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Fifth Quarterly Progress Report
September, October and November 1963

to

Aeronautical Systems Division
Wright-Patterson Air Force Base
Ohio

FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

F. Tepper
J. Greer

13 December 1963

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MSA Research Corporation

Subsidiary of Mine Safety Appliances Company

Callery, Pennsylvania

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⑩ by F. Tepper and
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Law
MSA RESEARCH CORPORATION
Callery, Pennsylvania

ABSTRACT

A device for the determination of the solubility of carbon in cesium is presently being constructed. Solubility studies of the alloys, Haynes-25, niobium-1% zirconium and molybdenum-0.5% titanium in liquid cesium are continuing and preliminary rates are given for Haynes-25. Investigation of the mechanisms associated with attack of liquid cesium on these alloys and TD-Nickel continue with the utilization of cesium containing carbon and oxygen additions.

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Fifth Quarterly Progress Report
on
FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

F. Tepper
J. Greer

INTRODUCTION

This is the fifth quarterly progress report on the ASD program "Factors Affecting the Compatibility of Liquid Cesium With Containment Metals" describing the work completed during the last quarter and correlating data obtained previously. A summary report, describing the work during the fourth quarter and summarizing the effort of the first year, has been released upon approval of the project engineer at ASD, Dayton, Ohio.

ANALYSIS OF CESIUM

A method for determining oxygen concentration in cesium by means of the freezing point depression has been investigated at MSAR. According to Brauer¹ the Cs-O₂ system has a eutectic at 10,000 ppm O₂ with a freezing point at -2°C. Freezing points obtained with measured oxygen additions give a linear relationship up to 500 ppm O₂ with a depression of 0.24°C per 100 ppm O₂. Absolute temperature measurements were made with a calibrated Beckmann thermometer and a Sargent thermometric bridge which are capable of determining the oxygen concentration in cesium with an accuracy of ± 5 ppm.

A cesium container with a thermometer well added was analyzed by this method after an oxygen-spike calculated to be 100 ppm was added. The oxygen concentration obtained from the freezing point depression was 110 ppm. This cesium is to be used in place of the Cs₂O-spikes to pure cesium in the future tests.

1. Brauer, Zeit. Anorg. Chem. 248, 1941.

DETERMINATION OF THE SOLUBILITY OF CARBON IN CESIUM

Carbon Solubility Study

Fig 1 shows a schematic diagram of an apparatus which will be used for the carbon solubility study. The apparatus consists of a 20 in. long x 3 in. diameter vessel in which the solubility will be studied and a 3 in. long x 3 in. diameter vessel for freezing point measurements. The vessel will be charged with ~ 6 lb of cesium and heated to 1200°F. A portion of the charge will be transferred to the freezing point apparatus and the oxygen content will be determined from the freezing point measurement. Samples will be extracted from the vessel and analyzed for carbon content.

Carbon is analyzed by a dry oxidation technique with a minimum limit of detection of 10 ppm and a sensitivity of ± 5 ppm. Procedures for this method include:

1. Extraction of the sample at temperature
2. Dissolution of the sample at 0°C with carbon-free water
3. Neutralization and evaporation to dryness
4. Oxidation of the dried salt with purified oxygen
5. Collection of the released CO₂ in a liquid nitrogen cooled trap
6. Measurement of CO₂ by mass spectrometry.

After the initial oxygen and carbon levels are established, carbon will be added to the system in the form of spectrographically pure carbon rods. Carbon concentration will be determined at 300, 600, 900 and 1200°F. Freezing point determinations will be made to determine if dissolved carbon in cesium has any effect on the freezing point. Finally the oxygen content will be varied to determine if oxygen has an effect on carbon solubility in cesium.

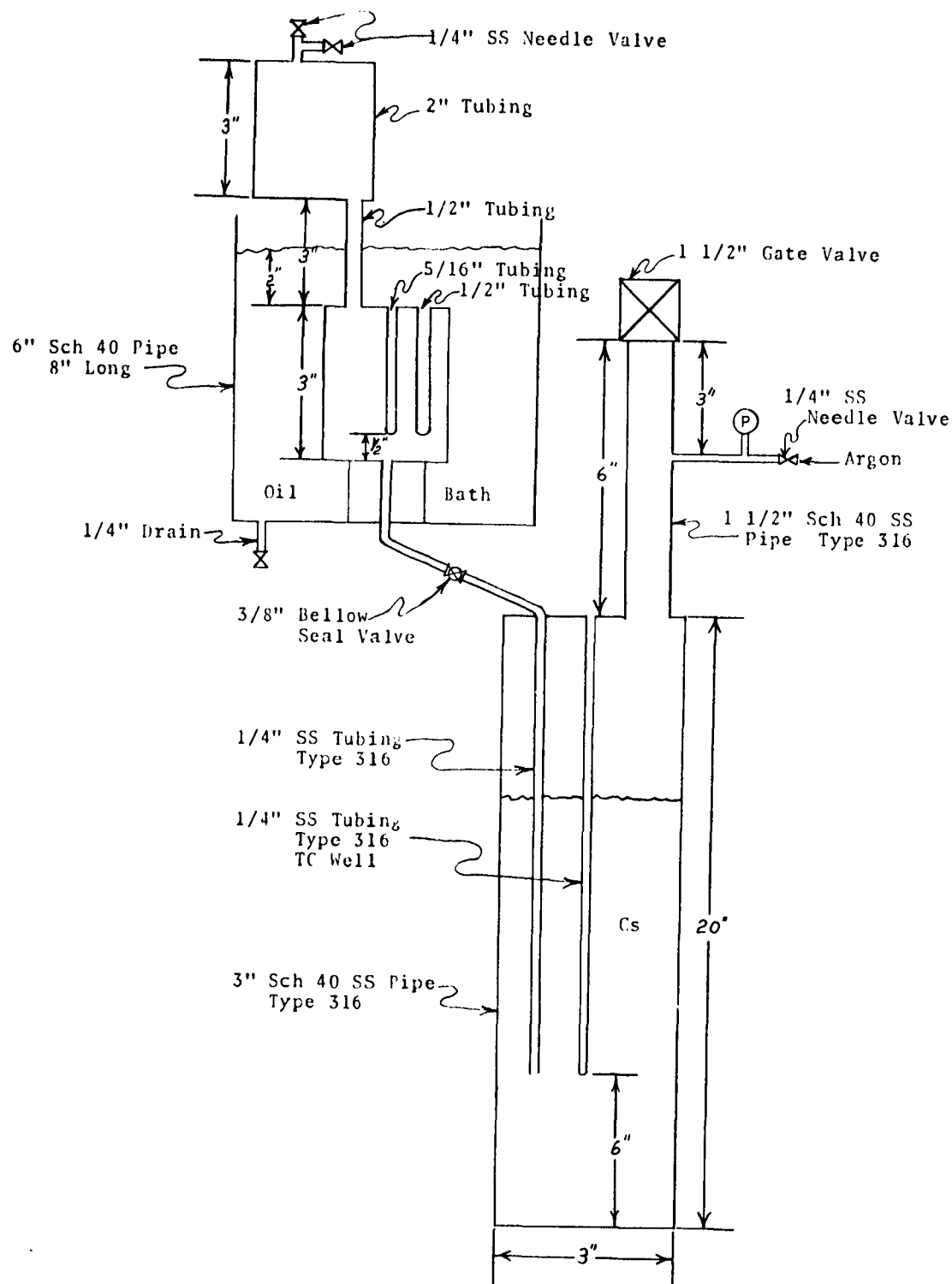


FIG 1 - SCHEMATIC DIAGRAM OF CARBON SOLUBILITY APPARATUS

SOLUTION STUDIES

Several tests have been done during this quarter in an effort to establish kinetics of solution, influence of dissimilar metal and "inert" material sample crucibles, and the saturation concentrations of the various constituents of the three alloys under investigation in this program. Identical solubilities have been measured with samples of Haynes-25 alloy and Mo-0.5%Ti equilibrated for as little as one half hour; essentially establishing the saturated solubilities but indicating severe difficulties in obtaining kinetic data using the present sampling technique. Comparison of the solubilities of Haynes-25 constituents measured from samples taken with metallic crucibles as opposed to the high purity alumina crucibles has shown that there are no differences observed when exposure at test temperature is short, but analyses diverge as equilibration time is increased. Analyses of samples from the refractory metal alloys taken with the high purity alumina crucibles show interaction varies in the order Mo-0.5%Ti < Nb-1%Zr. A spectrographic analysis of a high purity alumina crucible exposed 100 hrs to cesium vapor in a Nb-1%Zr capsule has been undertaken to establish the mode of the interaction.

Mo-0.5%Ti

Two samples, taken at 100 hrs and 14 hrs equilibration time, have shown the saturated solubility of molybdenum to be 20 ppm (± 7 ppm). This agrees with a sample previously taken in a 10 hr test using an alumina sampling crucible. The saturated solubility of titanium in the same two samples is 125 ppm (± 25 ppm). The preferential dissolution of titanium at 1371°C has not been explained as yet.

Establishing the rate of dissolution of the alloy constituents requires that a saturation time be assumed with the present limited data. Two more tests have been completed and samples taken after 45 minutes and 5 minutes equilibration times to more definitely establish the time necessary for saturation. Analysis of the cesium has not been completed but should provide sufficient data for establishing the feasibility of determining solution kinetics for this alloy.

Haynes-25 Alloy

A comparison of the results obtained in the solution studies with Haynes-25 is presented in Table 1. The test incorporating 1000 hrs equilibration time with an alumina sampling crucible shows great discrepancies with the others of this series.

TABLE 1 - ANALYZED SOLUBILITIES OF THE CONSTITUENTS
IN HAYNES-25 ALLOY

Capsule	H2	H3	H4	H5
Equilibration Time (hrs)	10	1000	100	0.5
Sampling Crucible	Al ₂ O ₃	Al ₂ O ₃	Mo-0.5%Ti	Mo-0.5%Ti
Metallic Content (ppm)				
Co	100	10	100	100
Cr	15	<5	50	50
Ni	15	<5	50	40
Fe	7	<1	30	30
Mn	5	<1	8	10

If it is assumed that saturation concentration is achieved upon 30 minutes equilibration time, a rate of dissolution of the major constituents may be calculated. The calculated rate for cobalt is 2.25×10^{-5} g/cm² hr and the others are respectively: Cr: 1.1×10^{-5} g/cm² hr, Ni: 1.0×10^{-5} g/cm² hr, Fe: 6.7×10^{-6} g/cm² hr, Mn: 2.0×10^{-6} g/cm² hr. The validity of these rate constants is very precarious not only in the assumption of the time for saturation but also in that there is no solute-solute interaction; no diffusion of the solute into the sampling crucible; and no adverse effects resulting from the long heating and cooling times.

Another test is planned in the solution studies of Haynes-25 alloy with a sample to be taken with an equilibration time less than 30 minutes.

Nb-1%Zr

Only three capsules have been successfully completed in the solution studies of Nb-1%Zr alloy. Previous studies incorporating the alumina sampling crucible created problems due to the low stress-rupture properties of this alloy. The change to Mo-0.5%Ti crucibles has resulted in two successful tests but has added serious problems in that niobium has been found to diffuse slightly into Mo-0.5%Ti. Microprobe analyses of samples from the dissimilar metals portion of this program have shown that diffusion is only slight and concentrated on the surface in exposures up to 100 hrs. Acid etching of the sampling crucibles should eliminate this problem as long as the precipitation remains a surface phenomenon.

Samples taken in the solution studies of this alloy indicate that saturated solubility of the constituents may not occur in 10 hr. The tests completed to date have had as their main objective the establishment of the time necessary to achieve equilibrium solubility. Variations in the metallic concentrations of samples taken after 100 hrs and 10 hrs indicate that equilibrium is achieved between these two times.

Two more tests are planned in the immediate future in which samples will be taken which will augment these tests. These, in conjunction with the tests already completed, should provide sufficient data for the evaluation of the sampling technique and the possibility of calculating solution rate constants.

DISSIMILAR METAL STUDIES

TD-Nickel vs Nb-1%Zr

TD-Nickel has been coupled with Nb-1%Zr and a capsule exposed 500 hrs at 1800°F. The capsule wall has cavities approximately 0.1 mm deep in the area exposed to liquid cesium (Fig 2) which have been shown by microprobe analysis to be the result of niobium precipitation on this surface. Several diffusion zones were apparent in the wall of the capsule when viewed under low magnification which may be due to ThO₂ diffusion, but these are not detectable by microprobe.

The presence of the niobium coating on the capsule wall does not significantly change the physical properties of the nickel capsule. Macrohardness tests show that this capsule, similar to a control capsule containing no Nb-1%Zr tab, experienced no changes in hardness in either the liquid or vapor zones. Precipitation of the transition metals present in the cesium after this test by cuferon reagent reveals less than 100 ppm of the metallic constituents soluble in this system.

The Nb-1%Zr insert placed inside the capsule experienced an 11% weight loss and considerable softening (from RB-37 to RB-20). The tab had a thin (~3 μ) precipitation layer which appeared under the microscope to be the same as the NbN identified in the studies of the Haynes-25 vs Nb-1%Zr couple. X-ray diffraction was unable to identify this precipitate and both niobium and nickel were found to be present in this zone with the microprobe. There is also a zone beneath the precipitate extending in approximately 8 μ in which the concentration of nickel is considerably higher than measured on the edge. This corresponds roughly to the diffusion of cobalt from Haynes-25 alloy into the Nb-1%Zr tab.

Only qualitative work has been done in the microprobe analyses of this couple at the present time. These tests have indicated several areas in which quantitative analysis may provide useful information concerning the diffusion of the metals within this system. Analysis of this couple will be continued during the next quarter.

Nb-1%Zr Vs Mo-0.5%Ti

Oxygen-spiked cesium has been charged to two Nb-1%Zr capsules to determine the influence of oxygen in the corrosion of this alloy



FIG 2 - TD-NICKEL CAPSULE EXPOSED 500 HRS (1800°F) TO
LIQUID CESIUM WITH A Cb-1%Zr TAB
Etchant: Aqua Regia 266X

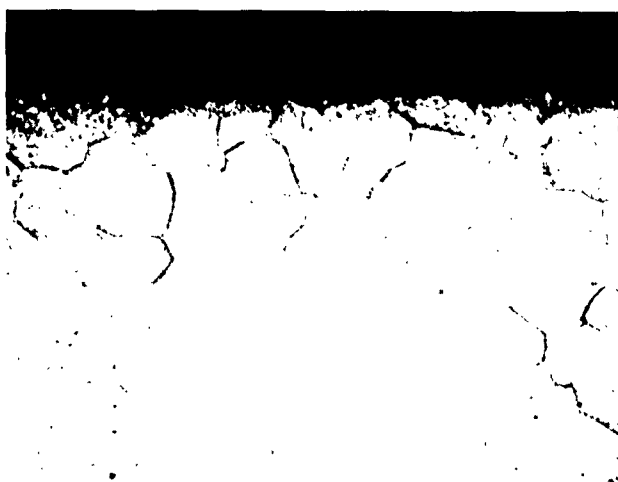


FIG 3 - Nb-1%Zr CAPSULE EXPOSED 100 HRS (2500°F) TO CESIUM
CONTAINING 150 ppm O₂
Etchant: Dupont's etchant 266X

by cesium. Only one capsule successfully completed a 100 hr test at 2500°F and it appears that an oxygen content in the cesium of 5 µg oxygen per gram Nb-1%Zr will sufficiently reduce the stress-rupture strength of this alloy as to make it undesirable for extended containment applications.

The first capsule contained cesium spiked to 150 ppm oxygen content but had no Mo-0.5%Ti insert. It successfully completed a 100 hr test but experienced considerable softening especially in the areas exposed to cesium vapor. The alloy decreased 15 RB hardness units where exposed to liquid cesium and 20 RB hardness units where exposed to cesium vapor.

Metallographic examination of the capsule reveals intergranular penetration along the inside (Fig 3). Although the strength of the alloy has been decreased and oxygen penetrates well into the matrix, there is no evidence of gross dissolution.

A second capsule was charged with cesium containing 190 ppm oxygen and also contained a Mo-0.5%Ti tab. This capsule ruptured in the section exposed to the vapor phase after 15 hrs exposure at 2500°F. The additions of both carbon and oxygen to the cesium contained in Nb-1%Zr capsules has repeatedly reduced the strength of this alloy enough to cause rupture after brief exposure.

Mo-0.5%Ti Vs Zr

During this quarter the influence of both carbon and oxygen in the corrosion on the Mo-0.5%Ti vs zirconium dissimilar metals couple have been observed. The influence of oxygen alone and the combined effects on these metals were studied in two 150 hr tests. These elements do not have analogous deteriorating effects on Mo-0.5%Ti vs zirconium couple as compared with the Nb-1%Zr vs Mo-0.5%Ti couple.

Cesium containing 550 ppm oxygen was charged to a Mo-0.5%Ti capsule also containing a zirconium tab and the capsule exposed 127 hrs at 2500°F. The effect of the oxygen addition was apparent in the Mo-0.5%Ti alloy where it was exposed to liquid cesium. The hardness in this area decreased 50 RB hardness units while the hardness of the area exposed only to vapor remained constant. The zirconium tab from this capsule also had no change in macrohardness and experienced only a 0.2% weight gain.

Samples taken from previous capsules in this series which were exposed to ultra pure cesium have experienced no changes in hardness where exposed to the liquid or the vapor phase. Massive

grain growth has been observed with a zone $\sim 150 \mu$ from the surface exposed to liquid cesium in the capsules exposed to ultra pure cesium. With the addition of 550 ppm oxygen this capsule has but very slight grain growth as seen in Fig 4. Since MoO_3 sublimates below test temperature, it is probable that this had decreased the grain growth in surfaces exposed to liquid cesium where oxygen content is highest.

The zirconium tab from this capsule underwent massive grain growth and a slight coating is evidenced in microscopic examination. The etchants commonly used in studying zirconium are not adequate for use on samples exposed to cesium, but must be diluted to one-half or less strength to avoid pitting and staining. After exposure to oxygen-spiked cesium the etchant had to be further diluted in order to stop excessive reaction. Chemical analyses on this zirconium tab and the Mo-0.5%Ti capsule should provide insight into the interpretation of these phenomena.

Carbon and oxygen additions were made simultaneously to the Mo-0.5%Ti vs zirconium couple in a 100 hr test at 2500°F to determine whether the corrosive effects of these contaminants was additive. The use of cesium containing 260 ppm carbon and 380 ppm oxygen had a pronounced effect on both the metals used in this test which was not encountered in tests using pure cesium but this contamination level did not prove to be ruinous to the metals. The physical changes brought about by the simultaneous addition of carbon and oxygen seem to be a compromise between those caused separately, even though the elemental reactions are additive.

The walls of the capsule, where exposed to the liquid phase are deeply etched, with the etching following closely the slight scores left during machining (Fig 5). Capsules of Mo-0.5%Ti exposed to pure cesium had a lustrous finish upon completion of a test and showed no tendency towards dissolution along the ridges caused by machining. The presence of these etched and pitted sections has no noticeable effect on the macrohardness.

Hardness of both the capsule and the zirconium insert were not changed appreciably nor was the transition metal content of the cesium increased. There is a slight softening of the Mo-0.5%Ti at the bottom of the capsule, but this is almost within the limits of the precision in measurement (RB-80 vs RB-85).

These phenomena do not follow from microscopic examination of the metals. The Mo-0.5%Ti exposed to liquid cesium experienced slightly more grain growth than capsules exposed to pure cesium.

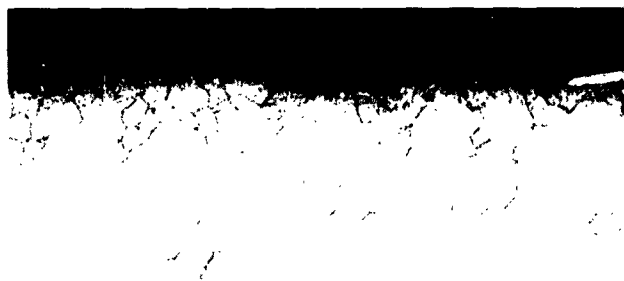


FIG 4 - Mo-0.5%Ti EXPOSED 125 HRS AT 2500°F WITH ZIRCONIUM
TO CESIUM CONTAINING 550 ppm O₂
Etchant: Murakamis reagent 266X

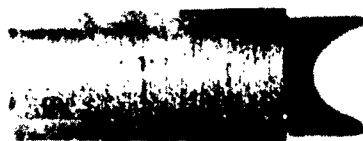


FIG 5 - Mo-0.5%Ti CAPSULE WALL EXPOSED 100 HRS AT 2500°F
TO CESIUM CONTAINING 260 ppm C and 380 ppm O₂
Actual size

The affected zone in this capsule extended about 350 μ into the sidewall whereas it extended only about 150 μ in the capsules containing pure cesium. Dissolution of the Mo-0.5%Ti is indicated by the ragged edges apparent in Fig 6. Mass transfer of molybdenum into the zirconium tab was found in a 725 hr test with this couple in pure cesium and, if these implications are judged correctly, may be enhanced by the combined effects of cesium and oxygen contaminations. The zirconium tab from this capsule experienced a 0.47% weight gain which is significantly greater than any of the others in this series of tests.

The zirconium insert, although undergoing no hardness change, did experience massive grain growth which diverged from that observed in previous tabs. Previously grain growth continued in the same pattern as the annealed material with the grains so large as to be easily visible to the naked eye. The pattern on this tab was broken irregularly by star-shaped patterns which resulted from the scavenging of carbon and/or oxygen.

Microprobe analyses of samples from these tests will soon be done. The results of these tests and the chemical analyses, which are also to be completed in the near future, should further illuminate the observed phenomena.

Haynes 25 Alloy Vs Nb-1%Zr

A capsule in this series was charged with cesium containing 620 ppm carbon and 180 ppm oxygen and exposed 100 hrs at 1800°F. The carbon and oxygen additions made no significant changes on the physical changes of Haynes 25 resulting from containment of cesium except that there seems to be a slight increase in solubility of the alloy constituents due to the presence of both non-metallics which was not observed when they were added separately. The Nb-1%Zr insert, however, was severely affected by the simultaneous addition of carbon and oxygen to this dissimilar metals system.

The Haynes-25 capsule underwent normal age hardening with no detectable changes observed between areas exposed to the liquid phase and vapor phase. Microscopic examination revealed a slight pitting along the walls exposed to liquid cesium indicating that dissolution of the alloy was greater in this capsule than those previously exposed to pure cesium although analysis of the cesium from this capsule did not reveal accumulation of the structural metals in the liquid metal.

The combination of carbon and oxygen spikes to the cesium had no effect on the hardness of the Nb-1%Zr tab contained in this capsule. The most conspicuous change incurred was a 27% weight

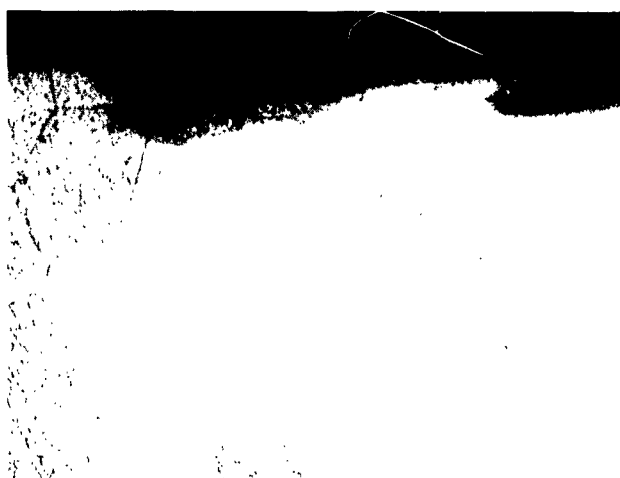


FIG 6 - Mo-0.5%Ti CAPSULE EXPOSED 100 HRS at 2500°F TO
LIQUID CESIUM CONTAINING 260 ppm C and 380 ppm O₂
Etchant: Murakamis 266X

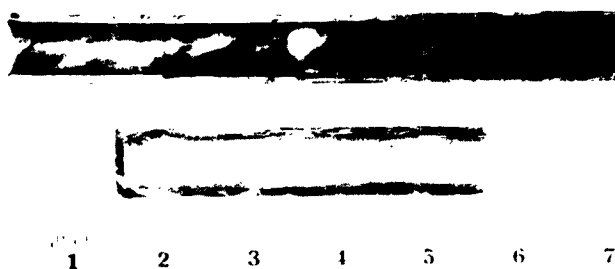


FIG 7 - HAYNES ALLOY-25 EXPOSED TO BOILING-REFLUXING
CESIUM FOR 500 HRS (liq. temp. 1800°F)

gain which is attributed to the diffusion of cobalt and other constituents of Haynes alloy into the tab. The diffusion of cobalt into Nb-1%Zr has been observed with samples exposed to pure cesium and it is believed that the combined effect of carbon and oxygen contamination increases the dissolution of the metals into the cesium where they are picked up by the Nb-1%Zr tab.

Comparison of the corrosive effects brought about by carbon and oxygen additions to the cesium used in this dissimilar metals couple reveals that the corrosion of Haynes-25 is slight unless both non-metallics are present in quite high concentrations while deleterious effects are observed on the Nb-1%Zr in all cases. The presence of Haynes-25 in this couple seems to mitigate the adverse effects of carbon additions by scavenging some of the excess carbon in the areas exposed to the vapor phase. The Haynes-25 in contact with the liquid phase of the contaminated cesium was decarburized to the same extent as the control sample exposed to pure cesium with no Nb-1%Zr tab. Analyses of the structural metals seems to indicate that there is an increase in the nitrogen content of the cesium during the test. This possibility is to be examined in the near future.

In contrast to this, an oxygen addition of 50 ppm to the cesium charged to this dissimilar metals couple decreased the carbon pick up of the Nb-1%Zr by a factor of 5. The oxygen spike was quite equally divided between the capsule and the insert with no differences observed between sections of the capsule exposed to the liquid phase and those exposed to the vapor phase.

The chemical analyses of the metals from the capsule containing both carbon and oxygen additions have not been completed as yet. These will help clarify the physical phenomena observed and also provide inferences for the microprobe work for which samples are now being prepared.

BOILING-REFLUX TESTS

Extrapolation of the results observed in capsule corrosion tests to be adapted to full scale units requires data from both static and dynamic systems. Extension of the present program into dynamic systems has begun and capsules of Haynes-25, Mo-0.5%Ti and TD-Nickel have been prepared.

The biggest problem associated with boiling-reflux tests is encapsulation under vacuum. The method used for sealing these capsules has been to weld a cap, through which a 0.25 in. tube extends, to the capsule immediately after charging the cesium in

the glove box. A stopper is placed in the tube while removing from the inert gas atmosphere and the capsule immediately moved to a vacuum system. After evacuation to approximately 1μ pressure the stainless steel tube is pinched closed and a cap welded over this to insure a seal. The deficiencies in this method are recognized and steps have been taken towards having all such capsules electron beam welded in the future.

A boiling-reflux test of 500 hrs has been completed with a Haynes-25 alloy capsule sealed in the manner mentioned above. Very few changes were observed in the alloy due to cesium containment during this test. The capsule wall exposed to liquid phase did not undergo age hardening (RC-26) while that exposed to the condensing liquid and the vapor phase experienced normal aging (RC 39).

The transition metals present in the cesium post-test were analyzed by means of Cupferron reagent and found to be present at approximately the same concentration as in the cesium analyzed from dissimilar metals static tests (~ 0.001 g of oxides per gram of cesium in the charge).

The walls of the capsule showed discolorations after opening and sectioning. The smaller section shown in Fig 7 is that exposed to the liquid phase during boiling. The clean surface is typical of what has been observed previously with Haynes-25. The larger section shows the condensing ring and section exposed to cesium vapor. Microscopic examination revealed no extensive corrosion in the boiling, condensing or vapor sections. A chromel-alumel thermocouple placed on the side of the capsule outside the furnace recorded a steady temperature of 1072°F for the section exposed only to cesium vapor. This section also experienced the least amount of grain growth but had considerable precipitation within the grains.

A boiling-reflux test with TD Nickel was also undertaken with a capsule similar to that used in the test with Haynes-25 alloy (10 in. long x 0.75 in. OD x 0.5 in. ID). The stainless steel tube which was pinched closed under vacuum parted after only one hour at temperature. The cap weld on this tube was also penetrated and the test interrupted. This capsule has since been thoroughly cleaned and prepared for a second charge.

The present method used in sealing the boiling-reflux capsules of the refractory metals requires the use of a Nb 1%Zr tube for pinching closed under vacuum. The first capsule prepared in this manner was Mo-0.5%Ti alloy but the Nb 1%Zr tube was severed during pinching and the vacuum broken. The refractory metal capsules are going to be electron beam welded in the future.