WORK FUNCTION DETERMINATION OF PROMISING ELECTRODE MATERIALS FOR THERMIONIC ENERGY CONVERTERS

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1 - FOREWORD

Part of the work presented in this report is the result of a combined effort between E. K. Storms and S. R. Skaggs at Los Alamos Scientific Laboratories and Arizona State University. Carbide sample fabrication and mass spectrometry has been done at Los Alamos.

2 - SUMMARY

The work function determinations of candidate materials for low temperature (1400°K) thermionics through vacuum emission tests are discussed. Two systems, a vacuum emission test vehicle and a thermionic emission microscope are being used for emission measurements. Some nickel and cobalt based super alloys have been preliminarily examined.

High temperature physical properties and corrosion behavior of some super alloy candidates are presented. The corrosion behavior of sodium is of particular interest since topping cycles might use sodium heat transfer loops.

A Marchuk tube is being designed for plasma discharge studies with the carbide and possibly some super alloy samples. Cesium, inert gas and combinations are planned for the discharge studies.

A series of metal carbides and other alloys are being fabricated and tested in a special high temperature mass spectrometer. This information coupled with work function determinations is being evaluated in an attempt to learn how electron bonding occurs in transition alloys. The results should be directly applicable to tailoring work functions of thermionic electrodes.

3 - HARDWARE DEVELOPMENT AND INSTRUMENTATION

3.1 Vacuum Emission Vehicle - The vacuum emission vehicle developed for taking measurements during this program consists of absorption roughing pumps, titanium sublimation intermediate pumping and 140 l/per sec noble gas vac-ion pumping. Samples are heated by electron bombardment from a high temperature counter-wound tungsten filament. Sample temperatures are measured with a micro-optical pyrometer, viewing a 10 to 1 depth to diameter hohlraum. The electron collector is of a plane 1/2 inch diameter radiation cooled molybdenum electrode. A large molybdenum guard ring is concentric with the collector, with a 10 mil spacing.

The vacuum system currently consists of a 12 inch diameter, 18 inch high pyrex tube, which has viton gaskets for sealing at each end. Pressures obtainable with this system have been consistently in the 10^{-6} to 10^{-7} torr range. Pressures in this range have been found to be unacceptably high when measuring the emission from super alloy samples. The current densities from the super alloy samples at the low temperatures in the range from 1000°K to 1200°K have been found to be quite low, and pressures in the 10^{-7} to 10^{-6} torr range appeared to be interferring with the electrical measurements. In order to obtain pressures in the range of 10^{-10} torr which we feel are essential for emission measurements in the low temperature range, a custom bell jar has been designed and ordered from Varian. The bell jar is stainless steel with a 12 inch female wheeler flange and clamps which mate to the top of the existing vacuum system. The bell jar is fitted with a sapphire window for hohlraum viewing and a rotary feed through will supply a shield to cover the sapphire window when readings are not being made. A second large 4 inch view port will also be put on the bell jar for viewing the inside of the system. The bell jar is due for delivery in 3 to 4 weeks.

Two vacuum emission gantries are available for a sample test. The system currently being used which was shown in Figure 1 dissipates heat from the collector and guard ring by radiative fins. One drawback with the use of this system is that the spacing between the emitter and the collector must be determined by first setting it at some specified value and then determining the spacing at temperature by calculation of the growth of various parts of the sample holder by knowledge of the temperature coefficient of expansion. The inter-electrode spacing information is required if one is to plot the log of the current density vs. the root of the field. This must be done if comparisons with theoretical curves are to be used. The work function can be determined accurately by plotting the log of the current density vs. the root of the applied voltage.

A second method of cooling the collector and guard ring assembly is by active cooling with transformer oil. It was necessary to install stainless steel bellows between the vacuum feed throughs and the collector and the guard ring. The stainless steel bellows were braised to copper tubes and the system eventually developed leaks. It was determined that the leaks were the result of galvanic corrosion. The stainless steel bellows have been eliminated in favor of copper and the leak problem has been eliminated.

When it is desirable to know the inter-electrode spacing at temperature, the second system is desirable since it also has a mechanical

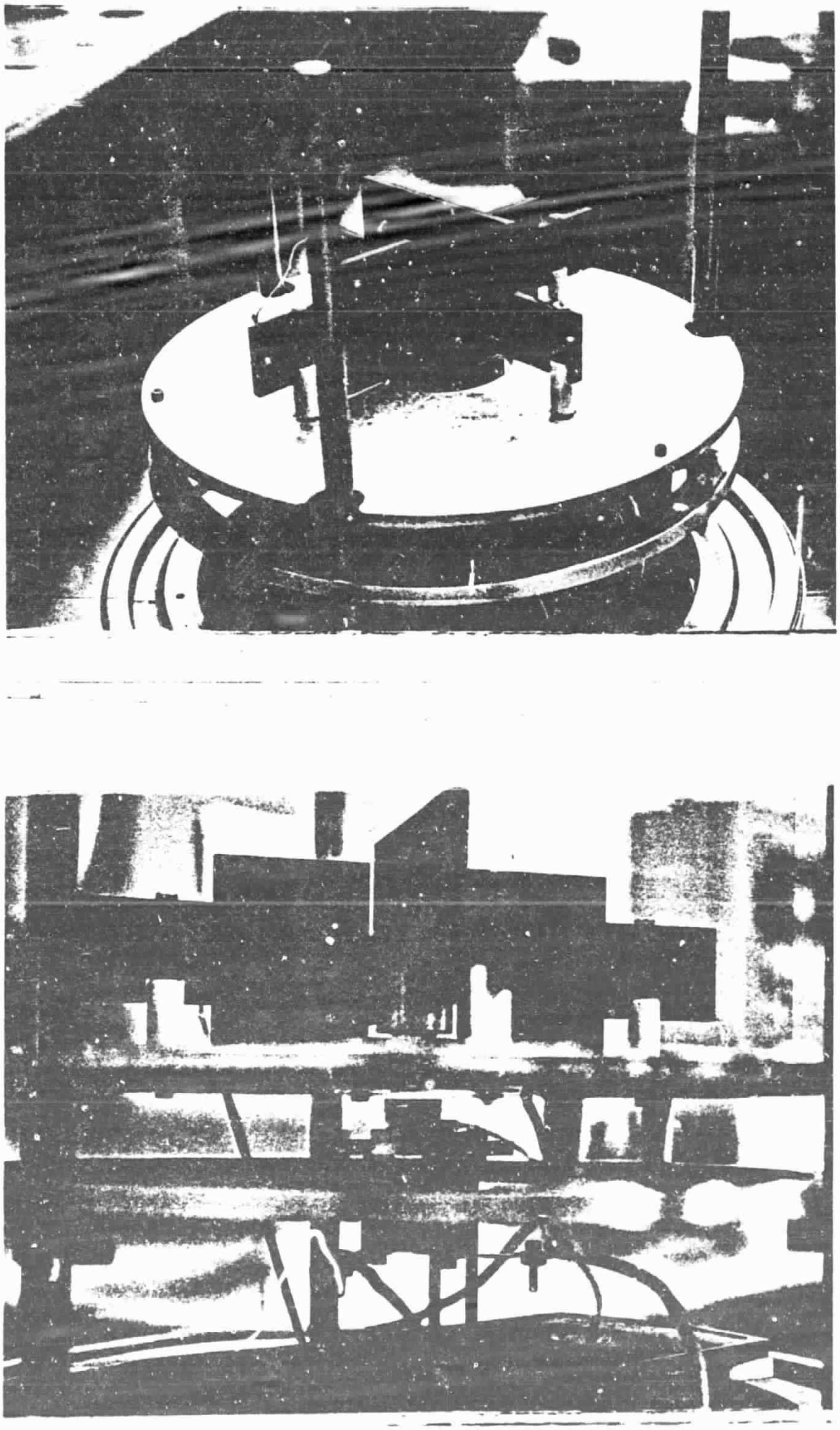

Fig. 1. Vacuum Emission Test Set Up

calibrated linear motion feed through. The feed through drives the emitter while the collector and guard ring are held in a fixed position. The inter-electrode spacing at temperature can be determined by first shorting the emitter to the collector and then driving the emitter away from the collector some distance which can be accurately determined from the calibrated linear motion feed through. The emitter does not actually have to touch the collector to establish the shorted condition. To prevent the collector surface from touching the sample, a shimstock of known thickness is braised to the guard ring and this is where contact takes place.

A polycrystalline molybdenum sample which has a documented work function of 4.48 electron volts at about 1789°K has been used as a standard sample in order to check out our system electronics. (Refs. 1, 2) Figure 2 shows two Schottky plots for the standard polycrystalline sample being used in the vacuum emission vehicle. The work function at a variety of temperatures has previously been reported in the literature. (Ref. 1) The sample was vacuum heated at 2323°K for over 16 hours to provide for grain growth and to stabilize the structure. The results shown in Figure 2 confirm the operation of the present emission system through the comparison with previous measurements on another system.

Problems that have arisen in attempts to measure accurately the emission from super alloys has been, first of all, that the evaporation rates are too high at reasonable temperatures, 1200°K to 1400°K and that at lower temperatures the current levels are so low that the measurements are being made very nearly in the noise levels of the electronic system.

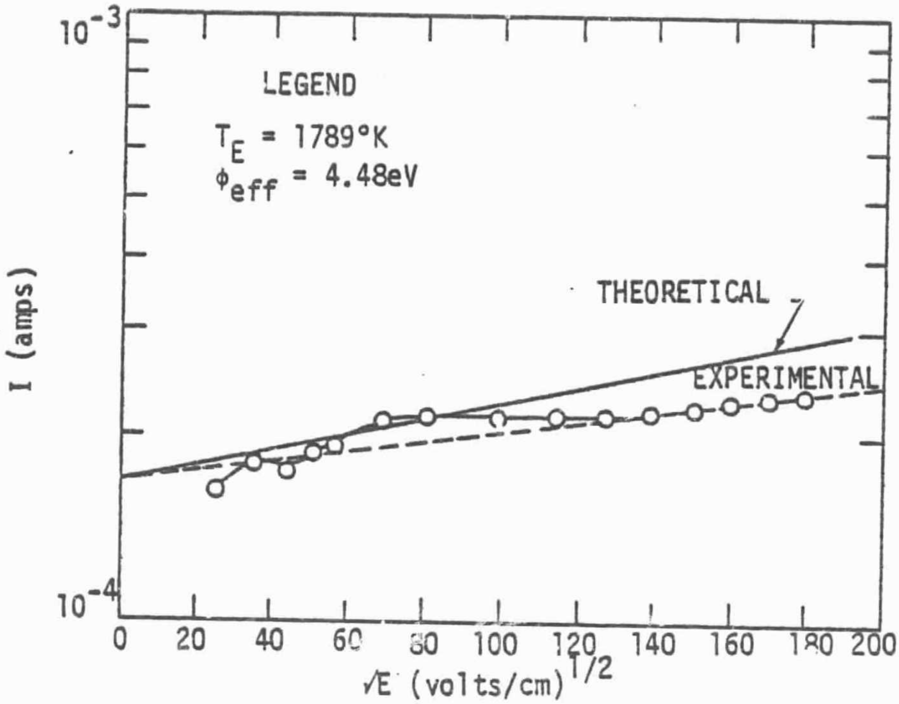

Figure 2A. Ref. 1,2.

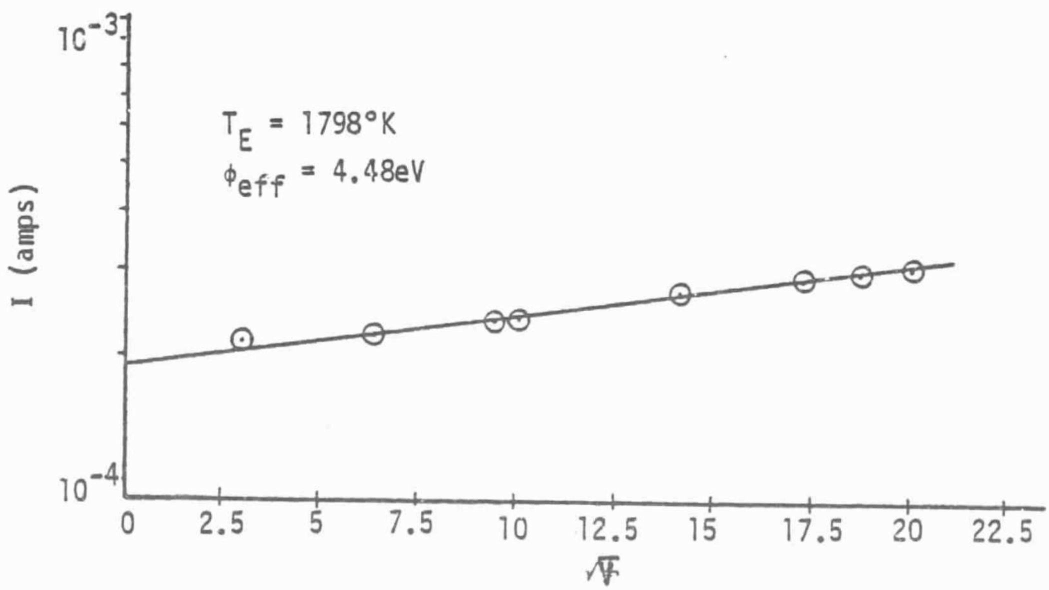

Figure 2B. Present Measurement

Figure 2. Schottky Plot of Polycrystalline Molybdenum Sample Determined from Vacuum Emission Vehicle Measurements.

It has also been determined that the pressures obtainable with the viton gasket bell jar, pressures on the order of 10^{-6} torr, are too high and appear to be interferring with the electrical measurements when the currents are in the 10^{-8} to 10^{-9} amp range.

A problem which has been encountered in the radiatively cooled collector-guard ring system is that the collector and guard ring short due to thermal distortions in the system. There is a 10 mil gap between the emitter and collector and unless the system is perfectly aligned at high temperatures, shorting occurs between the collector and guard ring. The elimination of the shorting problem is primarily one of repeated tedious re-alignment and re-heating of the system to obtain the stable position. A one-half inch thick, high purity alumina ring has been inserted between the top of the guard ring and the top portion of the collector in order to obtain a region of contact between the two. This has eased the alignment problem without reducing our ability to null current flow between collector and guard ring.

3.2 Thermionic Emission Microscope - A thermionic emission microscope will be utilized when appropriate to determine the fine structure of surfaces. The work function of individual grains within the sample can be determined with the microscope. The system is completely bakable and maintains the pressure at 10^{-9} to 10^{-10} torr. Emission micrographs of surfaces in situate temperature are obtained from a phosphorus screen at the end of the microscope. Qualitative measurements of emission from which work functions can be calculated are also available through a faraday cage.

The electrical feed through from the power supply to the vac-ion pump for the microscope has become inoperable because of electrochemical corrosion. Part of the feed through has been obtained and the system will be made operable again when a connector is received from Varian. The system should be operable again within 2 to 3 weeks.

3.3 Los Alamos Facilities - The experimental facilities available at Los Alamos Scientific Laboratories include the capability for the preparation of pure materials having the proper compositions. Characterization of these materials before and after evaluation is available using chemical and neutronic division analysis by x-ray and neutron defraction, by scanning electron microscope, and by metallographic examination. A unique mass spectrometer is located at LASL which permits the measurement of vapor pressure and diffusion rates over a very wide range of temperatures.

4 - SUPER ALLOY EVALUATION

(A bibliography for this section appears at the end of the References.)

The goal of this part of the program has been to measure the emission from a number of nickel and cobalt based super alloys to determine the effective work function of these alloys through measurements in the vacuum emission test vehicle and thermionic emission microscope. The compositions of a number of candidates plus a few other alloys are given in Table 1.

4.1 Mass Spectrometer Evaporation Measurements.

Two problems have been encountered in making vacuum emission measurements. The first involves the very high vaporization rates of some of the elements of which the alloys fabricated. The second involves the very low current densities which are obtainable from these materials in the temperature range of interest, 1000°K to 1400°K. The vaporization problem has been identified and discussed by Mr. Jim Morris at Lewis Research Center at the National Thermionics Meetings and also in informal discussions. The experience in this laboratory is that above 1200°K, very heavy deposits of evaporated material have been found on the collector and guard ring. A few selected super alloys have been sent to LASL for examination in the mass spectrometer. In this examination the samples will be held at the operational temperature while an evaluation is made by mass spectrometry of the elements which are being evaporated and the rate at which they are being evaporated. Incoloy 800, Hastelloy X, Haynes 25, Inconel 617 and other alloys will be examined in this manner.

The Incoloy 800 has been evaluated in the mass spectrometer. Vapor species between mass 24 and 80 were measured. In this range, Cr, Mu, Fe,

Table 1. COMPOSITIONS OF ALLOYS STUDIED FOR THERMIONIC ELECTRODES AND/OR FOR NA CORROSION CHARACTERISTICS

	Nominal Composition, %														
Alloy	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Ti	Al	B	Zr	Fe	Other
Incoloy 800	0.05	0.75	0.50	21	32.5	--	--	--	--	0.38	0.38	--	--	46	--
Refractaloy 26	0.03	0.8	1.0	18	38	20	3.2	--	--	2.6	0.2	--	--	16.2	--
Haynes alloy 188 (sheet)	0.08	--	--	22	22	Bal	--	14	--	--	--	--	--	1.5	0.08 La
Hastelloy alloy C	0.08	1.0	1.0	15.5	54.6	2.5	16.0	3.8	--	--	--	--	--	5.5	--
Hastelloy alloy N	0.08	0.8	1.0	7.0	67.9	0.2	16.5	0.5	--	--	--	0.01	--	5.0	0.5 Al + Ti
Hastelloy alloy X	0.15	1.0	1.0	21.8	45.5	2.5	9.0	0.6	--	--	--	--	--	18.5	--
Inconel 601	0.05	0.5	0.25	23	60.5	--	--	--	--	--	1.35	--	--	14.1	0.25 Cu
Inconel 617	0.07	--	--	22.0	54.0	12.5	9.0	--	--	--	1.0	--	--	--	--
Inconel 718	0.04	0.20	0.30	18.6	52.9	--	3.1	--	5.0	0.9	0.4	--	--	18.5	--
René 41	0.09	--	--	19	55.3	11	10	--	--	3.1	1.5	0.010	--	--	--
TAZ-8A	0.125	--	--	6.0	68.4	--	4.0	4.0	2.5	--	6.0	0.004	1.0	--	8.0 Ta
TAZ-8B	0.125	--	--	6	64.4	5.0	4.0	4.0	1.5	--	6.0	0.004	1.0	--	8.0 Ta
TRW VI A	0.13	--	--	6	61.6	7.5	2.0	5.8	0.5	1.0	5.4	0.02	0.13	--	9.0 Ta, 0.5 Re, 0.43 Hf
WAZ-20	0.15	--	--	--	73.7	--	--	18.5	--	--	6.2	--	1.5	--	--
Stainless Steel 304	0.08	2.0	1.0	19	10	--	--	--	--	--	--	--	--	67.8	0.045 P, 0.030 S
Stainless Steel 316	0.08	2.0	1.0	17	12	--	2.5	--	--	--	--	--	--	65.5	--

Ni and Cu were found to be present in the vapor. The composition of Incoloy 800 is given in Table 1. C, Si, Ti, and Al have mass numbers less than 24. Cu appears, apparently as an impurity. The percent of total pressure after various heating times is given at two interpolated temperatures in Table 2. Measurements were made between 1300°K and 1547°K.

Table 2. Mass Spectrometer Determination of Vapor Composition of Incoloy 800.

Vapor Composition: % of total pressure

T°K	Cr	Mn	Fe	Ni
		Initial		
1300	46	45	9	-
1500	56	15	28	-
		Heated at ∿ 1525K for 144m		
1300	48	31	21	-
1500	45	9	45	+ trace Ni and Cu
		Heated > 1600K for 35 h		
1300	54	18	25	3
1500	50	7	36	7

Evaporation at high temperatures tends to produce a surface which is richer in Ni and poorer in Mn than the bulk material. Also the surface will become richer in Fe compared to Cr. The total pressure decreases as evaporation proceeds. The amount of Ni being lost is lower than would be expected relative to pure element vapor pressure charts. The Ni appears to be bound tight in the lattice, possible partly with Al and one of the other lighter elements. Further analyses on the other mentioned alloys will continue in order to try to obtain more complete trends.

The spectrometer was calibrated with Fe and the resulting activities are plotted in Figures 3 and 4. The behavior of Fe can be treated, but the absolute activities of Mn, Cr and Ni are less certain, although the temperature variations should be accurate. Apparently, the activity of Fe is unity below 1430°K and drops rapidly above this temperature. Since other components behave in a similar way, compound formation may occur at a higher temperature, or a strongly enhanced mutual soluability may exist.

4.2 High Temperature Properties of Some Super Alloy and Other Alloys

Thermionic topping of large power installations such as a conventional steam power plant will probably require the use of relatively low cost materials. With this in mind super alloys and relatively low cost carbides and borides are being evaluated for electrode applications. The vapor pressure problem was discussed in the last section. The high temperature (1400°K) predicted for such applications also demands that the strength and corrosion characteristics of the electrodes be suitable for long life. A number of strength characteristics are examined in the next subsection, 4.2.1. The electrodes will probably be exposed to alkali metals, cesium on the convertes side, and possibly a heat transfer medium such as sodium on the opposite side. For economy and manufacturing convenience, it

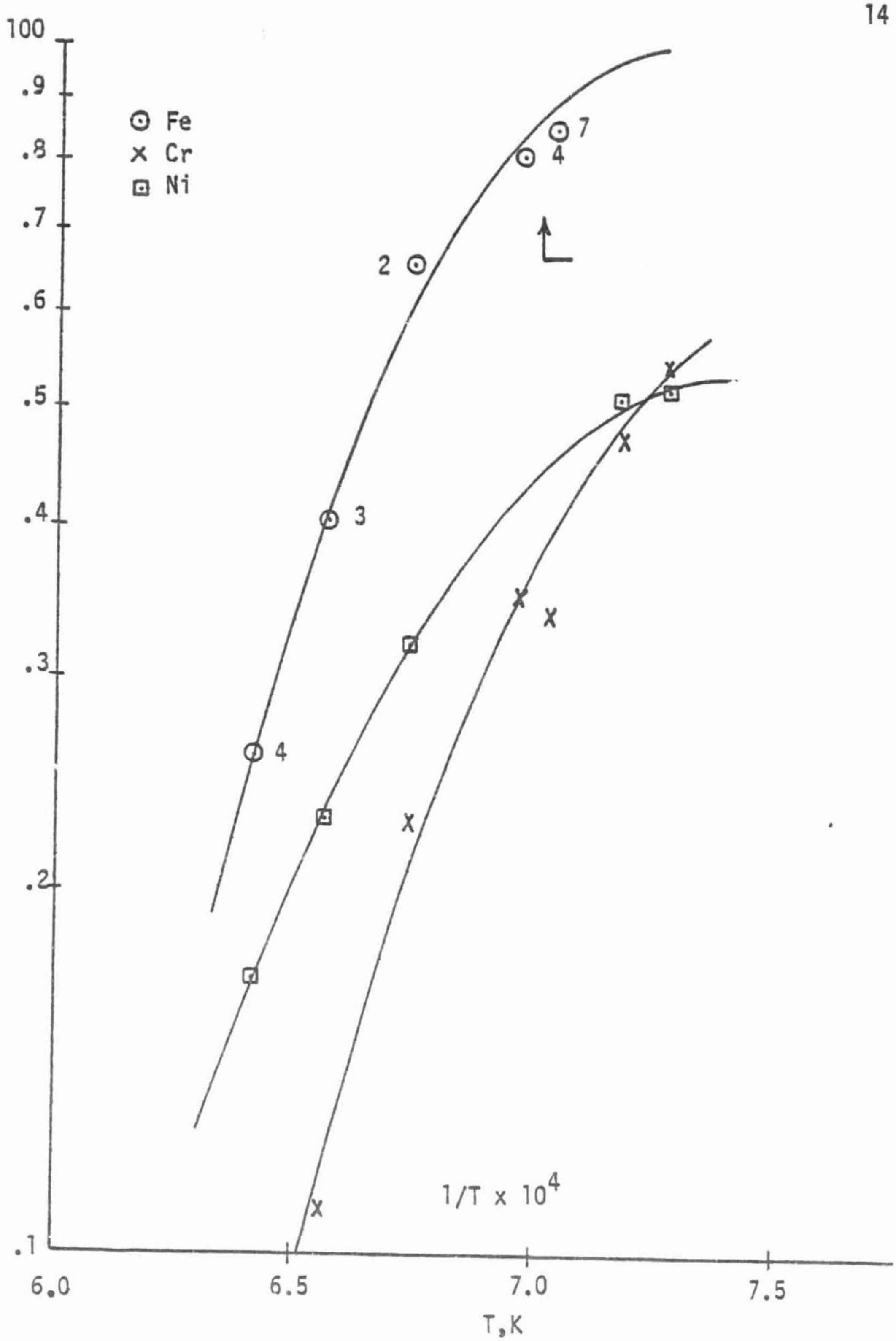

Figure 3. Activity v.s. Temperature for Incoloy 800 after 35 hours at 1600°K.

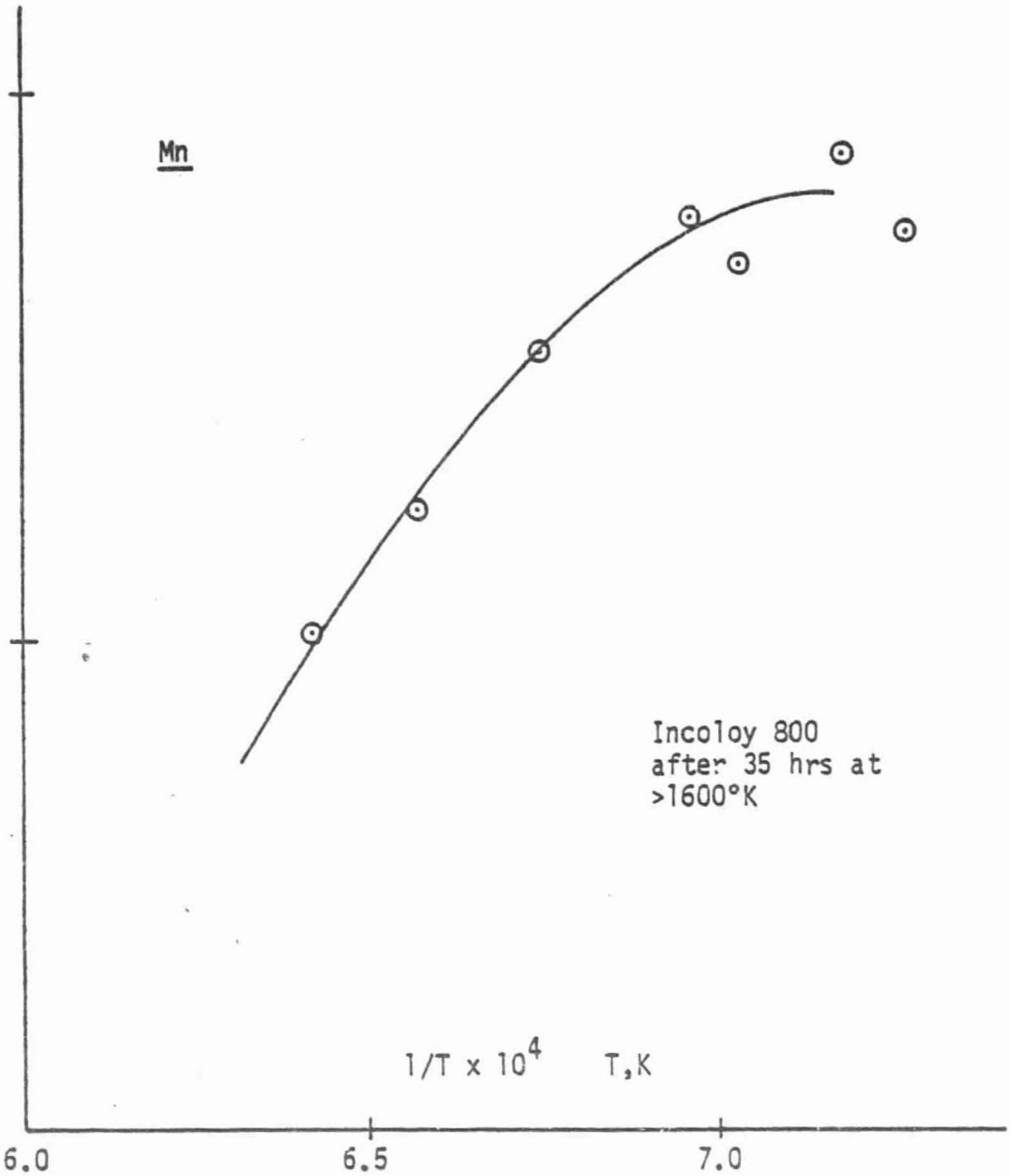

Figure 4. Activity v.s. Temperature for Incoloy 800 after 35 hours at 1600°K.

would be desirable to have a single material for the heat transfer medium and for the emitter. This would also be true on the collector side. In subsection 4.2.2 the compatibility of the selected alloys will be evaluated, primarily with sodium. Extensive literature is available regarding the compatibility of sodium with some materials, primarily austenitic stainless steels. These results have been obtained for the Liquid Metal Fast Bruder Reactor programs. Stainless steels have been tentatively selected for the heat transfer loops with sodium, but because of the limited strength at predicted high temperature applications, super alloys are now being promoted and entered into the strength and corrosion experiments being conducted in a number of laboratories.

4.2.1 High Temperature Mechanical Properties

Tables 3 and 4 list a number of mechanical properties for the alloys, at 1000°K in Table 3 and 4 at 1400°K in Table 4 except where data at other temperatures is specifically noted. Comparisons are difficult in many cases because the conditions of data acquisition are not exact. Relative values of strength can be seen in many cases through. Rene 41, the TAZ, TRW, WAZ and Refractalloy 26 alloys have superior high temperature mechanical properties. Some considerations such as the fabrication techniques applicable to these materials is important for practical applications. TAZ, WAZ and TRW alloys contain a reasonable percentage of tungsten, and are formed by arc melt castings. These materials along with Haynes 188 and Refractalloy 26 are difficult to machine and must be ground or electron discharge machined in many cases. The Inconel and Hastelloy series are more amenable to cost effective machining.

Table 3. NOMINAL ELEVATED TEMP. STR. OF CONTAINMENT ALLOY AT 1000°K

Alloy	Tensile Strength 1000 psi	Yield Strength 1000 psi	Stress-to-rupture in 1000 hr. 1000 psi	Creep Strength 1%, 1000 hr. 1000 psi
304 S.S.	30	20	3	1.2
316 S.S.	30	20	8	2.8
Hastelloy C	65	40	25	
Hastelloy N	56	29.5	5	
Hastelloy X	50	30	10	7.4
Inconel 601	55	25	12	
Inconel 617	60	24	28	5
Inconel 718	105	100	86	14
Rene 41	130	112	50	18.5 @ .2% 100 hrs.
TAZ 8A	130			
TAZ-8B	142			
TRW VIA			95	
WAZ-20				
Incoloy 800	35	24	6	5.5
Haynes 188	80	41		13.5
Haynes 25	50	35	17	9.0
Refractaloy 26	100	90	30	37
Nickel 270	7	2.5		5 @ 1% 1000 hrs.

Table 4. NOMINAL ELEVATED TEMP. STRENGTH OF CANDIDATE ALLOYS AT 1400°K

Alloy	Tensile Strength 1000 psi	Yield Strength 1000 psi	Stress-to-rupture in 1000 hr. 1000 psi	Electrical Resistivity Micro-ohm-cm	
				293°K	1400°K
304 S.S.	9 (1300°K)	10 (1200°K)	1.6 (1300°K)	75	
316 S.S.	5	20 (1200°K)	1.2 (1300°K)	74	
Hastelloy C	16		5 (1250°K)	129	
Hastelloy N	34 (1250°K)	25.9 (1250°K)			
Hastelloy X	10	10	0.9	118	
Inconel 601	5	5	1	119	130
Inconel 617			1.7		117
Inconel 718	10	10		124	135
Rene 41	40 (1300°K)	38 (1300°K)	20 (1250°K)		
TAZ 8A	8		9.6 (100 hr.)		
TAZ-8B	12		11.5 (100 hr.)		
TRW VIA			8		
WAZ-20			11.5 (100 hr.)		
Incoloy 800			1.4 (1255°K)	99	131
Haynes 188	20		2.2 (100 hr.)	92	
Haynes 25	12	12	4 (1255°K)	87	100 (1361°K)
Refractaloy 26	40 (1300°K)	40 (1300°K)			
Nickel 270	4 (1255°K)	2 (1255°K)		16	51

The overall strength characteristics of the alloys must be matched to the expected loads in the system and designed to minimize cost. Creep strength is very important for long term applications, and at 1400°K, little creep data is available for many of the materials.

4.2.2 Alkali Metal Corrosion

The alkali metal environment must be evaluated for a number of different corrosion phenomenon.

- dissolution of containment (leaching)
- embrittlement (grain, grain boundary)
- mass transfer
- erosion (flow velocity dependence)
- electrochemical
- galvanic (dissimilar metals)
- precipitation inducement
- stress corrosion

Some important parameters influencing some of the above mechanisms are:

- maximum system temperature
- maximum temperature differentials
- alkali metal oxide levels (and other impurities)
- alkali metal flow velvity
- heat flux

As stated considerable information is available for some stainless steels. A summary of some static corrosion tests in sodium is presented in Table 5. In static systems the corrosion appears to be limited,

Table 5. STATIC CORROSION IN SODIUM, 400 hr., 1273°K

METAL	INTERGRANULAR PENETRATION (in.)	SUBSURFACE VOIDS (in.)	DECARBURIZATION (in.)	GENERAL CORROSION
304 S.S.	0.000	0.003	--	Some surface voids
316 S.S./ 347 S.S.	0.000	0.002	0.004	Some surface voids
Inconel	0.000	0.0005	0.001	Very shallow attack
80 Ni - 20 Cr	0.000	0.000	0.000	None observed
Nickel	0.000	0.000	0.000	None observed

although the test duration of 400 hr. is not very substantial. The sodium corrosion of austenitic stainless steel for pumped loop experiments is given in Table 6. A verbal summary for 316 s.s. and for 304 s.s. from the experiments is that they can be used up to 850°K in sodium flow, provided that the oxygen and carbon impurity levels in the sodium are kept low. Transfer of interstitial elements to and from sodium exposed austenitic surfaces is possible in systems being considered here. When austenitic and ferritic steels are commonly exposed to the sodium environment migration of carbon can occur resulting in a decrease in strength of the carbon depleted material while embrittling the carbon rich system. In a pure 304 s.s., sodium flow system, acceptable performance appears to be obtainable as long as the oxygen level in the sodium is maintained to a few parts per million. 316 s.s. has characteristics similar to 304 s.s. Table 6 provides some data from various experiments.

Table 7 provides some data from the literature for sodium corrosion of super alloys. Except at the low temperature, 1088°K with no ΔT, corrosion appears. The oxygen level was not available in these experiments nor were the exact flow rates.

Table 8 summarizes some sodium heat pipe results from the literature. The oxygen contents of the sodium, and flow rates were again not available. The reports indicate that in most cases, the heat pipes did not fail. The studies in general, do not report post test analyses to provide data on corrosion that has taken place. Thus, it is impossible in most cases to make any predictions for long term behavior. Since heat pipes are important candidates for many thermionic applications, it will be necessary

Table 6. SODIUM CORROSION OF AUSTENITIC STAINLESS STEEL FROM LITERATURE (DATA)

(Pumped Loop Experiments)

SITE	MATERIAL	T_{max} °K	ΔT °K	V fps	Ox. ppm	TIME	CORROSION
G.E.	347 S.S.	660	(2)	∿10	220	3 years	None
LASL	316 S.S.	866	134	∿ 5	Low	18 months	T.S., Hardness increase
Babcock & Wilson	304 S.S.	866	0	∿55	Low	1,000 hrs.	Little attack
Babcock & Wilson	316 S.S.	866	0	∿55	Low	1,000 hrs.	Little attack
G.E. Vallecitos	316 S.S.	866	134	∿30	10	30,000 hrs.	Weight loss, intergranular penetration, carbon transport, surface transformation.
Soviet	18 Cr	894	--	--	Var.	5,500 hrs.	Corrosion attack; mechanical property changes.
ORNL ORNL ORNL	316 S.S. 304 S.S. 347 S.S.	1089 1089 1089	166 166 166	-- -- --	-- -- --	1,000 hrs. 1,000 hrs. 1,000 hrs.	Intergranular penetration 2 mils to 5 mils. Little mass transfer for 316, 304, and 347.
ORNL	310 S.S.	1089	166	--	--	1,000 hrs.	Intergranular attack, void formation to 13 mils, cold zone deposits.
ORNL	316 S.S.	1171	166	--	--	1,000 hrs.	Hot zone intergranular attack to 2 mils, small voids to 5 mils, cold zone deposit 3→5 mils thick.
ORNL	316 S.S.	1660	--	--	20 30	1,000 hrs.	Hot zone surface attack to 3 mils $\gamma \to \alpha$ transformation to 0.5 mils. Cold zone deposits.

Table 7. SODIUM CORROSION OF Ni and CO BASED ALLOYS FROM LITERATURE (DATA)

(flow systems)

MATERIAL	T_{max} °K	Time hr	ΔT °K	CORROSION
Hastelloy X	1088	1000		None
Hastelloy X	1200	305	361	Hot zone attack, voids intergranular attack
Inconel	1088	1000	167	Hot zone attack, 2 mils Heavy cold zone deposits
Hastelloy W	1088	1000		Ni deposits in cold zone

Table 8. SODIUM HEAT PIPE PERFORMANCE FROM LITERATURE

MANUFACTURER	CONTAINMENT MATERIAL	OPERATING TEMPERATURE	OPERATING TIME (HRS.)	FAILURE MECHANISM
Dynatherm	304 S.S.	923°K	16,500	None
RCA	304 S.S.	1073°K	7,200	--
Xerox/EOS	304 S.S.	1000°K	∿4,000	None
Hughes	304 S.S.	923°K	2,380	--
LERC	304 S.S.	1000°K	--	--
RCA	316 S.S.	1044°K	4,000	--
RCA	(A) Nickel	1073°K	20,000	None
RCA	Hastelloy X	988°K	20,000	--
RCA	Hastelloy X	988°K	8,000	--
BROWN-BOVERI	Nb - 1% Zr	1000°K	28,000	Two leaks (fixed)
LERC	Nb - 1% Zr	1000°K	3,000	--

to obtain more reliable corrosion data in order to design practical systems for long term reliable use.

Table 9 is a summary based upon a general culmination of literature corrosion studies and a qualitative prediction of behavior with temperature, flow rate and oxygen impurities as parameters.

Table 9. RELATIVE CORROSION OF AUSTENITIC STEELS AND SUPER ALLOYS

ALLOY	T °K	VELOCITY	LIFE	(Impurities) OXYGEN	GENERAL ATTACK	STRENGTH
304, 316, 347	850	High	Unlimited	Limited to few ppm	Minimum	Good
304, 316, 347	850 to 950	High	Dependent	Limited to few ppm	Moderate	Moderate
304, 316, 347	1050	Low	Limited	Limited	High	Poor
Super alloys (Ni Based)	<1000	Low	Good	Low	Low	Good
Super alloys (Ni Based)	>1000	Medium	Limited	Low	Several times greater than for stainless Ni leaching	Reduced
Super alloys	950 to 1100	Low	Limited	>20 ppm	Decarburization	Reduced creep strength
Super alloys	950 to 1100	Low	Long	Few ppm	Los attack as long as Oxygen content is low	Good

5 - CARBIDE ALLOYS

A primary portion of the current work is being done in conjunction with Los Alamos Scientific Laboratories. Metal carbides, borides, borocarbides and boronitrides have demonstrated application to very high temperature problems. In these investigations we are attempting to determine how the properties of these materials can be modified and to what extent they can be modified. The general properties which limit the usefulness of a high temperature material are strength, transport properties (including the diffusion and vaporization rates), and reaction rates with other materials or gases in the environment. Measurements will be made of the chemical activity and vapor pressure of the component elements as a function of composition. A special high temperature mass spectrometry system has been developed and tested for making these measurements at Los Alamos. As special candidate electrode materials are found, property measurements will be broadened to include thermal conductivity, thermal expansion and thermionic emission.

The intent of this work is to find the basic relationships between diffusion, work function and bond energy. The materials being studied, binary and ternary systems of the transition metal borides and carbides will be considered for application to thermionics. The relationship between bond energy obtained from vaporization measurements and the work function obtained from thermionic emission will be developed. The overall application of these materials as electrodes for thermionic energy converters will also be determined.

Preliminary work in Russia and Germany have shown that the class of materials to be studied have work functions which can be modified over a wide range. This, combined with good stability at high temperatures, opens new possibilities for the design for more efficient thermionic diodes by combining measurements of the vaporization behavior with maintenance of the work function using the same samples. This provides the unique position, not only to answer immediate practical questions, but to study the relationship between these basic properties.

The first sample shown in Figure 5 is a niobium carbide sample containing .98 to .99 percent carbon. It was hot pressed at 2773°K in a graphite die at 1000 psi. The sample was subsequently ground flat and outgased in vacuum at about 1773°K. The holder shown for the sample consists of a molybdenum base plate, a tantalum heat choke and a tantalum base plate just underneath the sample disk. The tantalum base plate will be heated by electron bombardment and the sample will then be heated by radiation coupling to the tantalum. This sample holder was used specifically so that sample disks could be used interchangeably with the same sample holder. The sample holder fits both of the existing vacuum emission systems and also the thermionic emission microscope. Both vacuum emission measurements and thermionic emission measurements in the thermionic emission microscope will be used to determine the work function and surface characteristics of these samples.

A series of niobium carbide, zirconium carbide and some boride alloys are intended for investigation during the current program. Ternary borocarbides and boronitrides will probably follow the examination of some of the binary alloys.

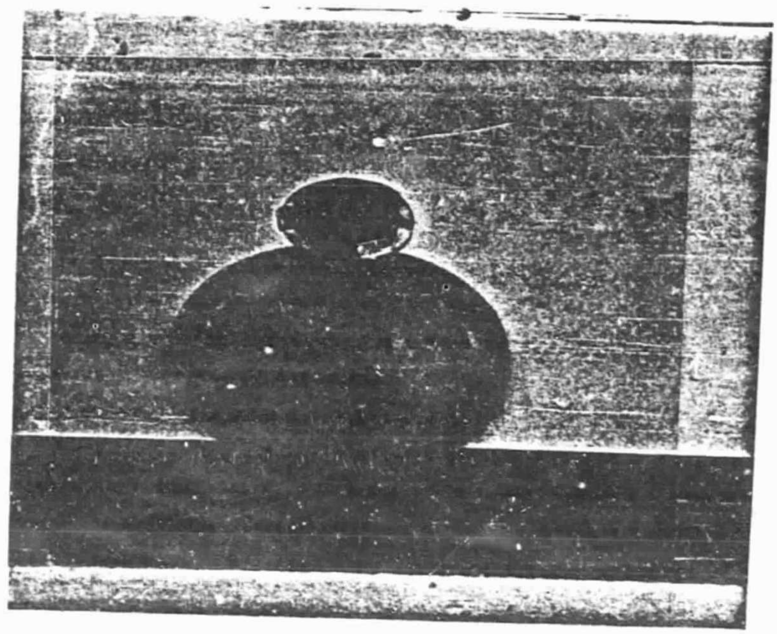

Fig. 5. NbC Test Sample

6 - MEASUREMENT OF GASEOUS EMISSION PROPERTIES USING A MARCHUK TUBE

The electron emission properties of candidate thermionic electrode materials will be investigated in a typical Marchuk experiment. (Refs. 3 and 4.) A glass test vehicle is being designed for these tests. Suitable emitter materials will be used as Langmuir probes in a plasma generated by secondary electrodes.

The Marchuk technique involves a plasma immersion process whereby materials of interest are allowed to emit thermionically into a surrounding plasma. Work functions may thus be measured at various plasma-gas pressures. Typically, wire probes have been utilized, their temperatures being determined by pyrometry at elevated temperatures, and by temperature-resistivity correlations at low temperatures.

A tentative probe design will employ either a button-type emitter, or a wire filament. This configuration will facilitate the use of thermocouples for precise measurement of low temperatures.

The data obtained will be mapped onto a plot of work function versus the ratio of the emitter temperature to the cesium reservoir temperature. Long-term variations in alloy work functions will be investigated. It might be expected that differential thermal segregation of individual grains and evaporation of particular alloying species might cause long-term changes in work functions. Low pressure cesium and inert gases and mixtures of the two are candidates for plasma production.

7 - SUMMARY OF RESULTS

The vacuum emission devices have been operational, although the high vapor pressures of some super alloy elements and low emission current densities at low emitter temperatures, 1200°K - 1400°K, have indicated that further refinements be made. These have included the acquisition of a metal bell jar in order to produce high vacuums, 10^{-9} torr, with an all metal gasketed system. Some of the super alloys appear to be unsatisfactory for thermionic electrodes because of high vapor emission characteristics of some elements such as mangenese. Mass spectrometer evaluations of some high temperature super alloys have confirmed the very high vaporization results of more super alloys are determined, the vaporization trends of the various elements will be evaluated. From these studies it might be possible to choose or design super alloys of particular compositions which might be suitable for thermionic electrodes.

High temperature physical properties including tensile strength, yield strength, stress to rupture, and creep strength have been obtained from the literature for a number of candidate super alloys. The high temperature corrosion behavior of some of these alloys and also of a couple of stainless steels have been obtained from the literature. An important application for low temperature, low cost thermionics is as topping a device for conventional steam power plants. It is probable that sodium could be used as a heat transfer medium from the conbusting gases to the thermionic element. Super alloys might be used both as a thermionic electrode and also as the plumbing for the sodium heat transfer lines. A good deal of information exists in the literature in regard to compatibility of various stainless steels with sodium. Most of the experimental work that is in the literature was produced for the liquid metal fast breeder reactor program. The same corrosion considerations would be necessary in utilizing sodium in thermionic topping, as would be required for the LFMBR programs. Little information currently exists in the literature in regard to the alkali metal compatibility with super alloys. The LFMBR programs are now beginning to examine alkali metal - super alloy compatibilities because the strength of the candidate stainless steels are not sufficient for some projected LFMBR applications. It is very probable that this information could become important to thermionics should such materials be used for thermionic topping. At the present the most important corrosion parameters appear to be the oxygen content of the sodium and the flow rate. The mechanical properties of super alloys must also be evaluated in the sodium atmosphere. At the present little information is available with regard to the behavior of super alloys of alkali metals in general.

One niobium carbide sample has been fabricated by Los Alamos Scientific Laboratories and is now being instrumented for vacuum emission tests at Arizona State University. After preliminary testing is done with this first sample, a series of closely controlled carbon alloys will be prepared by Los Alamos and tested in the mass spectrometer both before and after vacuum emission tests are made for work function determination. The results of these tests will be evaluated in order to try and determine the bonding characteristics of such alloys. If this is understood, it should be possible to tailor the work function of a given thermionic emitter hopefully to a given desired value. The series of other metals including zirconium with carbon, with boron, and possibly borocarbides or boronitrides are intended for investigation during this program.

Plans are underway for the fabrication of the Marchuk tube in order that cesiated emission from the carbide samples and possibly some super alloys can be performed at ASU. These systems have been used successfully in the past and are fairly simple to evaluate, and hopefully can provide a good deal of information.

8 - CONTINUATION PLANS

During the remainder of the current program, the primary tasks which will be pursued are to evaluate the work functions and vaporization characterizations of the chosen carbon, borocarbide or other alloys that are chosen. Activiation energies or vapor pressures will be determined by mass spectrometry at LASL and work functions will be determined at ASU. Vacuum work functions will be determined for all materials. Cesiated emission of some of the alloys will be determined dependent upon the success of fabrication of a Marchuk tube. Other physical properties of the alloys will be determined through thermionic emission microscopy, photomicroscopy, and other techniques. Super alloy or related materials will also be continually investigated, depending upon the results of the vaporization studies. These might also be implemented in a Marchuk tube experiment.

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