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Fourth Quarterly Progress Report
June, July and August 1963

to

Aeronautical Systems Division
Wright Patterson Air Force Base
Ohio

FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

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ABSTRACT

Work is continuing on investigation of mechanisms associated with the attack of liquid cesium on Haynes-25, columbium-1% zirconium and molybdenum-1/2% titanium. Preliminary evaluations have been performed on the compatibility of TD Nickel, a dispersion alloy, with liquid cesium. Dissimilar metal capsules of Haynes-25 vs Cb-1Zr and Cb-1Zr vs Mo-1/2Ti have been heated in a cesium environment at 1800°F and 2500°F respectively. Solubility studies of the alloys in liquid cesium are underway, utilizing refractory metal crucibles for sampling at temperature. A device for determination of the solubility of carbon in cesium is in the design stage.

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

F. Tepper
J. Greer

INTRODUCTION

This report describes work performed during the fifth quarter of effort. A summary report, which describes progress in the fourth quarter, and summarizes the effort in the first year, is to be released upon approval of the project engineer at ASD, Dayton, Ohio

DETERMINATION OF THE SOLUBILITY OF CARBON IN CESIUM

A device is presently in the design stage to permit determination of the solubility of elemental carbon in liquid cesium. The device will permit filtration of cesium samples at temperature to reduce the possibility of sampling suspended carbon. A bypass to permit determination of freezing point of the cesium charge will be incorporated into the device. It has been demonstrated that cesium melting point can adequately represent the oxygen content in a pure Cs-O mixture. Determination of the melting point concurrently with the solubility determination could permit evaluation of the effect of oxygen impurity on carbon solubility. Gratton* has shown the solubility of carbon in sodium to be oxygen dependant.

CORROSION OF TD-NICKEL BY CESIUM

Dispersion alloys, such as thoria-dispersed nickel, can have elevated temperature stress-to-rupture surpassing superalloys such as Haynes-25 and some refractory elements such as pure columbium. The ultimate tensile strength of as-received TD nickel sheet at 2400°F is approximately 7300 psi. The use of TD-Nickel as a structural material to 2200°F might offer distinct advantages over refractory metal alloys at this temperature, since it would not be as susceptible to embrittlement by oxygen and nitrogen. The particular disadvantage to this material involves joining, since fusion welding results in separation of the dispersed phase from the matrix nickel.

*Gratton, J.G., KAPL Report No. 1807 (1957).

Preliminary evaluation of TD-Nickel as a structural material for cesium has been undertaken during this quarter. A TD-Nickel capsule has been exposed to liquid cesium at 1800°F for 750 hours. Encapsulation of the cesium was accomplished by incorporating a threaded end-cap seal, followed by welding the end closure using Hastalloy W filler rod. While the end closure arrangement was thought to be the weakest part of the capsule, it was hoped that containment could be achieved to permit gross evaluation of the dispersion alloy with cesium. Unfortunately, after heating the capsule in air for 750 hours at 1800°F, failure of the seal resulted in release of cesium. The capsule was cooled and sectioned for post-test evaluation. External air oxidation resulted in a black scale, with a thick green oxide phase between the external scale and the metallic phase.

Metallographic examination of the surfaces exposed to liquid and vapor cesium was performed. Fig 1 shows the surface region exposed to liquid cesium, while Fig 2 shows that region exposed to vapor. The surface phase in Figs 1 (35 microns thick) and 2 (60 microns thick) have not as yet been identified. Macrohardness of the matrix was essentially the same as that of as-received material (R_B=91), while the affected surface was slightly softer than the matrix alloy. Little indication of dissolution attack was evident, however little was expected under the isothermal conditions of the test. The nitrogen and carbon contents of the alloy after test were respectively 16 and 27 ppm, which is only slightly less than that of the as-received material. Further evaluation of TD-Nickel with liquid cesium is in progress.

DISSIMILAR METAL STUDIES

Evaluation of isothermal mass transfer in dissimilar metal couples was continued. The effect of oxygen and carbon addition to purified cesium on mass transfer is also being evaluated.

Haynes 25 Vs Cb-12r

A dissimilar metal capsule fabricated from Haynes-25 and containing a tab of Cb-12r was charged with liquid cesium. Oxygen as Cs₂O was added to the capsule and corresponded to a level of 50 ppm oxygen.

Fig 3 shows a section of the Haynes-25 that had been exposed to liquid cesium (1800 °F, 100 hrs) containing oxygen. Oxygen analysis via the modified amalgamation technique of the hot-trapped cesium prior to oxygen addition was found to be 12 ppm. After the addition, the oxygen content is estimated to be between 60-80 ppm.



FIG 1 - TD-NICKEL CAPSULE EXPOSED TO LIQUID Cs FOR 800 HRS
Etchant: HCl-HNO_3 266X



FIG 2 - TD-NICKEL CAPSULE EXPOSED TO Cs VAPOR FOR 800 HRS
Etchant: HCl-HNO_3 266X

Fig 4 shows the Cb-12r tab exposed to liquid cesium within the Haynes-25 capsule shown in Fig 3. Fig 5 is a section of the Haynes capsule (H-4) which had been maintained at 1800°F for 100 hrs. The cesium in capsule H-4 had been spiked with the equivalent of 900 ppm carbon as high purity graphite. The accompanying Cb-12r insert is shown in Fig 6. A surface coating 3-4 microns thick is seen, which is significantly thinner than that coating resulting on the Cb-12r exposed to pure cesium in a Haynes-25 capsule (see Fig 12, Summary Report). The Cb-12r insert was harder ($R_p=48$) than as received material ($R_p=37$) but softer than any other tabs exposed to liquid cesium. Sections of the Haynes-25 capsule from regions exposed to cesium liquid and vapor are being analyzed for oxygen, carbon and nitrogen. Samples of the two Cb-12r tabs (figs 4 and 6) are being prepared for microprobe analysis.

Cb-1%Zr Vs Mo-0.5%Ti

Most of the analyses have been completed on the Cb-1%Zr vs Mo-0.5%Ti system which was exposed for 1000 hrs at 2500°F. This capsule was run simultaneously with a Mo-0.5%Ti capsule containing a Zr insert in a test which was interrupted after 725 hrs due to a failure in the vacuum system. This Cb-12r capsule was remounted in the furnace and was heated at 2500°F for the remainder of the 1000 hrs test without failure. The capsule maintained a bright clean surface after 1000 hours exposure at 2500°F.

The Cb-1%Zr capsule experienced a slight embrittlement in the vapor zone ($R_p=50$) while the area exposed to liquid cesium remained unaffected. The hardness of this alloy used in tests with a Mo-0.5%Ti insert has decreased as test duration has been extended (10, 100, 500 and 1000 hrs). The hardness of the Mo-0.5%Ti tabs employed in both the 500 hrs and 1000 hrs test were the same ($R_p=83$). This is slightly less than that hardness measured on Mo-0.5%Ti tabs exposed 10 and 100 hrs under cesium contained by a Cb-12r capsule.

The Mo-0.5%Ti insert experienced a 0.03% weight gain during this test possibly due to the mass transfer of Cb and Zr. Analysis of the Cb-12r capsule and Mo-0.5%Ti capsule are complete and are shown in Table 1.

The Cb-12r capsule has become enriched in oxygen and carbon, while there has been a resulting decrease of these elements in the Mo-0.5%Ti tab. The nitrogen appears to have been gettered from the Cb-12r by the Mo-0.5%Ti. It is evident that changes in oxygen, carbon and nitrogen content have occurred in the vapor phase of the capsule. Continued study of this dissimilar metal couple is underway.



FIG 3 - HAYNES-25 CAPSULE EXPOSED TO O₂-SPIKED Cs FOR 100 HRS
Etchant: HCl-H₂O₂ 266X



FIG 4 - Nb-1%Zr TAB FROM O₂-SPIKED HAYNES CAPSULE
Etchant: H₂O-HF-HNO₃-H₂SO₄ 266X



FIG 5 - HAYNES-25 CAPSULE EXPOSED TO C-SPIKED Cs FOR 100 F.S
Etchant: $\text{HCl-H}_2\text{O}_2$ 266X



FIG 6 - Nb-1%Zr TAB FROM C-SPIKED HAYNES CAPSULE
Etchant: $\text{H}_2\text{O-HF-HNO}_3\text{-H}_2\text{SO}_4$ 266X

TABLE 1 - Cb-1Zr DISSIMILAR METAL TEST
(2500°F - 1000 hrs)

	<u>Oxygen</u> <u>(ppm)</u>	<u>Carbon</u> <u>(ppm)</u>	<u>Nitrogen</u> <u>(ppm)</u>
<u>Cb-1Zr</u>			
As received	192	69	122
Exposed to liquid	938	146	63
Exposed to vapor	860	90	75
<u>Mo-1/2Ti</u>			
As received	80	186	46
Exposed to liquid	30	27	69

SOLUTION KINETICS STUDIES

During this quarter the solubility studies of the alloys, Cb-1%Zr, Mo-0.5%Ti and Haynes-25, have been undertaken using a metal sampling crucible in place of the Al_2O_3 crucible used formerly. Blackening of the Al_2O_3 crucible and a high Al content analyzed in the cesium indicated that the Al_2O_3 used was not pure enough to remain inert to cesium at elevated temperatures. The samples prepared from tests using Mo-0.5%Ti and Cb-1%Zr crucibles have not been completely analyzed at the present time, but will be compared with previous results which utilized Al_2O_3 sampling crucibles.

Solution Kinetics of the Refractory Alloys

Two capsule tests were undertaken in the solution studies of Mo-0.5%Ti alloy in cesium. These capsules contained Cb-1%Zr crucibles into which the cesium sample was decanted at temperature. The first of these capsules leaked at the cap weld just prior to sampling, but a second has been sampled after 100 hrs at 2500°F and the cesium was prepared for analyses. The data obtained from this test will be compared to that obtained in the 100 hrs exposure of the same alloy containing a high purity Al_2O_3 , "Lucalox", crucible. Similar tests with 10 and 0.5 hrs exposure are planned for the near future.

Two capsules were also undertaken in the solution studies of Cb-1%Zr alloy in cesium. The first ruptured after 98.5 hrs exposure in a 100 hrs test, but the second has been successfully sampled after 100 hrs at 2500°F and is undergoing analysis.

The effects of molybdenum from the sampling crucible on the solubility of Cb and Zr may possibly be ascertained by comparing the analysis of this capsule with those obtained on a similar capsule in which the sample was decanted into an alumina crucible.

Solution Kinetics of Haynes Alloy-25

Tests performed to determine the solubility of Haynes-25 have also incorporated a Mo-0.5%Ti crucible in place of the alumina. Capsules exposed 100 hrs and 0.5 hrs have been completed during this quarter and will be compared with previous results. The short duration test had achieved thermal equilibrium ($\pm 2^\circ\text{F}$) at 1800°F in 30 min, after which sampling was performed. It is thought that equilibrium solubilities may occur in less than 100 hrs, and shorter exposures or zero exposure times will aid in determining solution kinetics. Future tests in this series have been deferred pending transition metal analysis of these samples.

BOILING-REFLUXING TESTS

Boiling-refluxing tests of high purity cesium with Haynes-25, Cb-1Zr, Mo-0.5Ti and TD-Nickel are planned.

In an effort to extend the corrosion data on Haynes-25 into dynamic systems, a capsule has been fabricated for a boiling-refluxing test. A thermal gradient will exist along the capsule to a H₂O cooled section at the top. Haynes-25 capsules (Fig 7) will be sealed by pinching the stainless steel tube closed under vacuum and welding a sleeve over the crimp to assure closure during operation.

The initial charge of a Haynes-25 capsule was undertaken during this quarter and boiling-refluxing with a liquid temperature of 1800°F is underway.

Plans have been made and extra materials ordered for the fabrication of refluxing capsules from the other alloys being studied in this program.

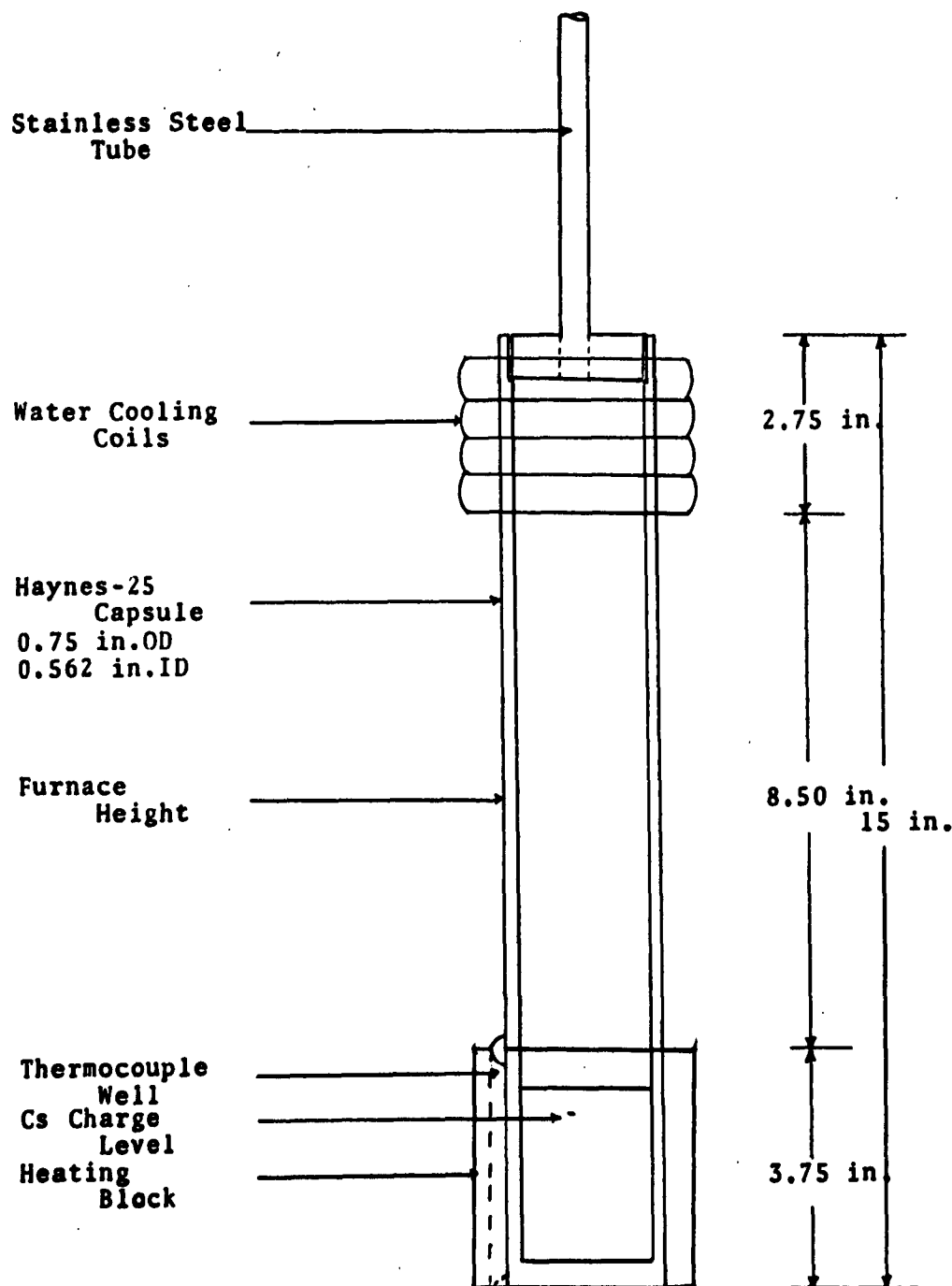


FIG 7 - CAPSULE CONFIGURATION FOR REFLUXING TESTS IN HAYNES-25

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17 September 1963

DCAS (DCLMT-TDC)
TDC-62-357-7
AF Unit P. O.
Los Angeles, California

Gentlemen:

Subject: Contract Number AF 33(657)-9168
Fourth Quarterly Progress Report

We are pleased to enclose one copy of the Fourth Quarterly Progress Report on the above-referenced contract.

Very truly yours,

MSA RESEARCH CORPORATION



C. H. Staub
Director - Marketing Division

CHS/fab

Enclosure: 1