12.2	3.2	
	5	2.580	8.6	3.3	
	6	1.548	12.6	8.2	
	7	2.060	12.7	6.2	
	Tube	0.305	66.5	218.0	
	Total	17.525	190.7	11.0 (Avg.)	
400	1	Section Lost			
	2	3.940	12.8	3.3	
	3	Section Lost			
	4	3.640	14.1	3.9	
	Tube	2.050	115.0	56.2	
	Total	9.630	141.9	15.6 (Avg.)	
600	1	3.600	52.4	14.5	Filtered Sample
	2	3.600	21.2	5.9	
	3	4.120	19.8	4.8	
	4	2.700	24.3	9.0	
	Tube 1,2,3,4	1.960	97.3	49.7	
	Total	15.980	215.0	13.4 (Avg.)	
600	1	1.302	21.0	16.1	Filtered Sample
	2	3.460	15.5	4.5	
	3	3.340	18.1	5.4	
	4	4.190	12.7	3.0	
	Tube 1,2,3,4	3.650	105.0	28.8	
	Total	15.942	172.3	10.8 (Avg.)	
600	1	3.220	15.5	4.8	Filtered Sample
	Tube 1	0.216	24.0	111.4	
	Total	3.436	39.5	11.6 (Avg.)	
800	1	2.570	22.1	8.6	Filtered Sample
	2	2.440	11.1	4.5	
	3	2.320	17.5	7.5	
	4	2.140	13.8	6.4	
	Tube 1,2,3,4	1.179	115.5	98.0	
	Total	10.649	180.0	16.8 (Avg.)	
800	1	3.400	48.0	14.0	Filtered Sample
	2	4.160	26.0	6.3	
	3	4.100	22.0	5.4	
	4	2.790	26.0	9.2	
	Tube 1,2,3,4	1.010	151.0	149.0	
	Total	15.460	273.0	17.6 (Avg.)	
900	1	3.120	28.0	8.9	Filtered Sample
	2	3.250	27.0	8.2	
	3	3.450	32.0	9.3	
	4	3.540	35.0	10.0	
	Tube 1,2,3,4	0.748	91.0	122.0	
	Total	14.108	213.0	15.1 (Avg.)	
1000	1	2.800	25.0	9.1	Filtered Sample
	2	2.520	31.0	12.0	
	3	2.400	27.0	11.0	
	4	2.200	35.0	16.0	
	Tube 1,2,3,4	1.210	166.0	138.0	
	Total	11.130	284.0	25.5 (Avg.)	
1000	1	2.210	26.0	12.0	Filtered Sample
	2	2.400	24.0	10.0	
	3	0.382	32.0	84.0	
	Tube 1,2,3	0.614	115.0	188.0	
	Total	5.606	197.0	35.2 (Avg.)	
1000	-	0.861	133.0	155.0	Nickel Bucket Dip Sample
1000	1	2.880	43.0	15.0	Filtered Sample
	2	2.560	41.0	16.0	
	3	2.270	27.0	12.0	
	4	2.260	50.0	22.0	
	Tube 1,2,3,4	0.680	230.0	340.0	
	Total	10.650	391.0	37.0 (Avg.)	
1000	1	3.060	33.0	11.0	Filtered Sample
	2	0.581	33.0	57.0	
	Tube 1, 2	0.332	68.0	204.0	
	Total	4.973	134.0	34.0 (Avg.)	
1200	1	2.690	54.0	20.0	Filtered Sample
	2	2.540	41.0	16.0	
	3	2.540	30.0	12.0	
	4	1.642	31.0	19.0	
	Tube 1,2,3,4	0.282	121.0	430.0	
	Tube 5	0.156	133.0	850.0	
	Total	9.650	410.0	42.0 (Avg.)	
1200	1	3.77	43.0	11.0	Argon cover gas flushed through tube to prevent surface sampling. Non-filtered sample taken below surface of cesium.
	Tube 1	2.94	314.0	107.0	
	Total	6.71	357.0	53.2 (Avg.)	
1200	1	2.20	37.3	17.0	Filtered Sample
	2	2.79	38.2	13.7	
	3	2.42	210.0	86.7	
	4	3.05	20.5	6.7	
	Tube 1	1.42	182.0	128.3	
	Tube 2	0.47	190.0	104.0	
	Total	12.35	678.0	54.7 (Avg.)	
1200	1	3.07	24.3	7.9	
	2	2.36	20.4	8.6	
	3	2.59	45.6	17.6	
	4	2.21	59.4	27.0	
	Tube	1.71	475.4	278.0	
	Total	11.94	625.1	52.4 (Avg.)	

For example, at 400°F, sections from the same tube gave results ranging from 8.6 to 29.5 ppm carbon while at 1200°F this range was from 6.7 ppm to 128 ppm carbon. Thus, the total weight of cesium melted from the rod was equated with the total amount of carbon found in each section to determine the average carbon content of the sample.

It also became evident that carbon was migrating to the sampler walls. In order to account for the carbon originally present in the sample, the individual tubes were washed free of cesium and the washes were combined and analyzed for carbon content. The weight of the cesium remaining on the walls of each tube as well as the total carbon analyzed in these sections had to be added to the values determined for the samples melted from the tube. These total values of cesium weight and carbon content were then used to determine the solubility of carbon in cesium at each temperature.

Cesium was transferred from the test vessel to the sampling tube by drawing a vacuum on the sampling tube. In this fashion cesium was extracted into the sampler through the micro-metallic filter. To retain the cesium in the sampling tube, it was necessary to freeze the cesium in place. Since the melting point of cesium was lower than the ambient temperature in the neighborhood of the test vessel, it was necessary to freeze the cesium in the tubing before extracting the tubing from the vessel. A liquid N₂ reservoir was installed on the sampling tube, and when the cesium came in contact with this area, it froze in place.

The possibility of overfilling the tube while under vacuum was recognized. Such an incident could result in injury to the individual extracting the sample, so a liquid level measuring device was incorporated in the sampling tube. This consisted of an insulated wire inserted into the sample tube to a level corresponding to the desired cesium level. The wire was connected to an audible alarm and when cesium metal was extracted into the tube and contacted the bare end of the wire, a circuit was completed and the alarm automatically activated.

Oxygen Analysis - Oxygen content of the cesium was determined by the freezing point depression method. A freezing point measuring device was incorporated with the cesium vessel and cesium was transferred under inert gas to this device when an oxygen determination was made. Oxygen remained at less than 10 ppm throughout the carbon solubility study. No effect of carbon on freezing point depression was observed.

Carbon Solubility Results

Cesium (3 lb) was charged to the stainless steel vessel and heated to 400°F. Samples at this temperature indicated the equilibrium concentration of carbon in cesium in contact with stainless steel was 12 ppm.

A spectrographic graphite rod weighing 14.6 grams was added to the cesium charge. The rod had been subjected to a vacuum at 1200°F for 72 hrs. Before the rod was added, dip samples showed excellent agreement. However, after the graphite rod was added, results were erratic showing from 250-860 ppm carbon at 400°F. This indicated that particulate carbon was floating on the cesium surface. Later dip samples showed better agreement with an average carbon content of 13.5 ppm carbon indicating that the particulate carbon on the surface had disappeared. It was recognized, however, that true solubility data could be clouded by the presence of particulate carbon in the cesium melt and all subsequent samples were filtered during sampling.

Data were collected at 400, 600, 800, 1000 and 1200°F (Table 1). The data are plotted in Figure 2 with the log of carbon concentration as a function of temperature. The data points from 600-1200°F indicates an ideal solution. The value at 400°F deviates from ideality. This may partly be a result of an analytical blank. At 1000°F a dip sample showed 155 ppm carbon compared to 35 ppm carbon in the filter sample, indicating the presence of particulate carbon on the surface. At 1200°F an unfiltered sample was taken from approximately 4 in. beneath the cesium surface. This value was 54.5 ppm compared with 53 ppm carbon for the filtered sample indicating that there was essentially no particulate carbon present in the bulk cesium.

Conclusions - The results indicate that the solubility of carbon in cesium is low (12 ppm at 600°F to 53 ppm at 1200°F) compared to the solubility of oxygen in cesium, ~3% at room temperature. The equilibrium solubility of carbon in cesium at 400°F was less than 12 ppm. The temperature dependent solubility of carbon coupled with the low solubility at lower temperatures suggest that cold trapping or filtration could be an effective means of removing carbon from cesium.

METAL SOLUBILITY STUDIES

Evaluation of the solubility experiments reported in reference 1 suggested the possibility of interaction of "high-purity" alumina (G.E. Lucalox) crucibles with either cesium or with the solute refractory metal capsule. Alumina was discarded as a sampling crucible material in favor of a "foreign" refractory alloy. The technique employed for solubility tests was that described in reference 1. Exposure duration was varied in order to ascertain the time necessary to attain equilibrium.

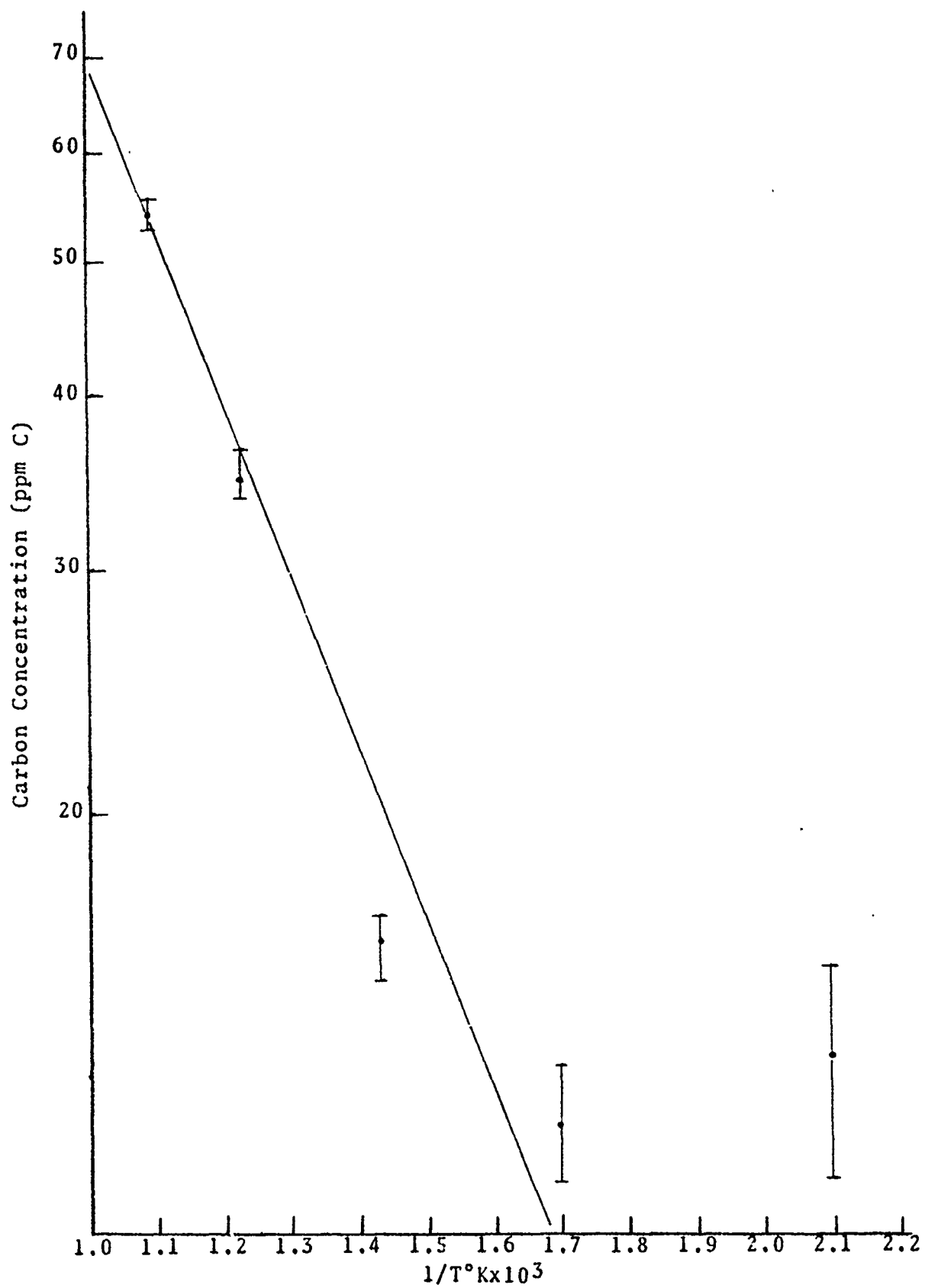


FIGURE 2 - SOLUBILITY OF CARBON IN CESIUM AS A
FUNCTION OF TEMPERATURE

Table 2 shows the solubility data derived using metallic sampling crucibles. The "solubility" of molybdenum in cesium at 2500°F is in the range 10-25 ppm. An increasing titanium content is apparent with increasing exposure time suggesting that equilibrium titanium solubility has not been attained and that titanium diffusion from Mo-1/2Ti is probably rate controlling. A possible synergistic effect of soluble titanium on the solubility of molybdenum in cesium is recognized.

Values for Cb-1Zr exposed to 2500°F cesium are also shown in Table 2. An increasing columbium content, from 10 to 30 ppm is seen from the data. These differences may be the result of analytical imprecision associated with the emission spectroscopic method. The values of zirconium are equal to or less than 10 ppm.

The experimental solubility studies performed during this program result in the following conclusions:

1. Synergistic solubility effects appear to exist between the components of an alloy in liquid cesium. This appears to be primarily the case in Mo-1/2Ti alloy studies.
2. The solubilities of the refractory metals columbium and molybdenum in cesium appear to be approximately 10-20 ppm at 2500°F.
3. The tip capsule sampling technique utilized in this program does not appear to be capable of obtaining kinetic solubility data due to a long heat-up time.
4. Improvements in methods of extracting solubility data at temperatures far in excess of the boiling point are necessary. This is particularly necessary where solubility values are of the order of 10 ppm or less.

REFLUX CAPSULE STUDIES

As a means of obtaining a qualitative description of the corrosion of alloys used in dynamic systems and screening possible containment alloys, reflux capsules have been prepared from the alloys Haynes-25, Nb-1%Zr, Mo-1/2%Ti, TD-Nickel, Ta-10%W and

TABLE 2 - "SOLUBILITY" OF METAL SPECIES IN 2500°F CESIUM

<u>Alloy</u>	<u>Temperature</u>	<u>Equilibration Time</u>	<u>Sampling Crucible</u>	<u>Metal Analysis</u>
Mo-1/2%Ti	2500°F	5 min.	Cb-1%Zr	Mo - 10 ppm Ti - <5 ppm
Mo-1/2%Ti	2500°F	14 hrs.	Cb-1%Zr	Mo - 25 ppm Ti - 100 ppm
Mo-1/2%Ti	2500°F	110 hrs.	Cb-1%Zr	Mo - 10 ppm Ti - 150 ppm
Cb-1%Zr	2500°F	0.5 hrs.	Mo-1/2%Ti	Cb - 10 ppm Zr - <10 ppm
Cb-1%Zr	2500°F	20 hrs.	Mo-1/2%Ti	Cb - 20 ppm Zr - >10 ppm
Cb-1%Zr	2500°F	100 hrs.	Mo-1/2%Ti	Cb - 30 ppm Zr - 10 ppm

Cb-27%Ta-12%W-1/2%Zr (FS-85). Encapsulation was accomplished under vacuum and tests were conducted at temperatures between 1800-2500°F for times between 250 and 1000 hours.

Exposure of containment alloys to refluxing cesium could accelerate corrosion by solution-deposition with pure condensate. These tests might not duplicate, but are qualitative representations of the corrosive conditions experienced in thermal or forced loop tests and may serve as a means of screening potential containment alloys and obtaining a qualitative measure of corrosion.

Refractory alloy capsules were fabricated from recrystallized rod 0.75 in. in diameter in such a manner that only one end-cap was required for encapsulation of the liquid metal charge. TD-Nickel capsules were similarly fabricated from as-received rod, while Haynes-25 tubing 0.75 in. OD x 0.65 in. ID was used as a starting material. The resulting refractory capsules were 8 in. long and had a wall thickness of 0.125 in. TD-Nickel and Haynes-25 capsules were 11 in. long. Capsules were individually charged under argon with cesium such that the height of the pot (at room temperature) was approximately two inches. The top seal cap having a small V-notch orifice was tamped into place and the capsule was placed within a mass spectrometer tested container, with a "quick-coupling" seal. The container was opened within the electron beam welding chamber and the chamber was pumped to less than 10^{-5} mm, after which the cap was seal welded and the V-notch was filled with weldment.

Reflux capsules of the refractory alloys were exposed under vacuum at temperatures between 2100 and 2500°F as shown in Figure 3. Temperature gradients experienced in these tests ranged between 350 and 500°F depending upon the thermal conductivity of the alloy.

Haynes-25

Two Haynes-25 capsules containing cesium were heated in an air environment with the boiling section being held at 1800°F. The condensing section of the capsules were air cooled. One test was run for 500 hours, while the second was run for 1000 hours. Due to a greater charge of cesium and a smaller ΔT through the capsule, the 1000 hour test experienced less cesium turnover than that exposed 500 hours. Approximate calculations show that the 500 hour capsule reflux rate was about 240 times/hr while that of the 1000 hour capsule was about 85 times/hr. Figures 4-6 compares the microstructures of the two capsules with that of a previously exposed capsule.

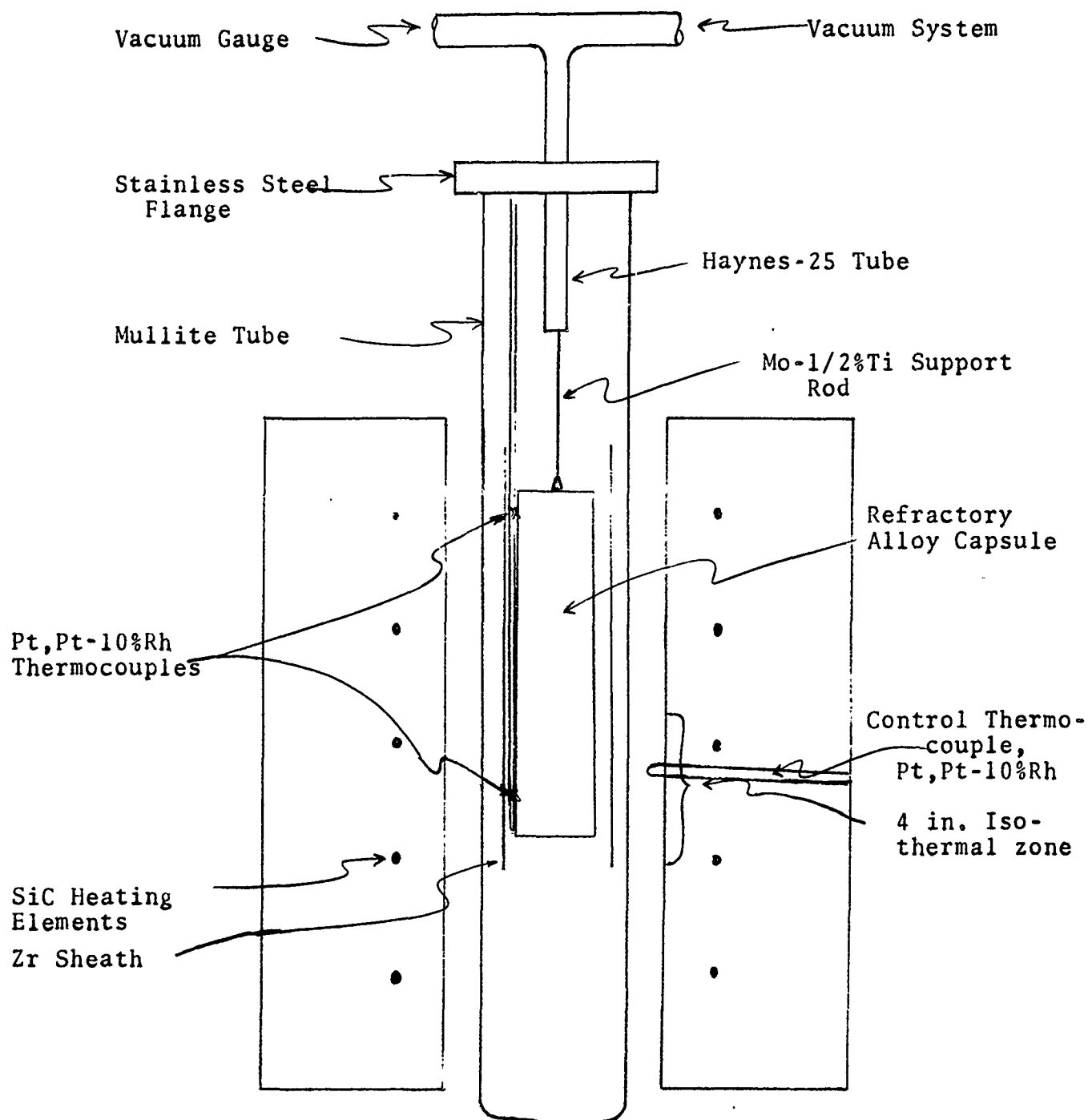


FIGURE 3 - HIGH TEMPERATURE REFLUX CAPSULE TEST FURNACE ASSEMBLY

FIGURE 4 - HAYNES-25 EXPOSED
TO BOILING CESIUM 500 HRS.

Etchant: $\text{HCl-H}_2\text{O}_2$

Magnification: 266X

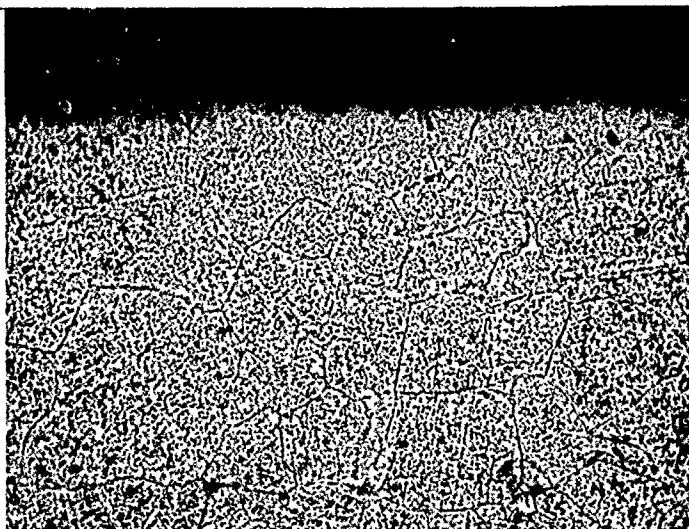


FIGURE 5 - HAYNES-25 EXPOSED
TO BOILING CESIUM 1000 HRS.

Etchant: $\text{HCl-H}_2\text{O}_2$

Magnification: 266X

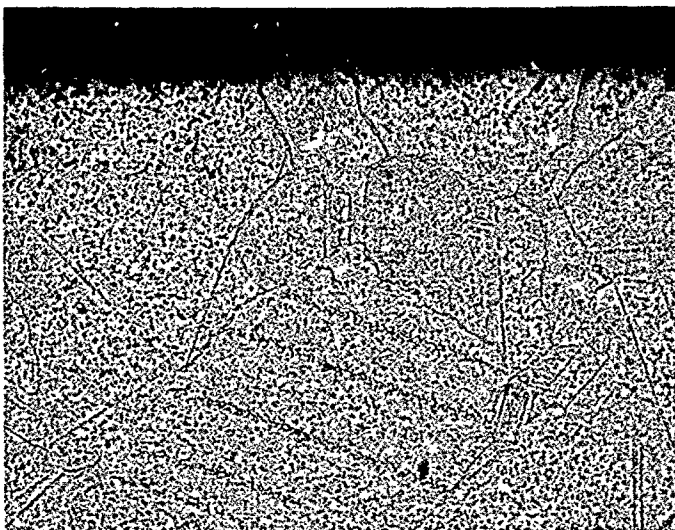


FIGURE 6 - HAYNES-25 EXPOSED
TO CONDENSING CESIUM 1000 HRS.

Etchant: $\text{HCl-H}_2\text{O}_2$

Magnification: 266X



The physical changes of this alloy upon exposure to refluxing cesium were not great. As observed in a static control capsule, the alloy exposed to the liquid phase did not show hardening when exposed 500 hours. The capsule showed increased hardness in the vapor zone, commensurate with the normal age-hardened condition. The capsule exposed 1000 hours at 1800°F showed equivalent hardness throughout.

It is apparent that considerably more aging occurred in the capsule exposed 1000 hours. The specimen from the boiling section of the 500 hour capsule shows considerable intergranular precipitation, but only a small amount of grain growth and segregation of the precipitating phases. The microstructure of each capsule show gradations of age-hardening from the vapor zone into the liquid zone where there is only slight aging in the 1000 hours exposure and almost none in the 500 hours exposure. The samples from the 1000 hour capsule show more twinning and better defined slip planes.

There was no evidence of any greater attack of the Haynes-25 in refluxing cesium than observed in static capsules, with little or no attack by either liquid or vapor phase cesium. In contrast with the static control capsule, however, which was decarburized by cesium, the reflux tests both showed increases in carbon content where exposed to the liquid phase. This was almost negligibly slight in the capsule exposed 500 hours, but was significant in the capsule exposed 1000 hours. The most important part of the transfer of carbon in the 1000 hour capsule was the observation of decarburization in the vapor zone and carburization in the liquid zone.

The capsules underwent the same amount of oxidation as in static capsule tests with the areas exposed to the vapor phase showing less tendency to scavenge oxygen than those exposed to the liquid phase.

TD-Nickel

Capsules fabricated from TD-Nickel were exposed to refluxing cesium at 1800°F for 260 and 500 hours duration. In each of the two capsules metallic crystallites were found adhering to the bottom of the capsule.

The hardness of the alloy was not substantially altered by exposure to liquid cesium at 1800°F, with the exception that slight softening was exhibited at the surface exposed to the liquid. As shown in Figure 7, the capsule exposed to refluxing cesium for 260 hours had a band approximately 30 microns thick along the inside surface. X-ray analysis indicates the surface to be FCC, and is probably nickel. A similar band found on the

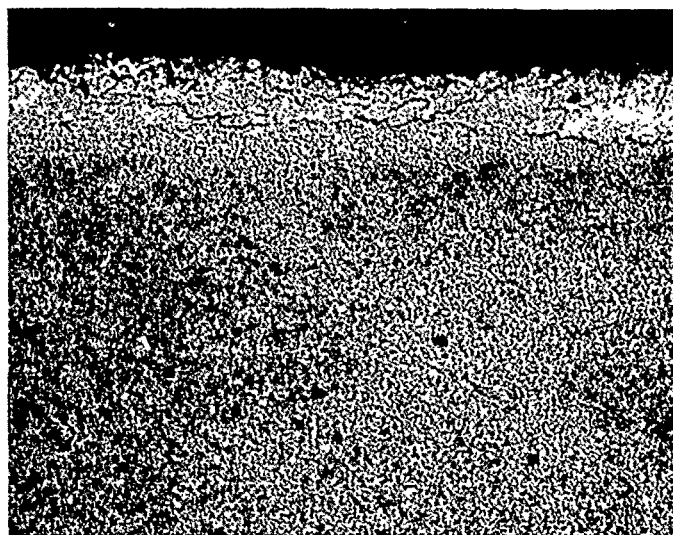


FIGURE 7 - TD-NICKEL CAPSULE EXPOSED 260 HRS AT
1800°F TO BOILING CESIUM

Etchant: Aqua regia

266X

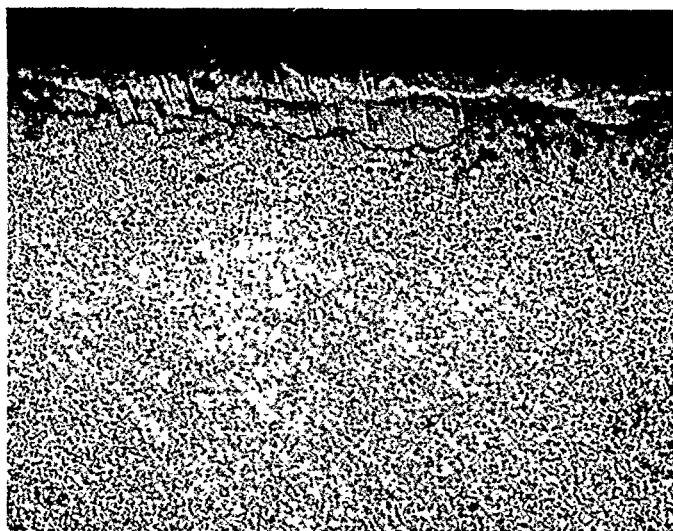


FIGURE 8 - TD-NICKEL CAPSULE EXPOSED 500 HRS AT
1800°F TO BOILING CESIUM

Etchant: Aqua regia

266X

inside surfaces of the capsule exposed 500 hours (Figure 8) is 30-35 microns thick. Microhardness measurements indicated the surface layer to be softer than the matrix TD-Nickel. Recrystallization and grain growth of the nickel, apparent in the photomicrographs suggests that the thoria dispersoid has been modified or possibly lost. Attempts to determine the possibility of selective leaching of thorium from the surface are underway.

Some decarburization (reduction from 50 to 25 ppm) of TD-Nickel was observed on the capsule exposed 260 hours to refluxing cesium with slight deviations between areas exposed to liquid and vapor phases, with the portion at the boiling ring essentially undergoing no changes. Decarburization of TD-Nickel was also observed in the 500 hours exposed capsule but was observed only in the section exposed to the boiling liquid.

While corrosion has not been considerable, the use of TD-Nickel as a containment alloy for boiling-refluxing cesium at 1800°F does not appear to be as effective as Haynes-25 alloy.

Cb-1%Zr

One Cb-1%Zr capsule successfully completed an 868 hour test with refluxing cesium with a liquid temperature of 2100°F. This test had to be terminated after 868 hours exposure because of difficulties with the vacuum system rather than with the alloy itself. The capsule showed no significant dissolution (Figure 9) with no deposited crystallites, and post-test hardness measurements indicated almost negligible hardness changes. The alloy experienced considerable grain growth within the matrix (Figures 10 and 11) but a small band 40 μ wide at the exposed surface did not show this change. This band gradually narrows and becomes less pronounced as one proceeds along the inside surface into the area exposed only to the vapor phase. Similar changes were noted in a static 2100°F control capsule. This alloy shows promise as a containment material at 2100°F but is limited for use at higher temperatures because of a lack of mechanical strength.

Mo-1/2%Ti

Three capsules of Mo-1/2%Ti were tested with boiling-refluxing cesium. The first test was performed with the liquid at 2500°F and was of 255 hours duration. A longitudinal section of this capsule, with an accumulation of metallic deposit adhering to the interface region is shown in Figure 12. The boiling zone, to the left of the photograph, is seen to have undergone attack resulting in a polishing action. The original machine marks are evident in the condensing portion.

FIGURE 9 - Cb-1%Zr CAPSULE EX-
POSED TO REFLUXING CESIUM
868 HOURS AT 2100°F



FIGURE 10 - Cb-1%Zr EXPOSED
868 HOURS TO BOILING CESIUM
(liquid zone)

Etchant: duPont's

Magnification: 266X

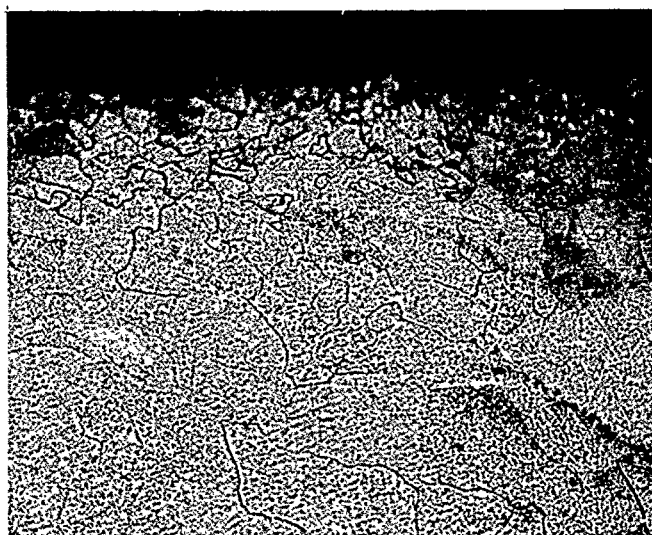
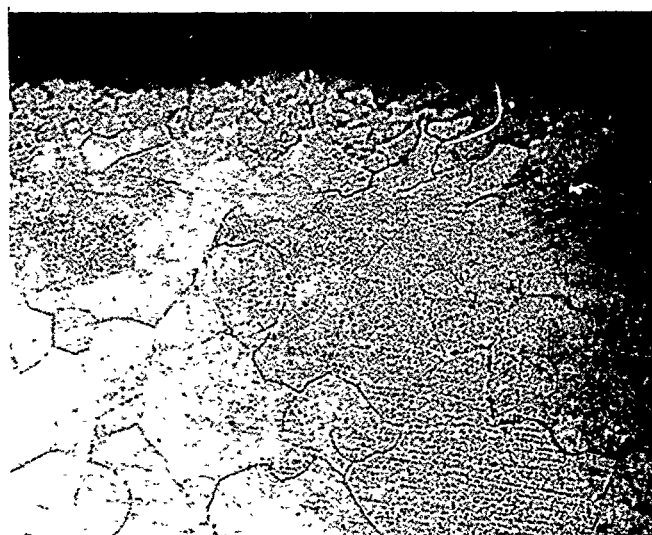


FIGURE 11 - Cb-1%Zr EXPOSED
868 HOURS TO CONDENSING
CESIUM VAPOR

Etchant: duPont's

Magnification: 266X



Regions from the boiling and condensing zone are shown respectively in Figures 13 and 14. Grain growth has occurred at the surface in the liquid region, but is not prevalent in the condensing region. The photomicrographs indicate that uniform dissolution has occurred, and that intergranular penetration is not significant.

Examination of the results of this test indicate greater dissolution from the boiling region than in the condensing region. This greater attack may have resulted by cooling of the ΔT occurring between the bottom of the capsule and the region where cooler condensate is being collected.

Reflux capsules of Mo-1/2%Ti were exposed to a 2100°F boiling condition for 292 and 1000 hours. Both 2100°F capsules experienced similar solution-deposition as observed in the single 2500°F test, but the attack was significantly lessened by the reduction of test temperature. The 292 hour test had but a few crystallites formed at the boiling interface. The interface region of the 1000 hour 2100°F test is shown in Figure 14. The surface irregularity is the result of deposition of molybdenum with the deposited crystallites obscuring edge clarity. The original surface is still evident.

Comparison of this test with a 2100°F Cb-1%Zr test described earlier indicates that solution-deposition in the molybdenum base alloy is more rapid than in the case of the columbium base alloy.

Ta-10W

One capsule of Ta-10W was exposed to 2100°F boiling-condensing cesium for 528 hours. A longitudinal section of this capsule with the original machining grooves intact is shown in Figure 15. No evidence of mass transfer could be detected. A section from the boiling region is shown in Figure 16. A substantial decrease in hardness (to $R_B=85$) of the alloy occurred as a result of exposure to test temperatures for 528 hours. Examination of the as-received material showed evidence of residual cold work and a carbide phase. The hardness reduction could thus be attributed to stress relief and carbide coalescence.

The absence of solution deposition when Ta-10W is exposed to boiling-refluxing cesium indicates that this alloy is one of the more corrosion resistant of those tested to date. A Ta-10W test capsule failed after 10 hours at 2500°F, due to rupture of a seal weld.

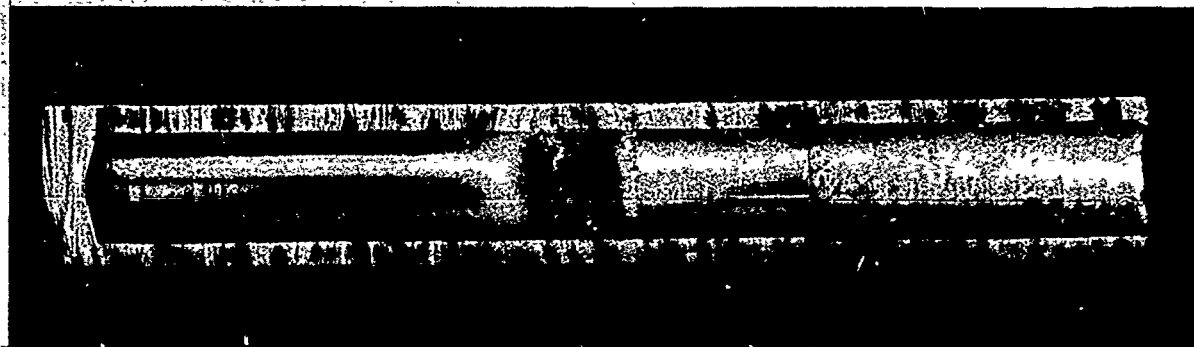


FIGURE 12 - Mo-1/2Ti CAPSULE EXPOSED TO BOILING-REFLUXING CESIUM (2500°F) FOR 255 HOURS

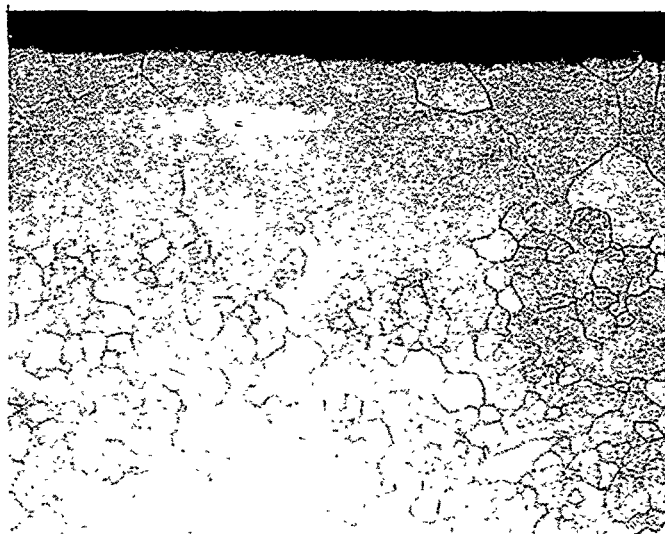


FIGURE 13 (Left) - SECTION FROM THE BOILING ZONE

Murakami's Reagent

133X

FIGURE 13 (Right) - SECTION FROM THE CONDENSING REGION

266X

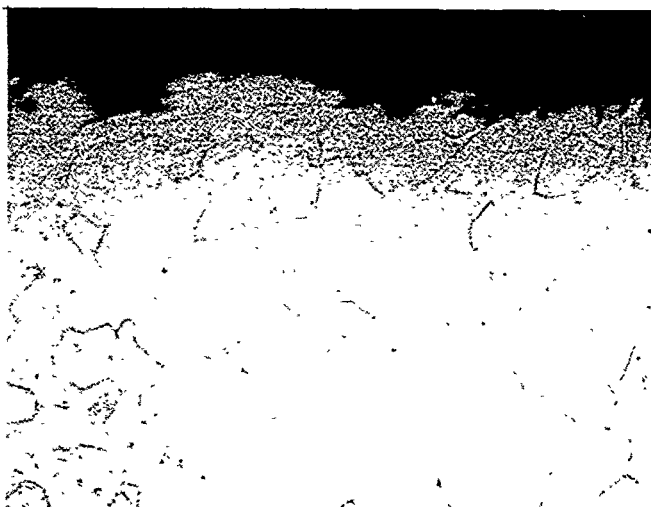
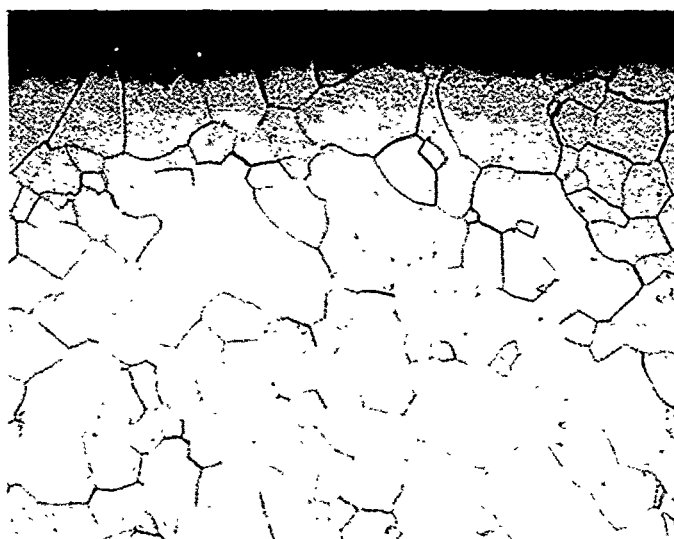


FIGURE 14 (Left) - INTERFACE REGION FROM A 2100°F 1000 HR TEST CAPSULE

266X

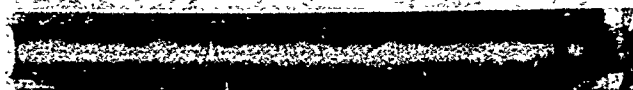


FIGURE 15 - Ta-10W CAPSULE EXPOSED 528 HOURS
TO BOILING (2100°F) CONDENSING CESIUM

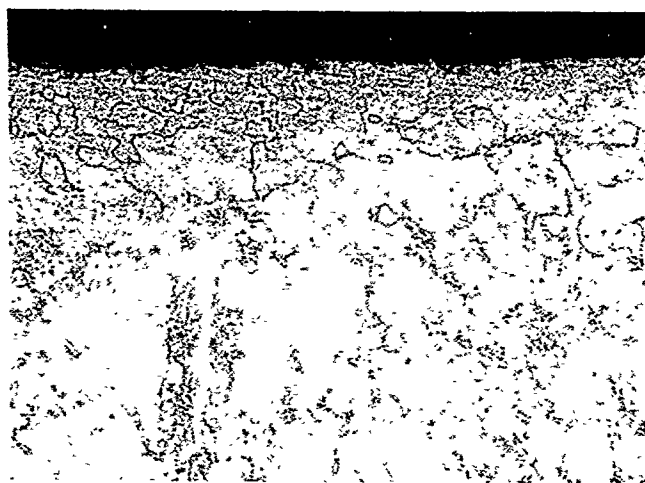


FIGURE 16 - BOILING ZONE OF Ta-10W CAPSULE
Etchant: Lactic-Nitric-HF 266X

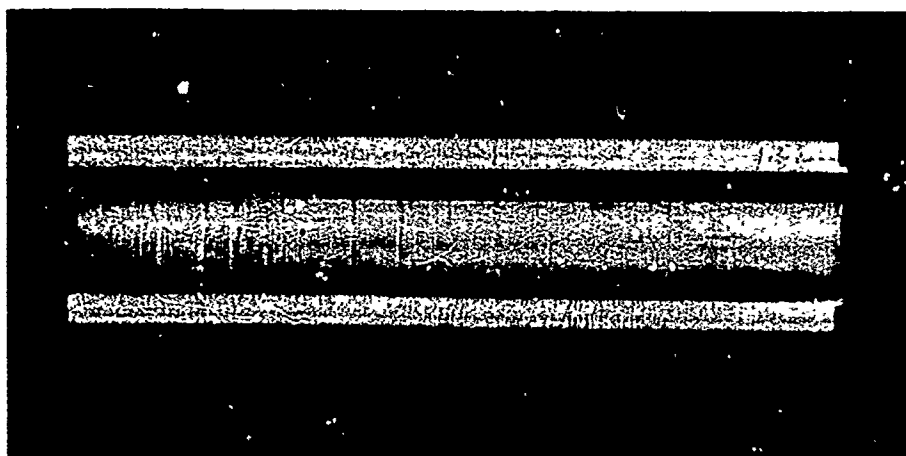


FIGURE 17 - FS-85 CAPSULE EXPOSED 817 HOURS TO RE-
FLUXING CESIUM. THE BOILING RING WAS LOCATED ~ 3cm
FROM THE LEFT END OF THE SAMPLE WHILE THE RIGHT SIDE
WAS EXPOSED TO CONDENSING CESIUM VAPOR.

Cb-25Ta-12W-1/2Zr (FS-85)

One capsule of this alloy successfully completed 818 hours testing at 2100°F. The test was terminated due to a pressure increase which threatened completion of the test. A photograph (Figure 17) shows a portion of the capsule taken from the interface section. Examination showed no dissolution or hardness change in any part of the capsule. There was no precipitation or foreign metal present in the cesium. FS-85 appears to be the equal of Cb-1%Zr for cesium containment and is superior in terms of strength.

DISSIMILAR METAL TESTS

Mo-1/2Ti versus Zirconium

Results reported in reference 1 indicated that zirconium initially scavenges both carbon and oxygen from Mo-1/2%Ti, but that with prolonged exposure (725 hours), there is a reversal of flow of oxygen and carbon back to the Mo-1/2%Ti. Three capsules consisting of this dissimilar metal couple were heated at 2500°F for a nominal 100 hour period. In each capsule impurity had been intentionally added, one with oxygen, a second with carbon and a third with both carbon and oxygen.

The test capsules exposed during this period were of the same dimensions as those described in reference 1. Each capsule contained approximately 7 grams of cesium.

Table 3 shows the average oxygen and carbon contents of both the zirconium tab and the Mo-1/2%Ti capsule after exposure.

The properties of the Mo-1/2%Ti alloy were not significantly altered by exposure to pure cesium liquid and vapor at 2500°F in the presence of zirconium.¹ Very little corrosion was experienced and no mass transfer of metallic species could be detected. Softening and grain coarsening were experienced by both the molybdenum and the zirconium as would be expected during long time high temperature exposure. Grain growth is restricted to the surface in the molybdenum and is coincident with the disappearance of the carbide dispersion due to surface decarburization. This latter is the only significant effect in the Mo-1/2Ti/Cs/Zr couple.

Although the effects of pure cesium were negligible, additions of carbon and/or oxygen as contaminants, produced measurable changes, some of which were abnormal.

TABLE 3 - Mo-1/2Ti Vs Zr DISSIMILAR METAL TESTS (2500°F)

	<u>M5</u>	<u>M6</u>	<u>M7</u>	<u>As-Received</u>
Impurity Added	Carbon*	Oxygen**	Carbon + Oxygen***	
Test Duration, Hrs.	100	126	100	
Mo-1/2Ti, post-test analysis				
oxygen, ppm	153	453	600	53
carbon, ppm	131	180	27	256
Zr tab, post-test analysis				
oxygen, ppm	750	2125	500	790
carbon, ppm	1470	355	1025	15
Hardness (R_B)				
Mo-1/2Ti - liquid zone	85	36	80	86
Mo-1/2Ti - vapor zone	87	86	85	86
Zr	75	91	90	78

* carbon added as spectrographic grade of graphite equivalent to 920 ppm in the cesium.

** oxygen added as Cs_2O equivalent to 550 ppm O in the cesium.

*** carbon (260 ppm) and oxygen (380 ppm) added.

Carbon was added as spectrographically pure carbon in an amount equivalent to 900 ppm. The major portion was gettered by the zirconium. The molybdenum was insensitive to the addition in terms of hardness and corrosion. Grain growth effects were minimized, due to a slow down in decarburization rate. The zirconium shows the effect of the carbon addition in the form of a surface carbide. Strangely, the zirconium appears to lose oxygen in the presence of high carbon cesium.

Oxygen, added as Cs_2O , in an amount equivalent to 550 ppm, did effect the molybdenum alloy. Even though the major portion of the addition was gettered by the zirconium as was the carbon, the molybdenum showed appreciable oxygen pickup, an absence of grain coarsening (Fig 18), a low decarburization rate, and a significant softening (R_B 86 to 36). These observances are difficult to explain. Conversion from a carbide to an oxide dispersion is possible and the finer oxide would show better control of grain growth and less effects on low temperature hardness. The oxygen gave little detectable effect in the zirconium. A slight hardness increase was observed, but it is probable that the hardening by oxygen was balanced by the annealing effects of time at temperature.

Concurrent additions of carbon and oxygen produced effects somewhat different from those of separate additions. Carbon was gettered by the zirconium in preference over oxygen; in fact, the loss of oxygen previously noted occurred in this test also. The molybdenum showed strong oxygen pickup with a decarburization rate higher than normal evidenced by the grain growth on the surface (Fig 19). No hardness change was observed but non-uniform surface attack was accelerated.

Of the several dissimilar metal couples investigated in this program, the Mo-1/2%Ti-Zr couple was the only one which did not exhibit measurable metallic mass transfer upon exposure to cesium at 2500°F. Weight gains of the zirconium tabs were usually less than 0.3% and electron microprobe analysis of the capsule exposed 725 hours at 2500°F supported the absence of metallic mass transfer.

Non-metallic scavenging by both metals produced some interesting effects. Mo-1/2%Ti experienced decarburization in almost all cases with the zirconium absorbing that amount and more from the cesium. The decarburization gave rise to some surface grain coarsening. Both metals tended to scavenge oxygen from the cesium. When oxygen and carbon levels were low, little if any corrosion was observed and hardness had a tendency to decrease in the molybdenum and zirconium. High levels of contaminants

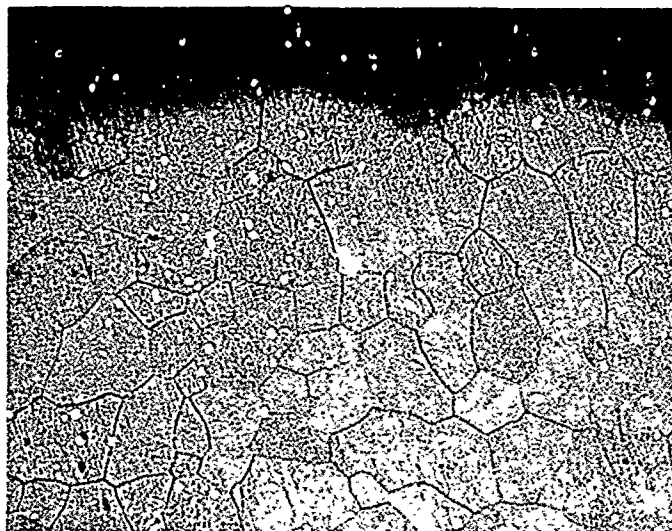


FIGURE 18 - Mc-1/2Ti EXPOSED 126 HOURS (2500°F)
TO CESIUM WITH ADDED OXYGEN 266X

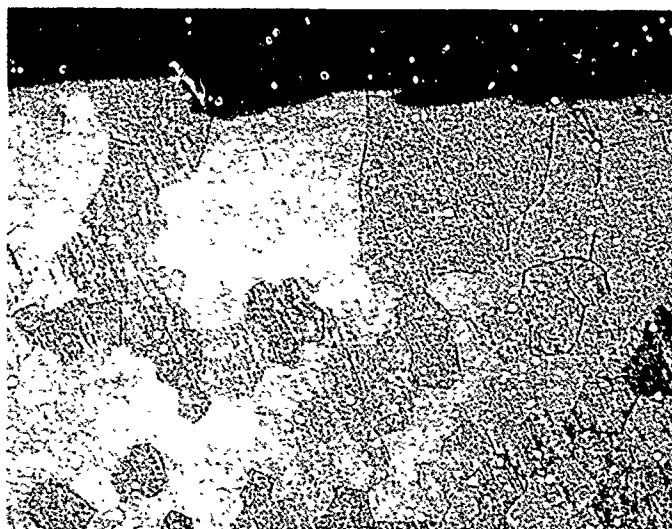


FIGURE 19 - Mc-1/2Ti EXPOSED 100 HOURS (2500°F)
TO CESIUM WITH ADDED CARBON AND OXYGEN 133X

altered results. Zirconium gettered the major portion of either oxygen or carbon additions, but showed a preference for carbon, absorbing only carbon when both carbon and oxygen were added. The molybdenum is basically insensitive to carbon additions but reacts to oxygen showing a tendency to extreme softening and increased corrosion. The former occurred in high oxygen only and the latter in high oxygen-carbon combination. The inconsistencies of the effects is puzzling, and may be the result of analysis of bulk samples which can only be considered as indicators since most effects are surface phenomena not truly represented by the bulk sample.

TD-Nickel Couples with Mo-1/2%Ti and Cb-1%Zr

TD-Nickel has been coupled with both Cb-1%Zr and Mo-1/2%Ti in dissimilar metal tests to determine the feasibility of using this superalloy with liquid cesium. In each case there was considerable mass transfer and diffusion of columbium and molybdenum through the thoriated nickel matrix. A coating of the refractory metal was found on the TD-Nickel and large cavities (~ 0.1 mm) were formed just beneath the interface (Fig 20).

When TD-Nickel was coupled with Cb-1%Zr, it was found that, although there was a considerable amount of columbium within the TD-Nickel, hardness did not change nor was there any appreciable change in the appearance of the metal under microscopic examination. The columbium appeared only as a coating on the TD-Nickel. Electron microprobe analyses of samples from this dissimilar metal couple showed that nickel diffuses into the Cb-1%Zr tab to a depth of approximately 8μ . The concentration of nickel within this narrow band was 5 wt % which is the reported solid solubility.⁵ The transfer of nickel was small for the tab experience a 7.93% weight loss.

Transfer of columbium to the TD-Nickel capsule created a zone approximately 35μ deep on the inside surface of the capsule where the columbium concentration was measured at 25.3 wt %. This composition is near the peritectic reported by Hansen⁶ (24 wt %) and it appears that the diffusion layer continues to increase in concentration until this composition is attained before continuing. The columbium concentration falls precipitously between 35 and 60μ , after which there is a gradual decrease. A plot of columbium concentration as a function of distance into the matrix appears in Figure 21. The overall mass transfer rate of columbium through the cesium and into the TD-Nickel capsule wall occurred at a rate of 8.9×10^{-5} g/cm²/hr. The influence of factors such as the surface area on the mass ratios of the metals cannot be assessed.

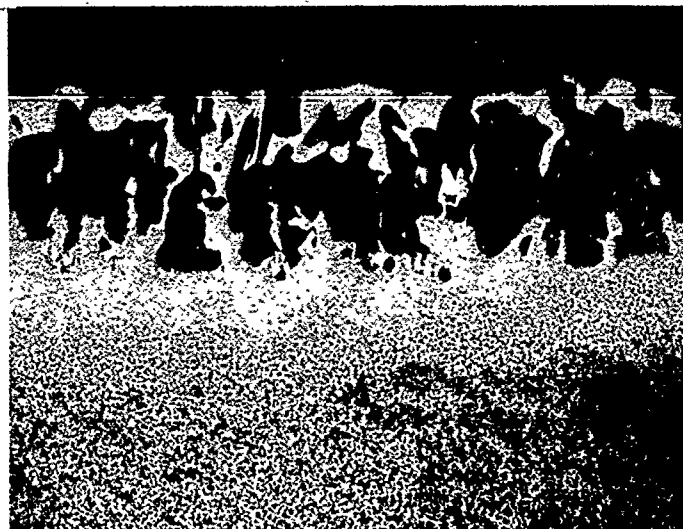


FIGURE 20 - TD-NICKEL CAPSULE FROM TD-Ni/Cs/Cb-1Zr COUPLE
EXPOSED TO LIQUID CESIUM AT 1800°F FOR 500 HOURS
Etchant: Aqua Regia 266X

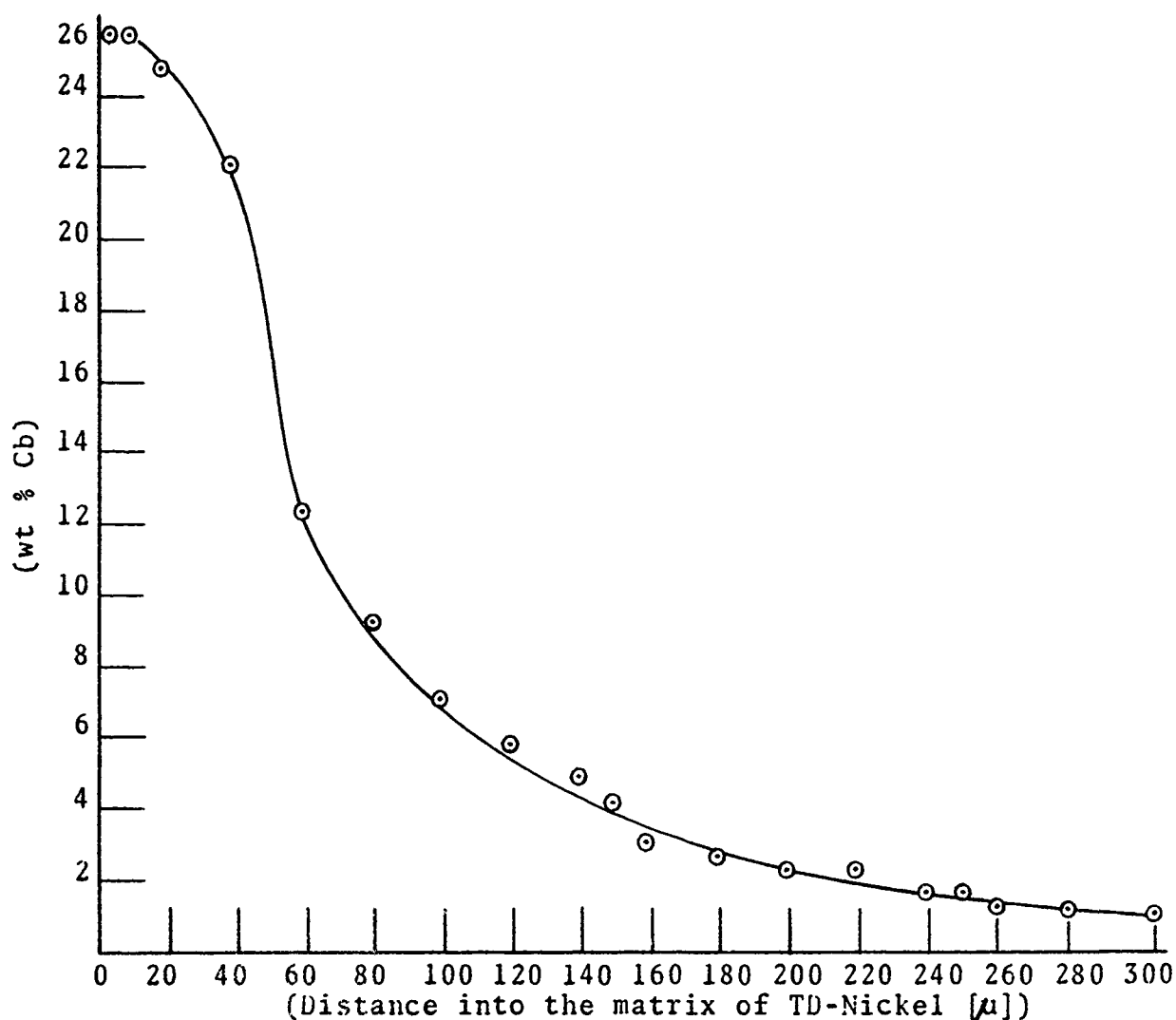


FIGURE 21 - Cb PROFILE IN TD-NICKEL DISSIMILAR METAL TEST

To further define the mass transfer occurring in this dissimilar metal system, a capsule was fabricated from Cb-1%Zr and tabs of nickel and TD-Nickel placed in the liquid cesium. This test was conducted at 1800°F for 500 hours exactly as the previous test with the exception that it was performed in vacuum. The mass transfer of nickel from the tabs to the Cb-1%Zr capsule was approximately one-tenth that observed when the relative masses were reversed. Overall mass transfer in this system was calculated from weight loss and microprobe analyses as 6.5×10^{-6} g/cm²/hr with approximately 75% of the total nickel transferred coming from the pure nickel tab.

The transfer of nickel to the Cb-1%Zr capsule was measured primarily by the electron microprobe. The nickel and columbium line profiles are shown in Figure 22. The high nickel end of the trace is not representative and is probably either a polishing or etching artifact. Adjacent to this there is evidence of an intermetallic compound corresponding to the composition CbNi (30-35 w/o Ni).

Other physical changes observed in the Cb-1%Zr versus both TD and pure nickel were similar to those of the previous tests where TD-Nickel was used as the capsule material. Hardness decreased in the Cb-1%Zr from R_B-45 to R_B-20 and in the nickel tab, from R_B-50 to R_B-25. Grain growth was observed in samples of both Cb-1%Zr and nickel, as can be seen in Figures 23 and 24. Both the TD-Nickel and pure nickel were decarburized from initial carbon contents of 45 ppm for TD-Nickel and 350 ppm for the nickel tab.

In a TD-Ni/Cs/Mo-1/2Ti couple, the results were similar with the Cb-1%Zr couple. There was little hardness change for either metal. TD-Nickel showed very little gettering of oxygen from liquid cesium by itself but did scavenge oxygen when coupled to Mo-1/2%Ti.

Mass transfer of metallic species proceeds in both directions. Nickel transfer to the molybdenum is the lesser of the two effects. Nickel shows as a band 20 μ wide on the molybdenum surface containing 35 wt % nickel. Microprobe analysis does not conform to the solid solubility of nickel in molybdenum as reported in literature¹, but corresponds with the data given for the solubility of molybdenum in nickel at these temperatures^{6,7} (34 wt % at 2010°F and 30 wt % at 1634°F).

The transfer of molybdenum to the TD-Nickel capsule accounts for the major portion of mass transfer in this system. In a 500 hour exposure at 1800°F the Mo-1/2%Ti insert experienced a weight loss of 9.43% while, in the same test conditions, a Cb-1%Zr tab experienced a weight loss of 7.93%. Mass transfer of molybdenum to the TD-Nickel capsule through liquid cesium occurred at a rate of 1.7×10^{-4} g/cm²/hr.

FIGURE 22 - Cb and Ni MICROPROBE
LINE PROFILES ON Cb-1Zr CAPSULE
FROM Ni AND TD-Ni/Cs/Cb-1Zr
COUPLE EXPOSED AT 1800°F FOR
500 HOURS

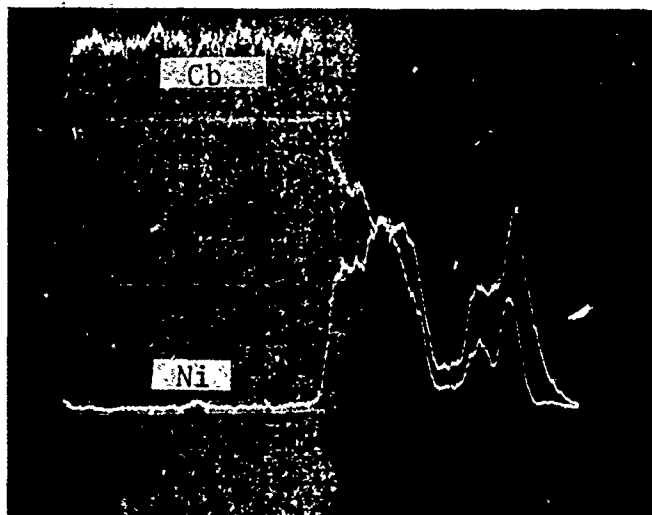


FIGURE 23 - Cb-1Zr CAPSULE FROM
Ni AND TD-Ni/Cs/Cb-1Zr COUPLE
EXPOSED AT 1800°F FOR 500 HOURS
Etchant: duPont's 266X

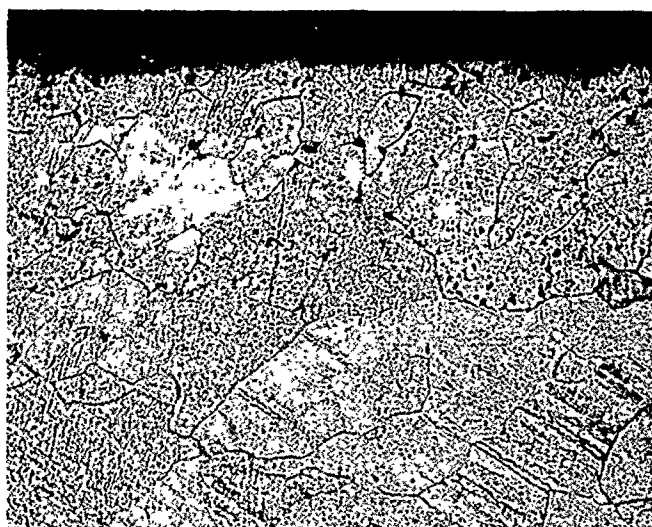


FIGURE 24 - NICKEL TAB FROM
Cb-1Zr CAPSULE SHOWN IN FIG 23
Etchant: Aqua Regia 266X



A plot of the transferred molybdenum concentration in the TD-Nickel matrix is shown in Figure 25. The molybdenum concentration was found to be approximately 10 wt % at the surface of the TD-Nickel which falls quite short of the reported solubility of molybdenum in nickel at these temperatures.^{6,7} The concentration of molybdenum gradually decreases until a depth of 100 μ where it remains constant at 1.4% for a depth of 130 μ . The molybdenum rich coating on the TD-Nickel capsule is seen in Figure 26.

Haynes-25/Cb-1%Zr Couple

Several capsules comprising this couple were tested and the results are described in reference 1. A capsule comprising the H-25/Cb-1Zr couple was prepared during this report period. Cesium containing both oxygen and carbon impurity (equivalent to 580 ppm C and 175 ppm O) was added to the Haynes-25 capsule and the sealed capsule was heated at 1800°F for 100 hours.

Post-test microstructures of the two structural metal components of the couple are shown in Figures 27 and 28. The Haynes-25 alloy had been attacked intergranularly and the microstructure of the Cb-1Zr tab had been grossly altered due to absorption of the metallic components of Haynes-25 alloy. The Cb-1Zr had experienced a weight gain of 27 percent, showing considerably greater mass transfer than in capsules of this couple tested previously.

Haynes-25/Mo-1/2Ti Couple

A H-25/Mo-1/2Ti dissimilar metal capsule was tested with pure cesium at 1800°F for 100 hours. Representative post-test microstructures are seen in Figures 29 and 30.

Mass transfer of metallic constituents across this couple was not as extensive as in the case of the H-25/Cb-1Zr couple. Decarburization of the Haynes-25 was slight and age hardening, at least in the portion in contact with liquid cesium, was as experienced with the Cb-1Zr couple. After 100 hours at 1800°F, the molybdenum showed a very slight increase in carbon (+38 ppm) and concurrent slight loss of oxygen (-20 ppm). Metal dissolution was small and equivalent to that experienced in the Haynes-25/Cb-1Zr couple where pure cesium was used.

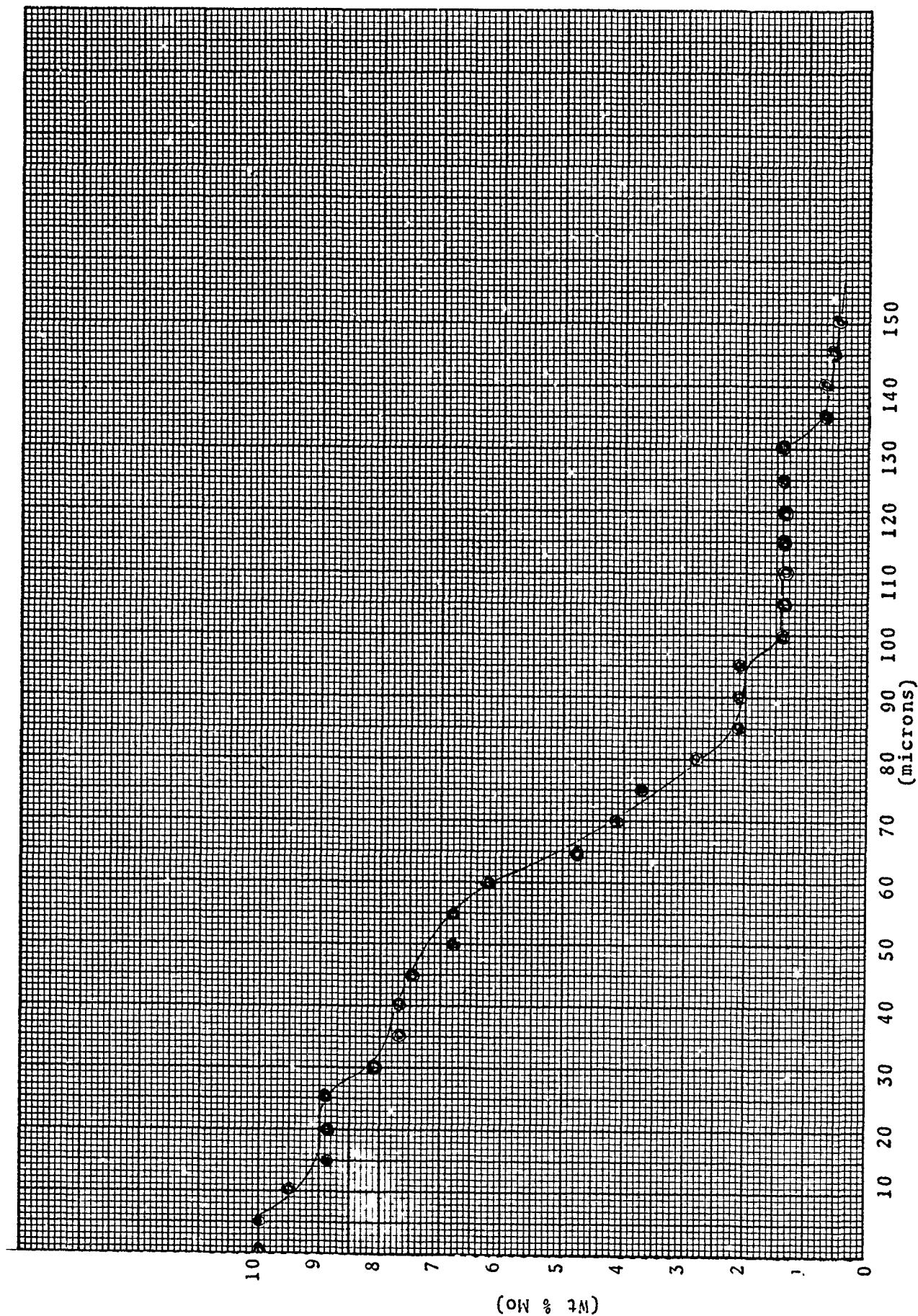


FIGURE 25 - MOLYBDENUM CONCENTRATION VS PENETRATION INTO TD-NICKEL

FIGURE 26 - TD-Ni CAPSULE FROM TD-Ni/
Cs/Mo-1/2Ti COUPLE EXPOSED TO 1800°F
FOR 500 HOURS
Etchant: Aqua Regia

266X

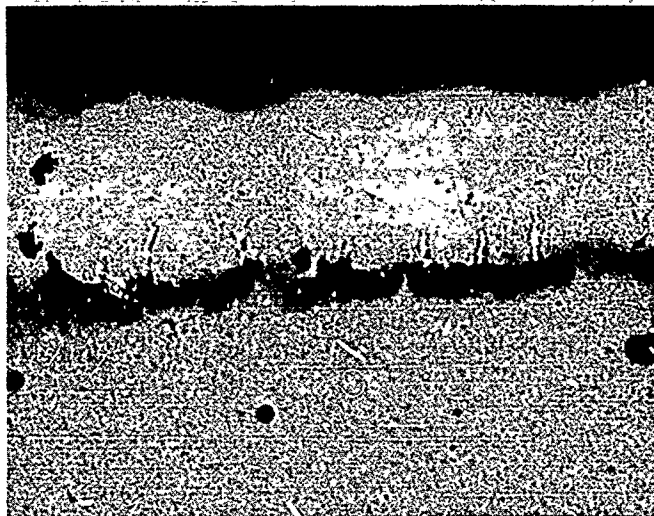


FIGURE 27 - HAYNES-25 CAPSULE FROM
H-25/Cb-1Zr COUPLE EXPOSED TO 1800°F
(100 Hrs) CESIUM CONTAINING CARBON
AND OXYGEN
Etchant: HCl-H₂O₂

266X

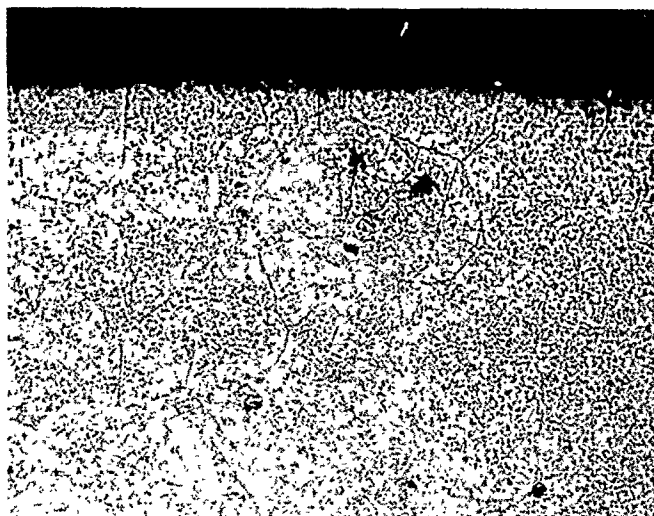
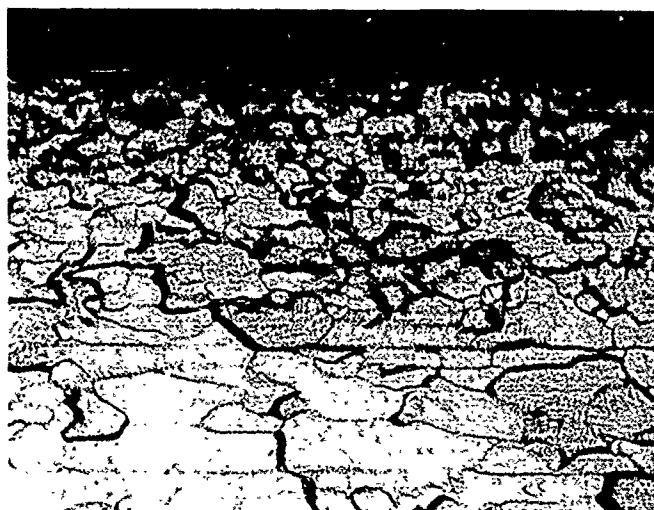


FIGURE 28 - Cb-1Zr TAB FROM COUPLE
SHOWN IN FIG 27
Etchant: duPont's

266X



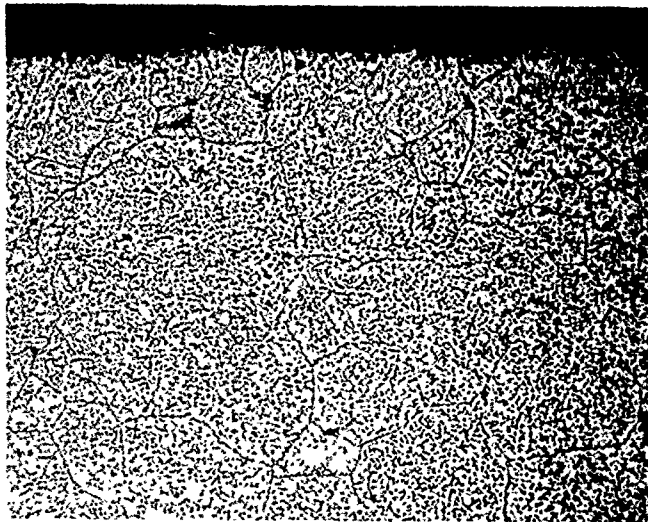


FIGURE 29 - HAYNES-25 CAPSULE FROM H-25/Cs/Mo-1/2Ti
COUPLE EXPOSED TO 1800°F FOR 100 HOURS
Etchant: HCl-H₂O₂ 266X

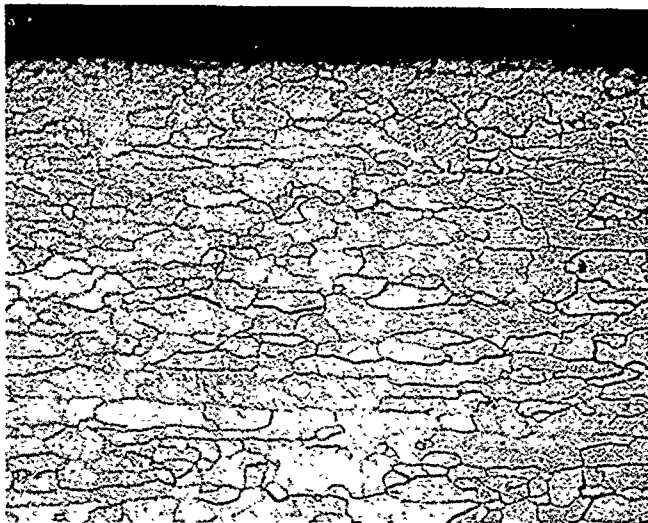


FIGURE 30 - Mo-1/2Ti TAB FROM H-25/Cs/Mo-1/2Ti COUPLE
EXPOSED TO 1800°F FOR 100 HOURS
Etchant: Murakami's 266X

Cb-1Zr/Mo-1/2Ti Couple

The results of a Cb-1Zr/Cs/Mo-1/2Ti dissimilar metal capsule test are described in reference 1. Mass transfer of columbium and zirconium to molybdenum had occurred in 500 hours at 2500°F while the Mo-1/2Ti was decarburized by Cb-1Zr. Subsequent analysis in this report period of a 10 and 1000 hour dissimilar metal test have verified the transfer. Quantitative microprobe scans revealed columbium rich (50-70 weight percent) surface layers up to 0.0005 in. thick.

Attempts were made to determine the effect of carbon or oxygen additions to cesium on mass transfer in the Cb-1Zr/Mo-1/2Ti couple. Two Cb-1Zr capsules with Mo-1/2Ti tabs containing cesium (to which carbon had been added) failed shortly after (14 and 14.5 hours) attaining a test temperature of 2500°F. Embrittlement of the Cb-1Zr by carbon are thought to be responsible for the failure.

One Cb-1Zr capsule containing cesium with added oxygen impurity (150 ppm) was heated at 2500°F for 100 hours. The oxygen content of a section of the Cb-1Zr adjacent to the liquid region had increased from an as-received value of 192 to 621 ppm. No change was noted in the carbon content.

Two Cb-1Zr/Mo-1/2Ti dissimilar metal capsules were prepared, where oxygen as Cs₂O had been added to the cesium. Oxygen levels in the two capsules were 100 and 190 ppm oxygen. Only the capsule with the lower oxygen level survived a 100 hour exposure at 2500°F without failure.

Analysis of the Cb-1Zr capsule in the surviving 100 hour test showed an increase in oxygen from 192 to 1385 ppm, and an increase in carbon from 69 to 132 ppm. The Mo-1/2Ti tab had been decarburized from an as-received value of 186 to 68 ppm. Microprobe analysis of this couple was performed, and metallic mass transfer could not be detected. Adsorption of oxygen by Cb-1Zr appears to have been responsible for minimizing the dissolution of metallic species, since with low oxygen cesium, metallic mass transfer was measurable.

Mo-1/2Ti was decarburized in each of the Mo-1/2Ti tests performed to date, with an attendant surface grain coarsening. The carbon is transferred to Cb-1Zr causing severe local embrittlement.

SUMMARY AND CONCLUSIONS

The solubility of carbon in cesium has been determined from 600°F (12 ppm) to 1200°F (53 ppm). The presence of carbon did not alter the freezing point of pure cesium, indicating that this element might not alter oxygen analysis by the freezing point method.

The quantity of solubilized transition metals in high temperature liquid cesium was measured. The solubility of the refractory metals columbium and molybdenum in cesium appear to be approximately 10-20 ppm at 2500°F. The tip capsule sampling technique utilized for solubility studies does not appear to be capable of producing kinetic dissolution data.

Boiling-refluxing studies performed at 1800°F have shown that Haynes-25 is more resistant to dissolution attack than is TD-Nickel. Boiling-refluxing studies with refractory base alloys at 2100°F indicate that columbium and tantalum base alloys are more resistant to dissolution attack than is molybdenum. Dissolutive attack of Mo-1/2Ti was not marked at 2100°F, but was appreciable at 2500°F.

The mass transfer of metallic and interstitial elements in dissimilar metal systems containing cesium under isothermal conditions was studied. Many such tests were performed where carbon and oxygen were added to the cesium. Of the several dissimilar metal couples investigated, the Mo-1/2Ti vs zirconium (2500°F test temperature) was the only one where metallic mass transfer was immeasurable. Columbium and molybdenum were found to transfer through 1800°F cesium to metallic nickel, where the driving force is the formation of stable nickel base inter-metallic compounds.

Mass transfer in the Haynes-25/Mo-1/2Ti system was less extensive than in the case of the Haynes-25/Cb-12r couple.

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