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EFFECTS OF LIQUID AND VAPOR CESIUM ON STRUCTURAL MATERIALS

R. L. Klueh
D. H. Jansen

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R. L. Klueh and D. H. Jansen

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ABSTRACT

The corrosion properties of cesium are of interest for applications in thermionic and turbine generator space-power systems. The present literature review of cesium corrosion properties was undertaken as part of a parametric study comparing the characteristics of cesium and potassium as working fluids in Rankine-cycle systems. In the past, cesium compatibility tests have consisted mainly of static capsule tests run for screening purposes, and in many instances, the effects of the impurities present in the cesium and structural materials were not evaluated. Despite these shortcomings, the tests have shown that the rates of corrosion of identical materials in cesium and potassium are qualitatively the same. Any further comparison must await more sophisticated tests that examine corrosion properties under environmental and boiling conditions that more accurately simulate the fluid velocities, heat fluxes, surface volume ratios, and temperature distributions of the Rankine-cycle space-power plant.

INTRODUCTION

This literature survey was undertaken as part of an analytical comparison of cesium and potassium as working fluids for Rankine-cycle space-power plants. This report, which deals only with cesium compatibility studies, will be supplemented with a report which directly compares the compatibility of cesium and potassium.

Cesium studies have generally been conducted in association with applications in power systems either as a working fluid in heat engines or to dissipate the current-limiting space charge in thermionic generators A literature survey reveals that information on the corrosion properties of cesium is considerably more limited than for potassium or sodium. Furthermore, much of the early work on cesium compatibility is of limited value, since it was acquired while organizations were familiarizing themselves with the handling problems of alkali metals. Subsequently, the literature contains many instances where attack of certain alloys by cesium was reported and then contradicted by later work. Such results are now attributed to liquid-metal contamination, especially by interstitial impurities. Generally no attempts were made to determine the amounts of impurities present in the cesium even in the later studies.

A comparison of the compatibility results of different investigators is also complicated by the different methods of testing employed and the different terms applied in describing the results. By far the majority of investigators relied on metallography to determine if a material had been attacked by cesium. In reporting their observations, these investigators often expressed the same findings in quite different terms. Nevertheless, in this survey we have adhered to the authors' original descriptions.

In compiling this review, we have drawn heavily on the recent survey of alkali-metal compatibility data published by Battelle Memorial Institute.[1]

Compositions of the alloys reviewed in this report are listed in Tables 1 and 2.

SOLUBILITY STUDIES

Quantitative solubility data for the transition and refractory metals in liquid cesium are essentially nonexistent. Tepper and Greer[2] attempted to measure the solubility of niobium and molybdenum in equilibrium with Nb-1% Zr and Mo-0.5% Ti, respectively, and reported solubilities of approximately 10 to 20 ppm. The majority of solubility data available is of a qualitative nature obtained by posttest analysis of cesium from compatibility tests. Generally such tests reveal a finite

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[1] J. H. Stang et al., Compatibility of Liquid and Vapor Alkali Metals with Construction Materials, Defense Metals Information Center Report DMIC 227, Battelle Memorial Institute (April 1966).

[2] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, Report No. AFML-TR-64-327, MSA Research Corporation (November 1964).

Table 1. Nominal Compositions of Nickel- and Iron-Base Alloys

Alloy Designation	Composition (wt %)								
	Ni	Fe	Cr	Ti	Mo	Mn	Si	C	Other
"A" nickel	Bal	0.15				0.2	0.05	0.1	0.1 Cu–0.005 S
"L" nickel	Bal	0.05				0.2	0.15	0.01	0.02 Cu–0.005 S
René 41	Bal	3	19	3	10			0.1	1 Co–1.5 Al
Ni-Span C	Bal	40	5.5	2.5					
Inconel X	Bal	7	15	2.5		0.7	0.3	0.04	0.9 Al–1 Nb
"B" monel	Bal	1.7				1.1	0.05	0.1	30 Cu–0.35 S
17-4 PH	4.25	Bal	16.5			0.4	0.5	0.04	0.25 Nb–3.6 Cu
AM 350	4.25	Bal	16.5		2.75	0.75	0.35	0.1	0.1 N
EN 58B stainless steel	8	Bal	18	0.6		0.4		0.12	
Type 310 stainless steel	20	Bal	25			2.0	1.5	0.25 (max)	
Type 304 stainless steel	10	Bal	19			2.0	1.0	0.08 (max)	
Type 321 stainless steel	9	Bal	18	5 x C (min)	2.5	2.0	1.0	0.08 (max)	
Type 416 stainless steel		Bal	13			1.25	1.0	0.12 (max)	
Type 430 stainless steel		Bal	16			1.0	1.0	0.12 (max)	

Table 2. Nominal Composition of Refractory Alloys

Alloy Designation	Composition (wt %)								
	Nb	Ta	W	Zr	Mo	V	Hf	Ti	C
D-43	Bal		10	1					0.1
B-66	Bal			1	5	5			
FS-82	Bal	33							
FS-85	Bal	28	10	1					
PWC-33	Bal			3					0.3
T-111		Bal	8				2		
TZM				0.1	Bal			0.5	0.01
TZC				0.1	Bal			0.5	0.1

but limited solubility of the material tested and show that excess oxygen, either in the cesium or the test material, increases the apparent solubility of the container material. Qualitatively, the solubility behavior of structural metals in cesium is analogous to that found in much more extensive investigations with potassium and sodium.

CORROSION OF NICKEL- AND IRON-BASE ALLOYS

Only limited data exist on the corrosion of iron- and nickel-base alloys in cesium. However, the tests that have been conducted generally reveal little or no surface attack within the temperature ranges where these materials can reasonably be used. Although surface attrition was quite minor, decarburization and leaching of carbide precipitates were commonly observed above 1200°F. Cesium purity, especially with respect to interstitials, was found to be extremely important in determining compatibility.

Unless otherwise stated, the tests discussed in this section (nickel- and iron-base alloys) were conducted by means of static capsules partially filled with liquid and generally containing a sheet-type corrosion specimen (of the same material as the capsule) in the liquid region. After test the specimens were generally checked for metallographic appearance, weight changes, and in a few instances for changes in chemical composition. The liquid and vapor regions of the capsules were also examined for attack.

René 41 was unaffected by cesium liquid or vapor for up to 500 hr at 750°F (ref, 3), but when the cesium was contaminated by oxygen as a result of weld failures, intergranular attack was observed. Similarly, nickel[4] was found to be compatible with liquid cesium in capsules at 1292°F,

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[3]P. M. Winslow, Synopsis of Cesium Compatibility Studies, CONF-650411, p. 334 (April 1965).

[4]C. R. Dulgeroff and G. D. Seele, Final Report for Experimental Electrical Propulsion Study for Period May 1, 1958 through May 31, 1960, AFOSR-TR-60-112, Curtis-Wright Corp. (1960).

but to be intergranularly attacked at 1832°F. This attack was attributed to impurity pickup from the liquid.[5] Decarburization was detected in Inconel X which had been exposed to cesium liquid for 720 hr at 1600°F (ref. 6); likewise Ni-Span C, on exposure to cesium vapor at 1200°F for 1000 hr (ref. 7), was found to lose subsurface precipitates which in turn caused a decrease in ductility and yield strength in room temperature tensile tests. In neither of these latter two alloys, however, were the surfaces attacked severely.

Lamberti and Saunders[8] and Slivka[9] conducted tests by simultaneously exposing several alloys to cesium vapor within a stainless steel chamber. The alloys, "A" nickel, "L" nickel, Inconel X, and "B" monel, were found to be compatible with cesium vapor for 48 hr at 500, 800, and 1200°F (ref. 8), whereas nickel was found to develop an external scale after 281 hr at 1652°F (ref. 9). Table 3 lists the results for nickel and nickel-base alloys tested to date.

The alloy "TD" nickel[2] appears to be the only nickel-base alloy that has been tested in cesium under refluxing conditions. Refluxing capsules were operated for 260 and 500 hr at 1800°F; and although corrosion was not extensive, metallic crystallites were found in the bottom of the capsules. Indications were that the thoria dispersoid near the surface had been modified or lost.

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[5]If true, this would contrast with the compatibility behavior of nickel in sodium, since, unlike chromium or iron, nickel is relatively insensitive to the oxygen content of sodium.

[6]W. T. Chandler and N. J. Hoffman, Effects of Liquid and Vapor Cesium on Container Metals, Report No. ASD-TDR-62-965. Rocketdyne Division of North American Aviation, Inc. (March 1963).

[7]D. W. Levinson, Stress-Dependent Interactions Between Cesium and Other Materials, IITRI-B215-22. Illinois Institute of Technology Research Institute (November 1964).

[8]J. M. Lamberti and N. T. Saunders, Compatibility of Cesium Vapor with Selected Materials at Temperatures to 1200°F, NASA-TN-D1739, NASA Lewis Research Center (August 1963).

[9]M. J. Slivka, "A Study of Cesium Vapor Attack on Thermionic Converter Construction Materials," Advan. Energy Conversion 3, 157-66 (1963).

Table 3. Corrosion of Nickel-Base Alloys in Cesium

Material	Temperature (°F)	Time (Hr)	Cesium Phase(s)	Results	Reference
Nickel	1112	100	Liquid and vapor	No attack	10
	1292	100	Liquid	No attack	4
	1832	100	Liquid	Intergranular attack	4
	1652	281	Vapor	Mixed bright and matte surface; reaction zone at surface	9[a]
"A" Nickel	500, 800, 1200	48	Vapor	No attack	8[a]
	1380	1000	Vapor	Surface grayed; no apparent attack	11
"L" Nickel	500, 800, 1200	48	Vapor	No attack	8[a]
Inconel X	500, 800, 1200	48	Vapor	No attack	8[a]
	1600	720	Liquid	Decarburization; no surface attack	6
Ni-Span C	1200	1000	Vapor	Loss of subsurface precipitates; no surface attack	7

[a]Tests were carried out in a stainless steel container with several specimens being run simultaneously.

Steels[3,4,6,8,9,10] and unalloyed iron[11] have generally shown high resistance to dissolution by cesium liquid and vapor in capsule tests, although decarburization has usually resulted. This was true for 17-4 PH, AM 350, and type 416 stainless steel[3] which were tested in liquid cesium at 750°F for 500 hr and type 310 stainless steel' after 720 hr at 1600°F. Type 321 stainless steel[4] was unattacked at 1292°F, but spectrographic analysis of the cesium after test indicated that titanium had been leached from the stainless steel. Lamberti and Saunders,[8] using the procedure described above for the nickel alloys, tested 1020 steel and type 304 stainless steel in cesium vapor and found slight tarnishing which was attributed to oxygen in the cesium. Table 4 summarizes the results for iron-base alloys.

CORROSION OF REFRACTORY METALS AND ALLOYS

Static Capsule Tests

Cesium Vapor

Several studies[6,8,9,10,12,13,14] have been conducted to determine the effect of cesium vapor on refractory alloys. These tests generally have been of three types:

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[10] R. G. Smith et al., "A Study of the Compatibility of Thermionic Converter Materials with Cesium," J. Nucl. Mater. 10, 191–200 (1963).

[11] W. B. Hall and S. W. Kessler, Cesium Conrpatibility of Thermionic Converter Structural Materials, N65-33774, Radio Corporation of America (1963).

[12] D. V. Rigney, Unpublished internal memorandum summarizing cesium corrosion data, Pratt and Whitney Aircraft-CANEL (July 15, 1965).

[13] J. A. DeMastry and N. M. Griesenauer, Investigation of High Temperature Refractory Metals and Alloys for Thermionic Converters, AFAPL-TR-65-29 Battelle Memorial Institute (April 1965).

[14] F. Hargreaves, G.T.J. Mayo, and A. G. Thomas, "A Study of the Long-Term Compatibility of Thermionic Converter Materials with Cesium," J. Nucl. Mater. 18, 212–18 (1966).

Table 4 Corrosion of Iron-Base Alloys in Cesium

Material	Temperature (°F)	Time (Hr)	Cesium Phase(s)	Results	Reference
Iron	1[illegible]00	1000	Vapor	attack	11
1020 steel	500, 800, 1200	48	Vapor	Tarnishing, probably due to oxygen in the cesium	8[a]
17-4 PH	750	500	Liquid and vapor	No attack	3
Fe Cr-Al-Y alloy	1[illegible]52	281	Vapor	Mild surface attack	9[a]
AM-350	750	500	Liquid and vapor	No attack	3
EN 58B stainless steel	1112	100	Liquid and vapor	No attack	10
Type 304 stainless steel	1600	1000	Vapor	No attack	11
	500, 800, 1200	48	Vapor	Tarnishing, probably due to oxygen in the cesium	8[a]
Type 310 stainless steel	1600	720	Liquid	Slight transfer of carbon from stainless steel to cesium	6
Type 321 stainless steel	1292	100	Liquid	Titanium leached from the stainless steel	4
Type 416 stainless steel	750	500	Liquid and vapor	No attack	3
Type 430 stainless steel	1652	281	Vapor	No attack	9[a]

[a]Tests were carried out in a stainless steel container with several specimens being run simultaneously.

1. Capsules may be partly filled with cesium liquid with the space above the liquid evacuated except for cesium vapor at a pressure determined by the equilibrium vapor pressure of cesium liquid at the test temperature.[10,12,14,15]

2. The amount of cesium introduced into a capsule may be limited so that the cesium will be completely vaporized at temperature.[13]

3. Stainless steel reservoirs containing test specimens may be connected to an outside source of cesium vapor.

In either of the first two methods the test specimens may be suspended in the vapor or else the capsule may serve as the test specimen.

When the capsule and the test specimen were of the same material (method 1 or 2), there was generally no metallographic evidence of attack. This was true for niobium,[15,11] Nb–1% Zr (refs. 15, 12), D-43 (ref. 12), PWC-33 (ref. 12), tantalum,[12] Ta–10% W (ref. 12), T-111 (refs. 15, 12), molybdenum,[15,12] Mo–0.5% Ti (ref. 12), tungsten,[15,12] W–3% Re (ref. 12), and W–5% Re (ref. 12) when exposed for up to 300 hr at 2500°F.

DeMastry and Griesenauer,[13] in what effectively were dissimilar metal tests, used method 2 with TZM as a container material with various refractory metals as test specimens and, in some instances, found evidence of corrosive attack and mass transfer effects. The alloy B-66 was found to experience slight surface dissolution after 1000 hr at 2500°F, and T-111, which was resistant to attack for 1000 hr at 2500°F, exhibited surface dissolution after 100 hr at 2800°F. After 100 hr at 2500°F, Ta–12% W was unattacked by cesium vapor, but showed surface dissolution after 1000 hr and showed surface dissolution and lamellar carbide or carbonitride precipitate after 600 hr at 2800 and 3100°F. The source of the carbon and nitrogen was thought to be the cesium and the TZM container. The tungsten-base alloys tested were unattacked after 1000 hr at 3100°F, but they experienced surface dissolution and grain boundary attack after 1000 hr at 3400°F.

[15]W. T. Chandler and N. J. Hoffman, Effects of Liquid and Vapor Cesium on Container Metals, Report No. ASD-TDR-62-965, Rocketdyne Division of North American Aviation, Inc. (March 1963).

Investigators in England[illegible] used the first method with a stainless steel container and found no indication of attack of tantalum and molybdenum after 100 hr at either 842 or 1112°F; but after 10,000 hr at 1062°F, tantalum, molybdenum, and niobium were all found to have a slight surface tarnish although there was no evidence of general corrosion. (The composition of the scale was not determined.) Lamberti and Saunders[8] and Slivka,[9] using the third method cited above, found that tantalum contained a surface film after test, but that molybdenum and tungsten were unattacked. Slivka[9] also tested FS-82 and found a surface film. Tables 5 and 6 summarize the results of the refractory alloys tested in cesium vapor.

Cesium Liquid

Chandler and Hoffman[illegible] have tested niobium, Nb–1% Zr, molybdenum, tantalum, and tungsten in static capsules containing cesium liquid for 300 hr at 1600°F and found no metallographic evidence of attack. Similar results were found by Winslow[illegible] for molybdenum and tungsten after 500 hr at 750°F. British workers[17] on the other hand, found a surface scale on niobium and tarnishing of tantalum and molybdenum after 10,000 hr at 1062°F. These latter tests, however, were conducted in stainless steel capsules.

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[16]P. M. Winslow, Synopsis of Cesium Compatibility Studies, CONF-650411, p. 334 (April 1965).

[17]F. Hargreaves, G.T.J. Mayo, and A. G. Thomas, "A Study of the Long-Term Compatibility of Thermionic Converter Materials with Cesium," J. Nucl. Mater, **18**, 212–18 (1966).

Table 5. Corrosion of Refractory Alloys in Cesium Vapor in TZM Containers[a] (Static Capsule Tests)

Material	Temperature (°F)	Time (Hr)	Results
B-66	2500	100	No attack
		1000	Slight surface dissolution
	2800	100	No attack
Ta-12% W	2500	100	No attack
		1000	Surface dissolution
	2800	100	Carbide precipitate
	3100	100	Carbide precipitate
Ta-8% W-2% Hf (T-111)	2500	100	No attack
		1000	No attack
	2800	100	Slight surface dissolution
TZM	2500	100	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	No attack
Mo-50% Re	2500	100	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	No attack
Tungsten	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	Slight surface dissolution
		1000	Grain boundary penetration
W-0.9% Nb	2500	100	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	Surface dissolution

Table 5(continued)

Material	Temperature (°F)	Time (Hr)	Results
W-15% Mo	2500	100	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	Surface attack and grain boundary dissolution
W-10% Re	2500	100	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	Grain boundary attack and surface dissolution
W-25% Re	2500	100	No attack
		300	No attack
		1000	No attack
	2800	100	No attack
		1000	No attack
	3100	100	No attack
		1000	No attack
	3400	100	No attack
		1000	Slight surface dissolution and grain boundary penetration

[a] J. A. DeMastry and N. M. Griesenauer, Investigation of High-Temperature Refractory Metals and Alloys for Thermionic Converters, AFAPL-TR-65-29, Battelle Memorial Institute (April 1965).

Table 6 Corrosion of Refractory Alloys in Cesium Vapor

Material	Temperature (°F)	Time (Hr)	Remarks	Results	Reference
Niobium	1062	10,000	Stainless steel capsule	Surface scale	17
	1600	300		No attack	12
	1600	720		No attack	15
	2500	300		No attack	12
Nb–1% Zr	1600	300		No attack	12
	1600	720		No attack	15
	2500	300		No attack	12
D-43	1600	300		No attack	12
	2500	300		No attack	12
FS-82	1652	281	Stainless steel container	Reaction zone at surface	9
PWC-33	1600	300		No attack	12
	2500	300		No attack	12
Tantalum	842, 1112	100	Stainless steel capsules	No attack	10
	1062	10,000	Stainless steel capsules	Slight surface tarnish	17
	500, 800, 1200	48	Stainless steel container	Surface tarnish	8
	1600	300		No attack	12
	1600	720		No attack	15
	2500	300		No attack	12
	1652	281	Stainless steel container	Internal pores and precipitate near surface	9
Ta–10% W	1600, 2500	300		No attack	12
T–111	1600, 2500	300		No attack	12
Molybdenum	500, 800, 1200	48	Stainless steel container	No attack	8
	750	500		No attack	16

Table 6(continued)

Material	Temperature (°F)	Time (Hr)	Remarks	Results	Reference
Molybdenum	842, 1112	100	Stainless steel capsule	No attack	10
	1052	10,000	Stainless steel capsule	Slight surface tarnish	17
	1600	300		No attack	12
	1600	720		No attack	5
	1652	281	Stainless steel container	No attack	9
	2500	300		No attack	12
Mo—0.5% Ti	1600, 2500	300		No attack	12
Tungsten	500, 800, 1200	48	Stainless steel container	No attack	8
	750	500		No attack	16
	1600, 2500	300		No attack	12
W—3% Re	2500	300		No attack	12
W—5% Re	2500	300		No attack	12
W—25% Re	2500	300		No attack	12

Dissimilar Metal Tests

Tepper and Greer[18,19] tested the following dissimilar metal couples in cesium liquid:

(1) Nb–1% Zr/"TD" Nickel (500 hr at 1800°F)
(2) Nb–1% Zr/Haynes alloy No. 25 (500 hr at 2500°F)
(3) Nb–1% Zr/Mo–0.5% Ti (500 hr at 2500°F)
(4) Mo–0.5% Ti/"TD" Nickel (500 hr at 1800°F)
(5) Mo–0.5% Ti/Haynes alloy No. 25 (500 hr at 2500°F)
(6) Mo–0.5% Ti/zirconium (725 hr at 2500°F)

For couples (1) through (5) considerable mass transfer of both metallic and nonmetallic constituents was observed. No detectable changes were noted in the Mo–0.5% Ti/zirconium couple after 725 hr at 2500°F, but when oxygen and carbon additions were made to the system, measurable changes were noted, especially in the zirconium which gettered both species.

Conclusions drawn from this investigation were that the utilization of dissimilar metal systems can often lead to premature failure if one is not cognizant of the effect of interalloying.

Refluxing Capsule Tests

Several investigators[15, 19–22] have conducted refluxing capsule experiments with cesium. Chandler and Hoffman,[15] in their tests, found

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[18] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, Report No. AFML-TR-64-327, MSA Research Corporation (November 1964).

[19] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, COW-650411, p. 323 (April 1965).

[20] J. R. DiStefano, High-Temperature Materials Program Quart. Progr. Rept. April 30, 1966, ORNL-TM-1520, Part I, pp. 27–34. (Official Use Only).

[21] A. Romano, A. Fleitman, and C. Klamut, The Behavior of Refractory Metals and Alloys in Boiling Sodium and Other Boiling Alkali Metals, BNL-10723, Brookhaven National Laboratory (1966).

[22] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, ASD-TDR-63-824, Part I, MSA Research Corporation (September 1963).

surface dissolution and severe attack of niobium and Nb–1% Zr after 720 hr at 1800 and 2500°F. These results, however, have been contradicted by more recent tests of niobium alloys.[20,21,22,19] Inserts removed from the condenser section of an Nb–1% Zr capsule tested by DiStefano[23] at ORNL for 5000 hr at 2192°F showed only slight weight changes on the order of 10^{-8} mg/cm^2; his data are given in Table 7. The only mass transfer noted was a change in oxygen concentration of the inserts. Analyses of the cesium following the test gave niobium and zirconium concentrations of 6 and 1 ppm, respectively, indicating little dissolutive corrosion.

Similarly, Romano, Fleitman, and Klamut[21] and Tepper and Greer[22] found no attack of Nb–1% Zr after 6000 hr at 2200°F and 886 hr at 2100°F, respectively. Two other niobium-base alloys which have been tested under refluxing condition – D-43 (ref. 21) (9000 hr at 2200°F) and FS-85 (ref. 22) (818 hr at 2100°F) – were also unattacked.

Chandler and Hoffman[15] found surface and dissolutive attack on refluxing capsules of tantalum tested for 720 hr at 1800 and 2500°F. Tepper and Greer,[22,19] on the other hand, found no mass transfer or attack of Ta–10% W after 528 hr at 2100°F. Finally, severe dissolutive corrosion of molybdenum[15] and Mo–0.5% Ti (refs. 22, 19) has been observed. Table 8 summarizes the refluxing capsule tests conducted to date.

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[23] J. R. DiStefano, private communication, Jan. 30, 1967.

Table 7. Summary of Weight and Chemistry Changes for Inserts of Nb–1% Zr Alloy Capsule Containing Refluxing Cesium[a]

Insert Number	Distance Above Liquid Vapor Interface (in.)	Weight Change of Condensate (mg cm^{-2} g^{-1})	Oxygen Change (mg/cm^2)	Oxygen Change (ppm)
1	5–6	0.0	-0.018	–20
2	4–5	0.0	b	b
3	3–4	2 × 10^{-8}	+0.261	+290
4	2–3	2 × 10^{-8}	b	b
5	2–1	0.0	+0.241	+270
6	0–1	0.0	+0.148	+160

(a)Refluxing capsule operated for 5000 hr at 2192°F.
(b)Not analyzed.

Table 8. Summary of Cesium Refluxing Capsules

Material	Temperature (°F)	Time (Hr)	Results	Reference
Niobium	1800	720	Surface dissolution	15
	2500	720	Severe attack	15
Nb–1% Zr	1800	720	Severe attack	15
	2500	720	Surface dissolution	15
	2192	5000	No attack	20
	2200	6000	No attack	21
	2100	886	No attack	22
D-43	2200	9000	No attack	21
FS-85	2100	81%	No attack	22
Tantalum	1800	720	Surface dissolution	15
	2500	720	Severe attack	15
Ta–10% W	2100	528	No attack	19,22
Molybdenum	1800	720	Severe attack	15
	2500	720	Severe attack	15
Mo–0.5% Ti	2100	292	Surface dissolution	19,22
		1000	Surface dissolution	19,22
	2500	255	Severe attack	19,22

Loop Tests

The literature contains only three references in which loop tests using cesium have been conducted for corrosion studies. Loop tests have been reported by Ammon, Begley, and Eichinger[24] of Westinghouse Astronuclear Laboratory (a two-phase natural circulation loop of T-111), Romano, Fleitman, and Klamut[21] of Brookhaven National Laboratory, and Young and Achener[25] of Aerojet General Nucleonics (the latter two were two-phase forced-circulation loops of Nb–1% Zr).

[24] R. L. Ammon, R. T. Begley, and R. L. Eichinger, T-111 Cesium Natural Convection Loop, CONF-650411 (April 1965).

[25] P. F. Young and P. Achener, Operation of 1850°F Pumped Loop System and Determination of Specific Heat, Density, and Vapor Pressure of Cesium Between 174 and 1800°F, AGN-8041, Aerojet General Nucleonics (May 1962).

T-111/Cesium Natural-Circulation Loop

A natural-circulation (two-phase) T-111 loop contained three tubular inserts, two in the boiler and one located in the condenser section.[24] The test, depicted in Fig. 1, was terminated owing to a high-temperature excursion, causing a failure in the boiler. Conditions during operation are given below:

Temperature, "F (max)	2500
Temperature, °F (min)	1940
Vapor pressure, psi	600
Power input, kw	3
Flow, lb/hr (max)	22
Vapor velocity, ft/sec	2.4
Condenser area, ft^2	0.061
Tubing sizes, in.	0.50 OD x 0.035 wall
Test duration, hr at "F	246 at 2400°F; 175 at 2000°F

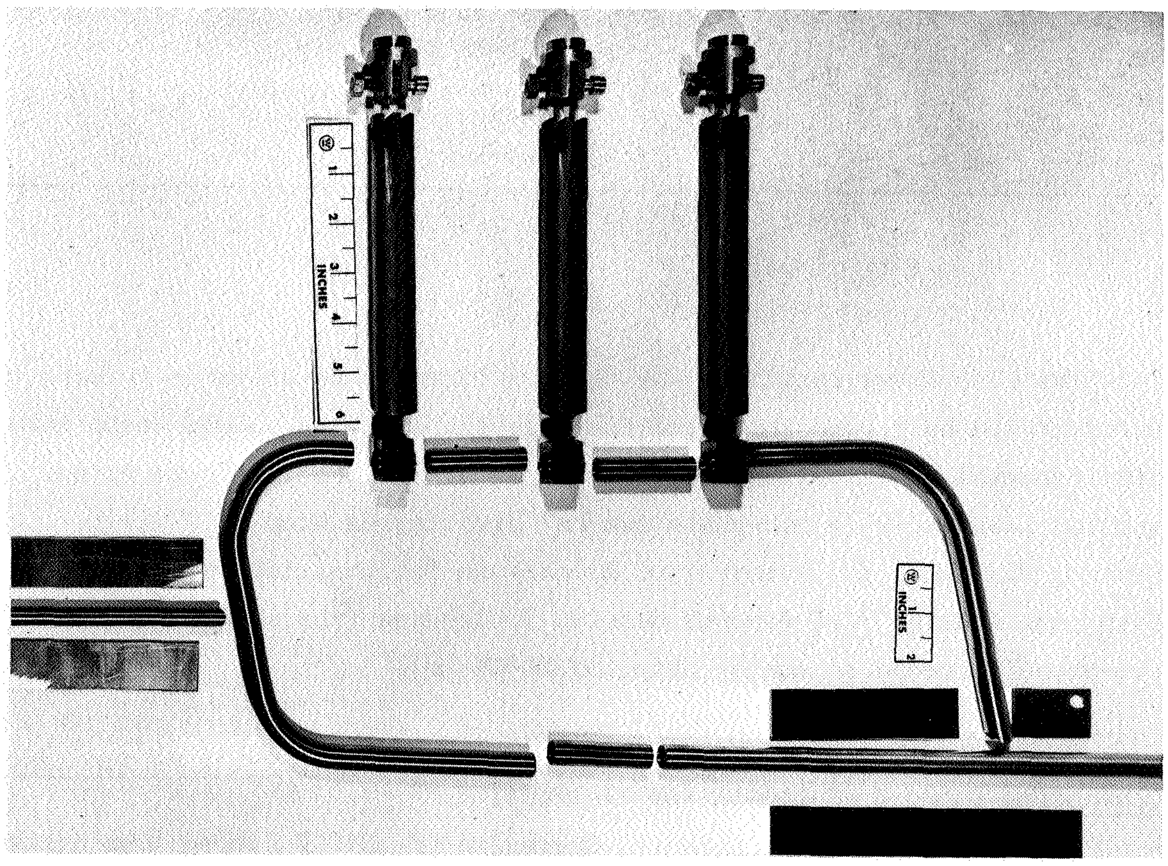

Fig. 1. Westinghouse T-111/Cesium Loop Prior to Welding.
Ref: R. L. Ammon, R. T. Begley, and R. L. Eichinger, T-111 Cesium Natural Convection Loop, CONF-650411 (April 1965).

Posttest analyses indicated a slight increase (26 to 40 ppm) of oxygen at the boiler region and a significant increase (20 to 110 ppm) at the condenser location. A decrease of oxygen in the cesium was also noticed. No evidence of corrosive attack was found in the loop.

Nb-1% Zr/Cesium Forced-Circulation Loops

Two forced-circulation loops have been operated with boiling cesium, one by Brookhaven National Laboratory, the other by Aerojet General Nucleonics. Operating conditions of the Brookhaven forced-circulation loop,[21] Fig. 2, are listed:

Test section material	
Nozzles	Nb-1% Zr
Blades	TZM, TZC
Number of stages	2
Temperature, °F	
Boiling	1760
Impingement (max)	1542
Vapor quality, %	80
Vapor velocity, ft/sec (max)	800
Mass flow rate, lb/hr	90
Test duration, hr	1100

The loop was constructed of Nb-1% Zr and contained a nozzle-blade test assembly with Nb-1% Zr nozzles and TZM or TZC blade specimens.

Posttest visual examination[21] of the nozzle-blade test section revealed a vortexing of the vapor on the underside (opposite to the impingement side) of the blades. Only a darkening of the high-velocity vapor impingement region was detected on the TZC and TZM alloy blade specimens. Results of metallographic examination of the blades indicated no evidence of corrosion or loss of materials, but rather an adherent metallic layer (identified as niobium) 1 mil thick.

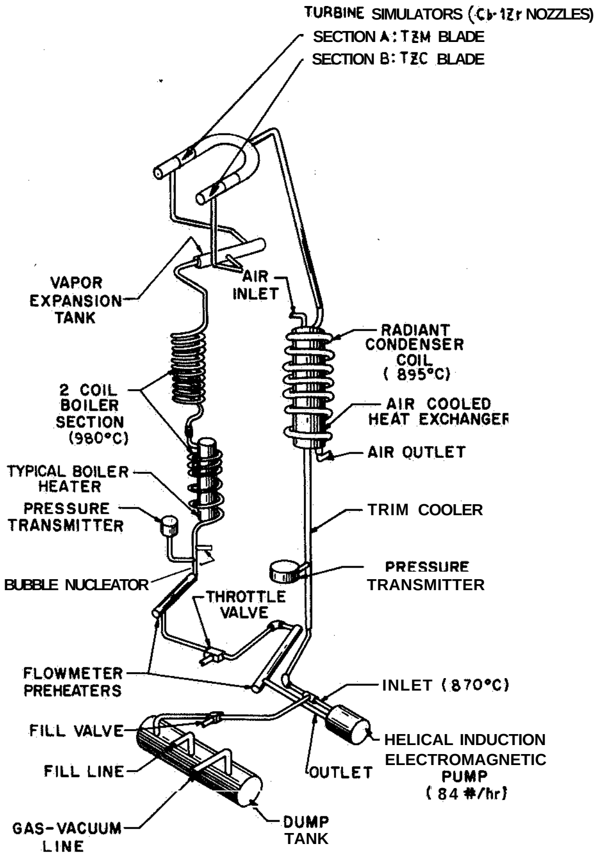

Fig. 2. Brookhaven Forced-Circulation Loop Operated with Boiling Cesium. Ref: A. Romano, A. Fleitman, and C. Klamut, The Behavior of Refractory Metals and Alloys in Boiling Sodium and Other Boiling Alkali Metals, BNL-10723, Brookhaven National Laboratory (1966).

The Nb-1% Zr forced-circulation loop containing boiling cesium that was operated by Aerojet General Nucleonics[25] was stable for 2014 hr with the cesium boiling and condensing at 1850°F. The pertinent operating conditions were:

Boiling temperature, °F	1850
Condensing temperature, "F	1850
Vapor quality, %	10 ± 3
Cesium flow rate, gpm (lb/hr)	0.84 (693)
Cold-leg temperature, °F	700
Power, kw	
To preheater	6.3
To boiler	8.5 to 9.6
Test duration, hr	2014

Oxygen content of the cesium increased from <10 ppm before the test to 57 ± 10 ppm at the conclusion of the test (method of analysis was not specified).

The loop did not contain nozzle and companion blade specimens but was designed to provide high-velocity vapor in various regions. Posttest examination revealed no corrosion of the loop piping and no mass transfer effects.

CORROSION OF MISCELLANEOUS MATERIALS

Static capsule tests in cesium liquid and vapor have been conducted on various materials other than those discussed above. Included in these are zirconium and hafnium at 1600°F for 720 hr (ref. 26); Ti–6% Al–4% V (ref. 27) at 750°F for 500 hr in liquid cesium; as well as rhodium, rhenium, vanadium, and palladium at 1380°F for 500 hr (ref. 28); and titanium at 1052°F for 10,000 hr (ref. 29) in cesium vapor. With the exceptions of vanadium, which became embrittled owing to oxygen pickup, and titanium, which appeared tarnished after the test, none of these materials was attacked by cesium. When rhenium was tested in cesium vapor contained in TZM capsules[30] it was found to be unattacked at 2800°F after 1000 hr but mass transfer of molybdenum to the rhenium occurred after 1000 hr at 3100 and 3400°F.

Tepper and Greer have investigated the compatibility of Haynes alloy No. 25 (50% Co–20% Cr–15% W–10% Ni–3% Fe–1% Si–1% Mo) under both static[31]

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[26] W. T. Chandler and N. J. Hoffman, Effects of Liquid and Vapor Cesium on Container Metals, Report No. ASD-TDR-62-965, Rocketdyne Division of North American Aviation, Inc. (March 1963).

[27] P. M. Winslow, Synopsis of Cesium Compatibility Studies, CONF-650411, p. 334 (April 1965).

[28] W. B. Hall and S. W. Kessler, Cesium Compatibility of Thermionic Converter Structural Materials, N65-33774, Radio Corporation of America (1963).

[29] F. Hargreaves, G.T.J. Mayo, and A. G. Thomas, "A Study of the Long-Term Compatibility of Thermionic Converter Materials with Cesium," J. Nucl. Mater. 18, 212–18 (1966).

[30] J. A. DeMastry and N. M. Griesenauer, Investigation of High Temperature Refractory Metals and Alloys for Thermionic Converters, AFAPL-TR-65-29 Battelle Memorial Institute (April 1965).

[31] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, ASD-TDR-63-824, Part I, MSA Research Corporation (September 1963).

and refluxing conditions[32,33] at 1800°F. There was no evidence of physical change in any of these tests and no evidence for any greater attack under refluxing conditions than under static conditions.

Finally, it should be pointed out that because cesium-plasma nuclear thermionic converters contain ceramic construction materials, several investigators[28,29,34-37] have looked at the compatibility of cesium vapor with alumina, beryllia, sapphire, and other ceramic materials. Thermionic diode development work has also led to studies of the compatibility of cesium vapor with copper, gold, silver, platinum, and other metals, which may be of use as metallizing and brazing components.[28,29,34-37] Since this report is concerned primarily with structural materials, these studies will not be further discussed.

EFFECTS ON MECHANICAL PROPERTIES

Essentially no data have been reported concerning the effect of cesium on high-temperature mechanical properties, Levinson,[38] however, has conducted an extensive program of low-temperature tensile and bend tests on ceramics and metals in cesium liquid as well as vapor. The effects of

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[32] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, Report No. AFML-TR-64-327, MSA Research Corporation (November 1964).

[33] F. Tepper and J. Greer, Factors Affecting the Compatibility of Liquid Cesium with Containment Metals, CONF-650411, p. 323, (April 1965).

[34] J. M. Lamberti and N. T. Saunders, Compatibility of Cesium Vapor with Selected Materials at Temperatures to 1200°F, NASA-TN-D1739, NASA Lewis Research Center (August 1963).

[35] R. G. Smith ~~et al.~~, "A Study of the Compatibility of Thermionic Converter Materials with Cesium," J. Nucl. Mater. 10 191-200 (1963).

[36] M. J. Slivka, "A Study of Cesium Vapor Attack on Thermionic Converter Construction Materials," Advan. Energy Conversion 3, 157-66 (1963).

[37] E. S. Keddy, Compatibility Evaluation of Materials with Cesium, LAMS-2948 (October 1963).

[38] D. W. Levinson, Stress-Dependent Interactions Between Cesium and Other Materials, IITRI-B215-22, Illinois Institute of Technology Research Institute (November 1964).

interest were those associated with the instant presence of cesium at the specimen surface rather than those associated with longer term effects of corrosion.

In particular the studies were designed to evaluate the effects of cesium on grain boundary decohesion, a classic stress corrosion effect notably exemplified in mercury-brass couples. Levinson's studies, which, were conducted at 86°F, suggest that exposure to cesium (both liquid and vapor) can lead to reductions in ductility and yield stress. The tensile properties of the stainless steels tested (types 302 and 430) were affected as shown in Fig. 3. It is interesting to note that, whereas the tensile properties of type 302 stainless steel are relatively unaffected by cesium when the material is in the cold-worked condition, these properties are significantly reduced when tested in cesium after annealing the cold-worked material. Of the refractory metals, only the tensile properties of molybdenum were found to be affected. This is shown in Fig. 4.

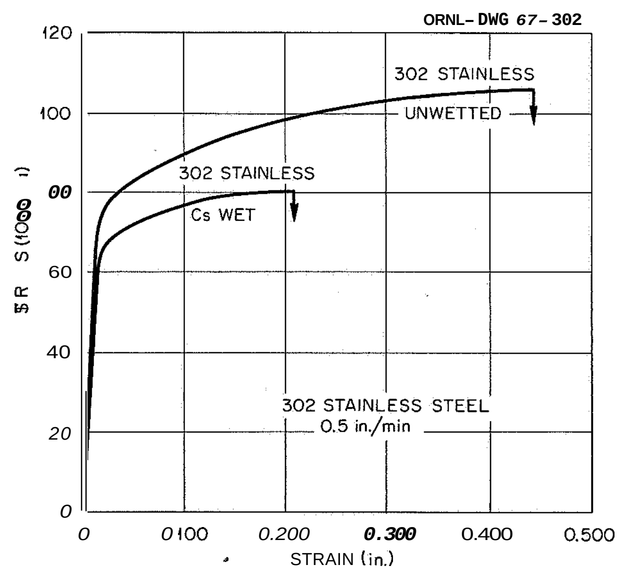

Fig. 3. Stress-Strain Curves for Type 302 Stainless Steel. Ref: D. W. Levinson, <u>Stress-Dependent Interactions Between Cesium and Other Materials</u>, IITRI-B215-22, Illinois Institute of Technology Research Institute (November 1964).

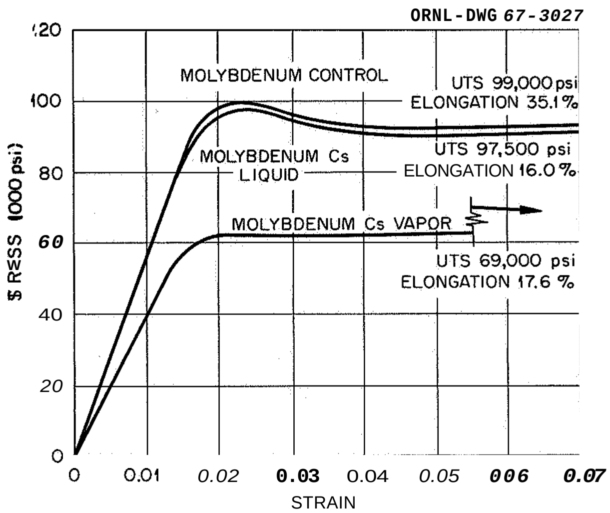

Fig. 4. Stress-Strain Behavior of Molybdenum in Cesium Vapor and Liquid. Ref: D. W. Levinson, Stress-Dependent Interactions Between Cesium and Other Materials, IITRI-B215-22, Illinois Institute of Technology Research Institute (November 1964).

Several materials, including 4340 steels, Ni-Span C, titanium alloys, niobium, and tantalum, were adversely affected by liquid cesium in dynamic bending at 86°F. These tests were conducted by coating the specimens with cesium prior to testing and comparing the results with noncoated specimens. Static bend tests were also conducted for 1000 hr at 86°F, but no instance of static fatigue was observed.

The authors pointed out that liquid metal embrittlement of this type is usually associated with a ductile-to-brittle transition temperature above which grain boundary decohesion is no longer detected. No transition temperatures were determined by Levinson[38] for the alloys tested; however, the actual service temperatures would probably be above the transition temperatures if the systems behaved in typical fashion.

DISCUSSION AND CONCLUSIONS

As in the case of rubidium, the corrosion properties of cesium have received only cursory study, and certainly the volume of compatibility data available today is but a small fraction of that existing for either sodium or potassium.[39] Unfortunately, a considerable proportion of the studies of cesium also have largely been pursued in the context of screening programs which provide only a gross indication of corrosion effects (i.e. light attack or heavy attack). Some of the earlier cesium compatibility tests showed inordinately high corrosion rates both for conventional and refractory metal systems. Recent data, in contrast, show corrosion results similar to those found for potassium, indicating that the early results were strongly influenced by impurities in the cesium. From what is now known from potassium and sodium studies, oxygen was probably the responsible impurity.

Sufficient corrosion data are now available to confirm that the solubilities of refractory metals in cesium are of the same low order as found in the more extensive studies of sodium and potassium. As in the case of these latter metals, the corrosivity of cesium is intimately related to its oxygen content, and, like potassium, the primary corrosion effects can be expected to be associated with partitioning of the interstitial impurities and transport of these impurities between zones of unlike temperature.

Although the corrosion data for cesium are nowhere so extensive as for potassium, our understanding of the behavior of cesium, in the writers' opinion, is at a stage where further simple screening tests can afford little new or useful information. Capsule tests, despite the shortcomings in chemical analysis, have verified that the corrosion properties of cesium, like those of sodium or potassium, are intimately associated with the effects of interstitial impurities and that, if these impurities are kept at low levels, corrosion studies of conventional and refractory metals give results that are qualitatively the same as for sodium and potassium.

**For information on potassium the reader is referred to two recent Publications which reviewed the compatibility of potassium with refractory alloys and conventional alloys: J. H. DeVan, A. P. Litman, J. R. DiStefano, and C. E. Sessions, Lithium and Potassium Corrosion Studies with Refractory Metals, ORNL-TM-1673, Oak Ridge National Laboratory (December 1966); and J. H. DeVan, Compatibility of Potassium with Structural Materials, ORNL-TM-1361, Oak Ridge National Laboratory (April 1966). (CONFIDENTIAL)

The next step in developing the technology of cesium, therefore, should logically define the specific effects of impurities on corrosion and examine the purity problems and corrosion behavior of cesium under environmental and boiling conditions which accurately simulate the fluid velocities, heat fluxes, surface-to-volume ratios, temperature distributions, and other conditions typical of the desired Rankine-cycle space-power plant.

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