VII. POTASSIUM RANKINE SYSTEM MATERIALS TECHNOLOGY

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INTRODUCTION

The discussion of the materials technology for advanced Rankine cycle systems presented herein mainly concerns the working fluid, potassium, and the containment materials, alloys of the refractory metals columbium and tantalum. Some of the problems inherent in the application of these materials to space power systems are presented, and the more significant results of recent materials investigations are summarized.

Before materials are considered in detail, however, the temperature regime of operation of the potassium-Rankine system should be defined. The working fluid can be used as a guide to delimit the temperature regime for the advanced Rankine cycle system. In figure VII-1 the vapor pressure is shown as a function of temperature for several liquid metals of interest: mercury and the alkali metals (cesium, rubidium, potassium, sodium, and lithium). The shaded area to the left is the area of operation of the SNAP-8 mercury system discussed in paper VI; the shaded area on the right is the operational regime of the advanced system discussed herein. The boundaries of the shaded areas are fixed by both system operation and materials considerations. The upper pressure limit, for example, is set by design stress limitations; the lower pressure limit reflects such operational considerations as vapor velocity, pump cavitation, and subcooling. The higher temperature boundary at approximately 2200° F for the advanced system is established by temperature limitations of available refractory alloys. The lower temperature boundary at 1400° F is determined by such operational considerations as optimum radiator temperature and cycle efficiency. Obviously, these maximum temperature and pressure limits can be extended as new materials with improved properties are developed.

There are four common refractory metals that can be considered for use in potassium Rankine systems: tungsten, tantalum, molybdenum, and columbium. Some of the important properties of these metals are listed in table VII-1. Tungsten has the highest melting point (over 6000° F) and columbium the lowest (about 4500° F). Even this temperature, however, is about 2000° F higher than the operating temperatures anticipated in potassium Rankine systems. Columbium has the lowest specific gravity (about the same as common nickel-base superalloys), while tantalum and tungsten are much heavier.

Columbium and tantalum are highly fabricable, ductile metals, while tungsten and molybdenum are relatively brittle, particularly in the welded condition. The poor fabricability of tungsten and molybdenum renders them unsuitable for use as containment materials for the complex

piping systems needed in Rankine systems; thus, columbium and tantalum alloys were selected for this application.

OXIDATION OF COLUMBIUM, TANTALUM, AND THEIR ALLOYS

Although tantalum and columbium alloys appear to be suitable containment materials, their use poses an unusual problem because of their high reactivity with contaminants, in particular with oxygen. At the high temperatures of system operation, oxygen is highly soluble in these refractory metals; they literally act as sponges and tend to absorb available oxygen from the environment. Since the addition of relatively small amounts of oxygen to a refractory metal alloy can produce marked changes in strength, ductility, and corrosion resistance of the alloy to potassium, the use of these materials hinges on the control exerted over the contamination reactions. Oxygen contamination, its control, and its effects on the properties of the structural materials are discussed throughout this paper. Concern with contamination of system materials that are expected to operate in space may seem somewhat peculiar, since there is little source of contamination in space. However, most of the research and development on these power systems will be carried out in ground-test vacuum facilities in which oxygen contamination is a real possibility. Therefore, if contamination is to be limited and controlled, the manner in which the oxidation process occurs must be understood and a quantitative determination of the oxidation rates made under test environment conditions.

The low-pressure oxidation of columbium and tantalum refractory metal alloys can be visualized as occurring in three consecutive steps. The overall rate of reaction is determined by that step which occurs at the slowest rate, called the rate-controlling step. The proposed steps, or processes, in the low-pressure oxidation of columbium, tantalum, and their alloys are shown in the simplified model given in figure VII-2. The first process is gaseous diffusion of oxygen molecules to the surface, wherein the number of molecules per second that impinge on the surface of the metal is described by the well-known kinetic theory of gases. The second process, surface reactions, covers the reactions of the molecules on the surface, such as adsorption of the molecules and dissociation of the molecules into atoms. The third process is simply the diffusion of oxygen atoms into the bulk solid. When gaseous diffusion is rate controlling, the oxygen weight gain w is directly proportional to time t:

$$w \propto t$$

When a surface reaction is the rate-controlling process, the weight gain is proportional to time to the n^{th} power:

$$w \propto t^n$$

For thin-walled specimens, comparable with tube thicknesses that would be employed in space power systems,

$$n < 1$$

When diffusion in the solid is rate controlling, the weight gain is proportional to the square root of time:

$$w \propto \sqrt{t}$$

An investigation to establish the rate-controlling process and to obtain quantitative data on oxidation rates was conducted. In this investigation, a novel method was used which has a sensitivity two orders of magnitude greater than available gravimetric methods. The experimental apparatus is shown in figure VII-3. Oxygen is admitted to the vacuum system through the controlled leak; it is simultaneously removed by means of two pumps. One is a conventional vacuum ion pump and the other is the heated refractory metal specimen itself. The oxygen pressure over the specimen P_2 can be set at the desired level by adjusting the oxygen leak rate. The value of P_2 is obtained from a measurement of P_3, which is then corrected for thermal transpiration effects. The rate of oxygen pickup by the specimen can be readily calculated from the oxygen pressure drop between P_0 and P_1 (as measured by the ionization gages and the mass spectrometers) and the known vacuum conductance. The oxygen weight gain rate R of the specimen is given by the relation

$$R = (P_0 - P_1)C$$

where C is the conductance. This relation is analogous to Ohm's law for electrical current flow. With this apparatus, continuous measurements of oxidation rate have been made for columbium, tantalum, and seven columbium and tantalum alloys of interest. Tests were run over the pressure range of 10^{-8} to 10^{-5} torr and over the temperature range of 1600° to 2000° F. Shown in figure VII-4 is a plot of the experimental data for the oxidation of columbium at a temperature of 1800° F and an oxygen pressure of 3×10^{-8} torr. The weight gain was linear with time for a test run of over 200 hours. This result is typical of the refractory metals tested, inasmuch as all these metals exhibited a linearity between oxygen weight gain and time. These results are significant because they identify gaseous diffusion as the probable rate-controlling process in the oxidation of refractory metals over the range of conditions covered in these tests.

Further, since flux of oxygen molecules to the surface controls the oxidation rate and since this flux is proportional to pressure, the rate of oxygen weight gain for the refractory metals tested should be directly proportional to the oxygen pressure. This conclusion is confirmed as indicated in the typical case given in figure VII-5. Shown is a plot of oxidation rate as a function of oxygen pressure for the columbium-zirconium alloy Cb-1Zr over the temperature range of 1600° to 2000° F. The weight gain rate is, in fact, linear with pressure. The equation of the oxidation rate - pressure line is shown on the figure. The quantity in the parentheses is the kinetic theory of gas expression for the flux of oxygen molecules to the surface of the specimen under the test conditions. The factor ϵ is termed the "pumping efficiency" of the material. The value of ϵ of 0.15 determined for the Cb-1Zr alloy indicates that for every 100 molecules of oxygen that hit the surface of the alloy, 15 penetrate into the bulk metal. Values of pumping efficiency obtained

for columbium, tantalum, and the columbium and tantalum alloys tested were between 0.02 and 0.20; the columbium alloys had generally higher values than comparable tantalum alloys.

In regard to the problem of oxygen contamination of refractory alloys during operation in ground-test vacuum facilities, it is evident that the pumping efficiency values can be used to calculate test vacuum requirements as a function of alloy wall thickness and test time. As an illustration, oxygen pressure is plotted against the time needed to pick up the indicated oxygen contamination in figure VII-6 for T-111 (Ta-8W-2Hf) alloy with one side of the 20-mil-wall tube exposed to the vacuum environment and operated at 2000° F. If, for example, it is desired to limit contamination to no more than 100 ppm oxygen during a 1000-hour test, the oxygen partial pressure must be no more than 1×10^{-8} torr.

The pressures discussed so far have been oxygen partial pressures; however, vacuum gages measure the total system pressure. The oxygen partial pressure is approximately a decade or more lower than the total pressure. In the example just given, in order to ensure a contamination pickup of less than 100 ppm in 1000 hours, the total system pressure should be maintained at 1×10^{-7} torr or less, as measured by the vacuum gage.

SPACE POWER SYSTEM CONTAINMENT MATERIALS

Requirements

The prime requirements for a containment material are as follows. First, it must have good high-temperature creep strength. Second, since the containment material will be utilized primarily in the form of thin-wall tubing which must be welded into a highly reliable, leak-tight piping system, the material must be readily fabricable and possess good ductility in the welded condition. Finally, the containment material must be resistant to corrosion by boiling potassium.

Creep Strength

The first requirement, creep strength, is particularly important since space power systems must operate at high temperatures for long times. Allowable creep deformation, for example, might be limited to less than 1 percent in 10 000 hours. Although there are many columbium and tantalum alloys which could be considered for use as containment materials, no long-time creep data for these alloys were available when Rankine system feasibility studies were initiated. Thus, the first goals were to identify the most promising alloys and to generate the long-time creep information required for preliminary design studies.

The chemical compositions of some of the alloys evaluated are shown in table VII-2. Columbium - 1-percent zirconium is a highly fabricable but relatively weak columbium-base alloy which was in the most advanced stage of development when the study was initiated. The other four materials listed are newer alloys which attempt to combine the good fabricability and weldability of columbium - 1-percent zirconium with better high-temperature strength. The alloys FS-85 and D-43 are columbium-base alloys while T-111 and T-222 are tantalum-base materials.

There are two basic strengthening mechanisms utilized in these alloys. First, other high-melting-point metals, such as tungsten, are added as solid-solution strengtheners; that is, the tungsten replaces columbium or tantalum in the base metal lattice. The difference in atomic sizes produces strains in the lattice and increases strength. Second, smaller amounts of the very reactive metals, zirconium or hafnium, are added to promote dispersion or precipitate strengthening. These metals react with residual or intentionally added interstitial elements such as carbon, oxygen, or nitrogen to form a very fine dispersion of second-phase particles which act as barriers to the high-temperature deformation process.

The high reactivity of these columbium and tantalum alloys with oxygen and other interstitials poses a problem in high-temperature creep testing of these materials. If the test environment is not sufficiently pure, the creep specimen will absorb contaminants such as oxygen from it. This continuous contamination would progressively change the composition of the material and thus affect the creep properties being measured. In general, contamination with oxygen in amounts greater than 200 or 300 ppm makes the material stronger but less ductile. Such contamination during high-temperature creep testing in the laboratory could lead to an overly optimistic estimate of the strength of the material in service. In the high vacuum of space where contamination is absent, the material would be weaker than in the laboratory test.

In order to minimize the problem of oxygen contamination in creep tests, strict limitations were imposed on the vacuum level at which tests were conducted and on the test duration. For an initial screening study which was used to identify the most promising alloys, for example, the tests were limited to durations of a few hundred hours and conducted at total pressures of 10^{-6} to 10^{-7} torr. For tests with durations of thousands of hours, ultrahigh-vacuum creep equipment was designed and constructed.

In the screening program, the creep behavior of twelve columbium alloys and three tantalum alloys was evaluated at temperatures from 2000° to 2400° F and at a constant stress of 4000 psi. This stress was selected as being in the range of interest for typical components of the containment system. Some of the results from the 2200° F screening tests are shown in figure VII-7. Plotted is creep strain in percent against the test time in hours. Under these test conditions, Cb-1Zr crept 1 percent in only 30 hours. The strongest alloys were the tantalum alloys, T-222 and T-111, and the columbium alloys, FS-85 and D-43. These alloys all crept less than 1/2 percent in 300 hours. The other 10 alloys generally fell in the intermediate region between the strongest alloys and Cb-1Zr, although a few were even weaker than Cb-1Zr. On the basis of these results, attention was focused for longer time tests on the four alloys, FS-85, D-43, T-111, and T-222.

The ultrahigh-vacuum creep units developed for these tests are shown in figure VII-8. These creep units are bakeable stainless-steel systems which utilize copper gaskets for all demountable joints. They are evacuated by ion pumps and routinely operate at total pressures of 10^{-8} to 10^{-9} torr. With such units, contamination of 30-mil tantalum alloy sheet has been held to less than 100 ppm in 10 000-hour creep tests.

Although extensive long-time creep data are not yet available, a preliminary comparison of the creep properties of the selected tantalum and columbium alloys at 2200° F are shown in figure VII-9. Since weight is an important consideration in space power systems, the tests were conducted at a constant ratio of stress to density. The actual stresses are indicated in paren-

theses. Despite the fact that the tantalum alloys were tested at higher stress levels to compensate for their higher density, they are significantly more creep resistant than the columbium alloys. The T-222 alloy ran for 7500 hours at 8000 psi before exceeding the 1-percent creep limit. At somewhat lower stresses or temperatures, this alloy would meet the goal of less than 1-percent creep in 10 000 hours.

The effect of stress on the creep rate of the T-222 alloy at 2200° F is shown in figure VII-10. Plotted is the creep curve at 8000 psi which was shown in figure VII-9 and the creep curve at 12 000 psi. Increasing the stress level to 12 000 psi decreases the time for 1-percent creep from 7500 hours to approximately 2500 hours. For low stresses and small strains, the stress dependence of creep appears to follow the relation

$$\dot{\epsilon} = \sigma^n$$

where $\dot{\epsilon}$ is the creep rate, σ is the applied stress, and n is a constant. From available data on tantalum and columbium alloys, the value of the exponent n is approximately 3.

As is known, creep strength is strongly dependent on metallurgical structure. Heat treatments which alter the size and distribution of oxide or carbide precipitates in these alloys will affect their creep strengths. The effect of annealing temperature on creep strength is illustrated in figure VII-11 for the tantalum alloy T-111, creep-tested at 2200° F and 8000 psi. The material annealed for 1 hour at 3000° F before testing was approximately three times as creep resistant as the material annealed at 2600° F for 1 hour before testing. This effect is attributed to the residual carbon present in the alloy. At temperatures between 2800° and 3000° F, the carbon in the alloy is taken into solution, and relatively rapid cooling traps the carbon in the dissolved state. Subsequent testing at elevated temperatures allows the carbide to precipitate from the matrix during creep testing. It is this precipitate which enhances the creep properties of the alloy.

The results of these long-time creep studies to date indicate that existing commercial tantalum-base alloys have adequate creep strength for use as potassium containment materials to temperatures approaching 2300° F. For higher temperatures, stronger alloys will be required. Shown in figure VII-12 is a Larson-Miller creep-strength plot for one of the more promising advanced alloys, Astar 811C, and the two tantalum alloys just discussed, T-111 and T-222. On figure VII-12 the stress for 1-percent creep is plotted against the Larson-Miller time-temperature parameter φ. The temperatures indicated correspond to those for the Larson-Miller parameter at a 10 000-hour test time. The Astar 811C alloy (Ta-8W-1Re-1Hf-0.025C) is solid solution strengthened with rhenium as well as with tungsten and is also precipitation strengthened since it contains hafnium and carbon. This new tubing alloy, at comparable stresses and times, has a temperature advantage of about 150° F above commercially available tantalum alloys.

Fabricability

The strength situation for the refractory metal alloys seems promising. However, as was previously mentioned, another prime requirement for a containment material is that it be fabricable. As of the present time, all alloys discussed herein with the exception of the advanced

tantalum-base alloy, Astar 811C, have been fabricated into small-diameter tubing, which is a practical measure of fabricability.

One quantitative measure of the fabricability of an alloy is its ductile-to-brittle transition temperature. It is a characteristic of these columbium and tantalum alloys that they exhibit a change from ductile to brittle behavior over a relatively narrow temperature range, as illustrated in figure VII-13. The transition temperature is easily determined by bending sheet specimens over a radius equivalent to the thickness of the sheet until brittle failure occurs or until a maximum angle of 100^{o} is reached.

Bend transition tests of this type have recently been run on the refractory alloys of interest, and the results are shown in figure VII-14. The transition temperatures for the base material and for tungsten - inert-gas (TIG) arc-welded material are presented. A number of weld variables, such as welding speed, heat input, and spacing, were evaluated. The length of the black bars represents the temperature range over which the transition temperature occurred.

Although the Cb-1Zr alloy does not have the requisite strength characteristics, it is included for comparison since it is known to be readily fabricable. The FS-85 base material had a relatively low transition temperature, but in the as-welded condition the transition temperature was near room temperature. The relatively long bar for the as-welded D-43 alloy indicates the high sensitivity of this columbium alloy to the welding variables investigated; this sensitivity is one reason why it was dropped from further consideration. The alloys with the short bars are preferred since they indicate a low sensitivity to the welding variables. The tantalum-base alloys, as a class, exhibited very low transition temperatures and little sensitivity to the welding variables.

At Lewis special procedures have been developed to minimize contamination and to control welding variables. Personnel are required to put on clean-room coats and shoe covers before entering the welding room. The parts to be welded are chemically and ultrasonically cleaned and carefully handled so as to prevent contamination. Tungsten - inert-gas welding is performed in a controlled environment chamber. After the pieces to be welded are placed into the chamber, it is sealed and evacuated to a pressure of less than 1×10^{-5} torr. The chamber is then backfilled to atmospheric pressure with dry argon or helium containing less than 2 ppm oxygen. During the welding process, water vapor and oxygen levels are continuously monitored and controlled to assure a contaminant level of less than 5 ppm oxygen and 10 ppm water vapor. Electron-beam welding is performed in a large vacuum chamber at pressures below 1×10^{-4} torr. In this welding facility, electron beam welds have been made of refractory metals and alloys in thicknesses ranging from 5 mils to 1/8 inch. With the use of such procedures, high-quality welds with a minimum amount of contamination can be obtained with all the alloys discussed.

In addition to the problem of obtaining good as-welded ductility, however, the problem of embrittlement of the weld zone as the result of precipitation during long-time service must be considered. This precipitation phenomenon, called age hardening or simply aging, has led to serious problems in earlier systems. During long-time ground testing of space power systems, scheduled or inadvertent shutdowns often occur, and it is essential that the weld joints be ductile enough to accommodate the resulting thermal strains.

An experimental program is currently being conducted to determine if the more promising

columbium and tantalum alloys are susceptible to this aging embrittlement. In these tests, welded sheet specimens are aged at temperatures and times of interest and the bend transition temperatures determined after this exposure. Available results for the alloys FS-85 and T-111 are shown in figure VII-15, where the bend transition temperature is plotted as a function of aging temperature. Aging time, in all cases, was 1000 hours. Both alloys were postweld-annealed at 2400° F before aging. For FS-85, the bend transition temperature of the as-welded material is about -200° F. However, on aging for 1000 hours at 1800° F, the transition temperature increases to approximately 75° F; that is, the weld is likely to be brittle at room temperature. On the other hand, however, although the alloy T-111 also exhibits the aging phenomenon, the transition temperature is always well below room temperature. No problems from aging of welds would thus be anticipated for this alloy.

As refractory metal test facilities are run on the ground, another practical consideration encountered is the necessity of cutting into the facilities after numerous hours of operation and then rewelding. Since some contamination is bound to occur during thousands of hours of operation, even at pressures as low as 10^{-8} torr, the effect of contamination on the properties of the alloys must be considered. Shown in figure VII-16 is the effect of preweld oxygen content on the as-welded transition temperature of the alloys T-111, T-222, and FS-85. Materials evaluated in these tests were doped with oxygen prior to welding, and the welding was performed with the procedures previously described. The T-111 alloy is relatively insensitive to the oxygen content over the range investigated. The FS-85 alloy shows a relatively gradual increase in the transition temperature with increased oxygen and reaches room temperature at 600 ppm oxygen. The T-222 alloy shows a relatively high sensitivity to the increased oxygen. This difference between the two relatively similar tantalum alloys, T-111 and T-222, may be ascribed to the intentional addition of 100 ppm carbon to the T-222 and 10 percent tungsten in T-222 as against the 8 percent in T-111. Additions of tungsten to tantalum appear to reduce the solubility of all interstitials (carbon, oxygen, and nitrogen) in the alloy. It is expected that oxygen additions above 300 ppm to the T-111 alloy will result in an increase in its transition temperature.

Up to this point, the strength characteristics and fabrication and weldability properties of several columbium and tantalum alloys have been discussed. Attention is now given to a critical materials area, that of compatibility of the refractory alloys with potassium.

Corrosion

It is now commonly accepted that corrosion by potassium, and alkali metals in general, is highly dependent upon the presence of oxygen. It has been proposed that oxygen (O) present in the metal will react with the refractory metal (M) and potassium (K) to form a complex oxide, such as potassium columbate or tantalate:

$$K + M + O \rightarrow [KMO]_{complex}$$

These complex oxides are believed to be highly soluble in potassium and thus are taken rapidly into solution. The potassium - refractory-metal - oxygen reaction is therefore expected to continue until all available oxygen is consumed.

Some alloys contain an element called a gettering element, which is a highly reactive element such as zirconium or hafnium which tends to form a very stable oxide. When a gettering element is present in the alloy, the getter reacts and combines with the oxygen. A reduction in the amount of available oxygen results in the formation of less of the complex oxide, which thereby imparts a degree of corrosion resistance to the alloy.

This mechanism is supported by several observations. First, oxygen distribution studies indicate that oxygen migrates from columbium to potassium, contrary to the expected behavior based on the free energies of formation of the respective oxides. These results imply the formation of an intermediate compound. Second, solubility studies show a high dependency of refractory metal solubility on oxygen content, which indicates the active role of an oxide. Third, complex refractory-metal - alkali-metal oxides are known and have been identified as corrosion products. Last, the nature of the corrosive attack is consistent with this mechanism.

In regard to the subject of solubility, as was just discussed, the amount of oxygen available for the formation of a complex oxide should control the amount of metal taken into a solution by potassium. The solubility of iron in potassium in the presence of materials with different gettering potentials can be used to illustrate this point. The solubility of iron in potassium was measured with a capsule similar to that shown in figure VII-17. The body of the capsule was made of iron and the sampling cup, of a different metal. The sampling cup was positioned within the capsule body as indicated in figure VII-17(c). After equilibration of the potassium with the iron, the capsule was inverted while still at temperature. Then the capsule was allowed to cool, and a sample was removed for analysis. The cup not only served to isolate the potassium sample but in this series of experiments also acted as an oxygen getter.

In figure VII-18 measured iron (Fe) solubility is plotted against estimated available oxygen. As indicated at the bottom of the figure, the cup metals used were nickel, molybdenum, tantalum, columbium, and zirconium. Because of their differing gettering abilities, each material sets a unique value for the amount of oxygen available for the reaction,

$$K + Fe + O \rightarrow [KFeO]_{complex}$$

The expected variation in measured solubility was indeed obtained; the oxygen effect for iron is quite significant, with approximately two orders of magnitude difference between the solubility results with sampling cups of nickel, a relatively poor getter, and zirconium, a good getter.

This example illustrates the point of enhanced solubility of iron in the presence of oxygen. Presently, similar data are being sought for the refractory metals. Preliminary results of solubility tests, with Cb-1Zr alloy and pure columbium, have shown that the presence of zirconium in the alloy reduces the measured columbium solubility by about one order of magnitude below that obtained for the ungettered columbium. Thus, the information obtained for iron also appears to apply to columbium.

Now that the fundamental processes behind the corrosion reaction have been outlined, attention can be turned to material screening tests which are employed to determine the compatibility of possible containment materials with potassium. Inasmuch as oxygen appears to have a serious effect on corrosion, adequate precautions must be taken to ensure that oxygen is not inadvertently

introduced into the test. Careful handling and control of all test conditions are needed to minimize oxygen contamination so that test results will be meaningful.

Material screening tests were carried out in capsules with 0.5-inch diameter, 1.75-inch length, and 0.040-inch wall thickness. The capsule wall served as the test specimen. To minimize contamination of the metals during loading and capsule sealing, a special vacuum-handling facility was constructed, containing a potassium extruder, a work table, a remote manipulator to position the capsules within the vacuum enclosure, a welding fixture, and an electron beam welder. A measured amount of potassium was extruded from a sample tube and dropped into a capsule. The capsule was placed in the welding fixture and capped. The welding fixture was rotated and the electron beam welder was activated to seal the capsule. Since the entire operation was carried out rapidly and in a vacuum of less than 10^{-5} torr, contamination was minimized.

The capsules were then instrumented with thermocouples and inserted into individually controlled heaters clustered on a test bed. The capsules were tested in a vacuum chamber at a pressure of less than 1×10^{-7} torr, an acceptable vacuum level for the test times and temperatures. Heat input to the capsule was such that the potassium refluxed within the capsule. Potassium vapor rose to the upper part of the capsule where it condensed and then streamed down the wall of the capsule to produce a continuous circulation of fluid. At the end of the tests, the bed was removed from the chamber and the capsules were prepared for metallographic and chemical analyses to determine the extent of corrosion.

Thirteen columbium and tantalum tubing alloys were screened in this manner in the temperature range of 1800° to 2400° F for times up to 10 000 hours. The materials tested are given in table VII-3; both gettered and ungettered columbium and tantalum alloys were included. The potassium used in these tests was of high purity and contained less than 20 ppm oxygen.

The results of tests run on columbium alloys can best be shown by comparing the zirconium gettered alloy FS-85 with the ungettered alloy SCb-291. Figure VII-19 shows a sectioned capsule of SCb-291 which has been tested for 1000 hours at 2200° F. As shown in the accompanying photomicrographs, general dissolution occurred at the top of the capsule and attack along grain boundaries at the bottom of the capsule. Figure VII-20 shows a sectioned FS-85 capsule tested for 2000 hours at 2300° F. Despite the more severe test conditions imposed upon FS-85, it shows essentially no corrosive attack.

A comparison of reflux corrosion capsule results for an ungettered tantalum alloy, Ta-10W, with a hafnium gettered alloy, T-111, is given in figures VII-21 and VII-22, respectively. The ungettered Ta-10W alloy was tested at 1800° F. Termination of the test occurred at 128 hours, after the potassium had leaked out by penetrating the grains in the weld area. This penetration is shown in the bottom photomicrograph on figure VII-21. Intergranular attack was also found in the fine-grained structure at the top of the capsule. In contrast, the gettered alloy, T-111, under more severe test conditions, showed essentially no attack in the weld zone and only a slight roughening at the top of the capsule.

With larger capsules than those previously described, encouraging results were also obtained in long-time tests on the gettered columbium alloys AS-55, D-43, and Cb-1Zr. The results for D-43 are typical of these alloys. As indicated in figure VII-23, there was no detectable corrosion after 10 000 hours at 2000° F.

The effect of both stress and strain on corrosion of columbium alloys in potassium was

investigated. For this purpose, the standard corrosion capsule was altered as shown in figure VII-24. Just above the midregion of the capsule, the wall thickness was machined down to provide a highly stressed region. The capsule was then heated to 2300° F for 1000 hours. Internal pressure in the capsule resulting from the vapor pressure of potassium imposed an initial hoop stress of about 4000 psi on the thin-wall section, which caused it to bulge. The maximum strain in this test after 1000 hours was approximately 37 percent.

After the test, the capsule was sectioned and examined metallographically. A typical photomicrograph from the highly stressed section is shown in figure VII-24(c). There is no evidence of stress corrosion despite the high temperature and large amount of strain. These results are for the columbium alloy D-43, but similar results were also noted for other alloys. Thus, it is believed that stress corrosion is not likely to be a problem in potassium Rankine systems constructed from columbium or tantalum alloys.

The initial screening of the alloys and the determination of basic properties such as solubility limits are most readily obtained in capsules of one type or another as described. The alloy finally selected for a system, however, should be proof-tested in an engineering test loop specifically designed to simulate the proper temperature and flow conditions of the actual system. Since experience has been limited in the construction and operation of such complex test loops, a prototype loop was fabricated from the Cb-1Zr alloy. The choice of this alloy was dictated by the fact that it was the only refractory metal alloy available as tubing in 1963 when the test program was initiated. This loop is shown in figure VII-25. The vacuum chamber in which the loop is mounted was capable of maintaining a vacuum better than 2×10^{-8} torr during loop operation.

Shown in figure VII-26 is a schematic diagram of the corrosion loop. The two-loop system consisted of a primary sodium heater loop and a secondary potassium boiling and condensing loop. In the primary circuit, the sodium is discharged from a pump and flows through an electrical resistance heater to a tube-in-tube counterflow boiler, where heat is transferred to the potassium. The sodium loop operated at a maximum temperature of 2130° F, a minimum temperature of 1990° F, and a flow rate of 2.6 gallons per minute.

In the boiling and condensing secondary loop, the potassium is discharged from the pump through an electrical resistance preheater, where the temperature of the potassium is increased to a temperature near the saturation temperature before it flows into the boiler. In traveling through the boiler, the potassium is converted from liquid to superheated vapor and then passes through the first nozzle of the turbine simulator. Heat is rejected in the crossover line of the turbine simulator, and wet vapor then passes through stages 2 to 10 of the turbine simulator to the condenser. Condensed vapor is returned through the subcooler to the pump. Potassium in this circuit was boiled at 1850° F, superheated to 2000° F, and condensed at 1425° F. The potassium circuit had a flow rate of 0.1 gallon per minute.

The loop was operated stably at these conditions for 5000 hours. Posttest metallurgical evaluation of the potassium circuit revealed no significant corrosion.

Since the design and operation of the Cb-1Zr prototype corrosion loop was successful, additional corrosion loops are now being constructed from the T-111 tantalum alloy.

Test Instrumentation

With a test of the complexity of that just described, success rests heavily upon instrument performance. The instrumentation used must not only be able to operate reliably for long periods, but in some applications must be capable, in terms of materials, of withstanding high temperatures and contact with potassium.

In the consideration of pressure measurements, the pressure-pickup material in direct contact with the potassium must be corrosion resistant. This requirement precludes the use of stainless steel in the pressure instrumentation, even in the low-temperature portions of the loop. A successful technique of solving this problem is the use of the well-known slack-diaphragm pressure transmitter, shown schematically in figure VII-27. The slack diaphragm forms a separating membrane between the potassium of the loop and the NaK which fills the rest of the pressure measuring system; yet it allows the pressure to be transmitted to the pressure pickup. The spring properties of this high-temperature diaphragm have little effect on the pressure measurement; all that is required is that the stiffness be low compared with that of the pressure transducer. The choice of material for the diaphragm and its housing can therefore be dictated by a materials consideration without regard to its characteristics as a spring. Further, because the precision-spring measuring element of the transducer can be maintained at room temperature, the accuracy of the technique is good. Probable errors of the order of 1 percent of full scale are typical.

An example of a Cb-1Zr alloy slack-diaphragm assembly is shown in figure VII-28. This pressure pickup was used on the corrosion loop previously described. Comparable assemblies of T-111 alloy are being made for the T-111 corrosion loops presently under construction.

Response time is the major limitation of this slack-diaphragm technique. The relatively long NaK-filled line that allows the transducer to operate at room temperature also limits the frequency response of the system to the order of 0.1 cps. Making transient pressure measurements generally requires the use of very short connecting tubing, which results in requirements for high-temperature pressure transducers. A transducer of the type shown in figure VII-29 was used on the previously described corrosion loop to measure boiler inlet pressure and indicate loop stability. This transducer is a commercial design, which was modified by the substitution of refractory alloys for the stainless steel normally used. The diaphragm and its housing are made of tantalum alloys. The diaphragm deflection is measured with a differential transformer. The transducer is restricted to operation at temperatures no more than 900° F because of temperature limitations on this differential transformer. The usable frequency response was limited to about 20 cps by the nature of the installation.

A more truly high-temperature transducer is shown schematically in figure VII-30. This transducer is being developed for operation at 1800° F. The pressure capsule is about 1 inch in diameter and made from W-25Re alloy. A vacuum diode operated in the space charge limited mode is used to measure capsule deflection. A linear output signal can be obtained by utilizing a double-diode technique, with one diode a variable-spacing collector-emitter combination and the second, a built-in fixed-spacing reference diode. As stated, this transducer is in development; prototype models are being built for testing in a two-phase potassium loop.

Since the material tests described earlier involve thousands of hours of operating time, thermocouple drift can be a serious problem. In a recent test at 2200° F, for example, a ther-

mocouple drift of 100° F was observed in 150 hours. There are a great many interrelated factors that affect thermocouple stability. These factors include choice of material, purity of material, wire size, handling and assembly techniques, and the environment to which the thermocouple is subjected. With proper control of these factors, good stability can be achieved, as indicated by recent high-vacuum stability tests summarized in table VII-4. In one set of 1000-hour tests, stability was within ±18° F for temperatures ranging from 2200° to 2600° F. The alloys tested included both platinum-rhodium (Pt-Rh) and tungsten-rhenium (W-Re) alloys. In another test at 3200° F for 4000 hours, stability to within 30° F was obtained. The alloys used in this test were W-3Re/W-25Re. In all these tests 20-mil-diameter thermocouple wires were insulated with very high purity alumina. These results reflect the state of the art attainable with proper care in fabricating and using available high-temperature thermocouples.

System Working Fluid

In the past few years, property measurement programs supported by NASA and other government agencies have bridged the last of the engineering property gaps. Currently, the major engineering properties of potassium, such as vapor pressure, density, thermal conductivity, and viscosity, are known over the temperature range of interest to the advanced space power system. For the most part, small amounts of oxygen impurities appear to have a negligible effect on the engineering properties of potassium. This effect, however, is not negligible in relation to corrosion.

As has been previously described, the presence of oxygen enhances the corrosion attack. It is therefore of the greatest importance (1) that the impurity concentration of the potassium be low (preferably 20 ppm or less), (2) that special handling procedures be employed to preclude contamination of the potassium, and (3) that there be a reliable method for the analysis of oxygen in potassium at concentrations below 20 ppm.

Currently, the first requirement can be met. Purification procedures such as distillation and hot gettering allow the routine production of potassium with oxygen concentrations between 5 and 15 ppm.

The second requirement can also be satisfied if rigid standards of cleanliness and handling are maintained. With the use of clean metallic transfer lines which have been vacuum-leak-checked for integrity, potassium has been transferred from system to system and from apparatus to apparatus without introducing measurable contamination.

The third requirement, a reliable analytical method for measuring low concentrations of oxygen, has proved to be the most difficult of the potassium problems. Currently, three principal methods are employed in the analysis of oxygen in potassium: amalgamation, distillation, and neutron activation. The amalgamation method uses the principle of selective solubility to separate the potassium from the oxygen impurity. The potassium is dissolved in mercury; the insoluble oxygen impurity is thus allowed to float to the surface of the mercury. In the distillation method, the volatile potassium is distilled from the less volatile oxide impurity. In the neutron activation method, an encapsulated potassium sample is irradiated with fast neutrons followed by a measurement of the activity of the decay products from the neutron-oxygen reaction.

Until recently, little was known of the accuracy and precision of these methods, in spite of the fact that two of these methods, amalgamation and distillation, have been in use for over a

decade. This state of affairs was further apparent in the results obtained between laboratories. When two or more laboratories performed analyses on equivalent samples of potassium, the results were usually in poor agreement.

Investigations at Lewis have indicated that the major cause of these difficulties is the inadvertent contamination of the potassium during the act of sampling, transfer, and analysis. To minimize such contamination, special vacuum analytical techniques and equipment were devised. The results obtained with two such techniques, vacuum amalgamation and vacuum distillation, on replicate samples are given in table VII-5. For batch 3, a neutron activation analysis was obtained in addition to the amalgamation and distillation analyses. As is apparent, the oxygen values obtained by all three independent methods show good agreement. Thus, for the first time, a high degree of confidence may be had in the accuracy of these methods.

Establishment of the accuracy and precision of results, however, does not complete the analytical situation. The matter of the lack of agreement between different laboratories must still be considered. This problem was attacked through a series of Round Robin Analyses, sponsored by Lewis, the AEC, and the ASTM. Standard samples prepared by Lewis were distributed to 15 participants in government and industrial laboratories throughout this country. The results of the third and most recent Round Robin Analysis were as follows. Amalgamation was the method used by most of the 15 participants; however, a few used distillation or neutron activation. The total number of determinations made was 77; the mean value obtained was 14.7 ppm oxygen; the range of values was 4 to 26 ppm with a standard deviation of 5.1 ppm. These results of this third Round Robin Analysis are encouraging, for they show that reasonable agreement can be obtained among laboratories. Also, these results indicate a more general awareness of the need for environmental control and careful handling.

SUMMARIZATION

Reviewed in this paper are some of the more significant results of recent potassium Rankine system materials investigations. In summary, the oxidation problem, present in all ground-test operations, has been brought into focus: in terms of fundamentals, the probable rate determining process in the low-pressure oxidation of columbium and tantalum alloys has been identified; in terms of engineering, the requirements for vacuum test environments have been defined. As for the structural properties of container materials, test results indicate that the creep strength of available commercial columbium and tantalum alloys is adequate for system operating times and temperatures, as currently envisioned. Moreover, newer tantalum-base alloys such as Astar 811C promise as much as 150° F increased temperature capability, if needed. The fabricability and weldability of the high-strength alloys, such as T-111, appear to be satisfactory, if care is taken to minimize contamination and proper heat treatment is employed. The important question of compatibility of container materials with potassium has been investigated by means of solubility, screening, and pumped loop tests. The results to date indicate that the gettered columbium and tantalum alloys have adequate corrosion resistance. Further, instrumentation for the variety of material tests described, with suitable response and reliability, appear attainable with the proper choice of materials and installation techniques. Finally, as for the working fluid, potassium, the engineering properties are known over the temperature range of interest to the Rankine system, and, in the main, techniques have been established for purification, handling, and oxygen analysis

TABLE VII-1. - PROPERTIES OF REFRACTORY METALS

Metal	Melting point, ^{o}F	Specific gravity	Fabricability
Tungsten	6170	19.3	Poor
Tantalum	5400	16.6	Good
Molybdenum	4750	10.2	Fair
Columbium	4470	8.6	Good

TABLE VII-2. - COMPOSITIONS OF TYPICAL COLUMBIUM AND TANTALUM ALLOYS

Alloy	Composition, wt %					
	Cb	Ta	W	Zr	Hf	C
Cb-1Zr	Bal.	----	--	1	---	----
FS-85	Bal.	28	10	1	---	----
D-43	Bal.	----	10	1	---	0.1
T-111	----	Bal.	8	--	2	----
T-222	----	Bal.	10	--	2.5	.01

TABLE VII-3. - POSSIBLE COLUMBIUM AND TANTALUM TUBING ALLOYS

Alloy	Composition
Columbium base	
B-33	Cb-4V
SCb-291	Cb-10Ta-10W
Cb-1Zr	Cb-1Zr
D-14	Cb-5Zr
AS-55	Cb-5W-1Zr-0.2Y-0.06C
B-66	Cb-5Mo-5V-1Zr
D-43	Cb-10W-1Zr-0.1C
FS-85	Cb-27Ta-10W-1Zr
Cb-752	Cb-10W-2.5Zr
C-129	Cb-10W-10Hf
Tantalum base	
Ta-10W	Ta-10W
T-111	Ta-8W-2Hf
T-222	Ta-9.6W-2.4Hf-0.01C

TABLE VII-4. - RECENT THERMOCOUPLE STABILITY DATA

	Test duration, hr	
	1000	4000
Measured stability, ^{o}F	Within ±18	Within +0, -30
Temperature, ^{o}F	2200 to 2600	3200
Thermocouple alloy	Pt-10Rh/Pt, Pt-6Rh/Pt-30Rh W/W-26Re, W-5Re/W-26Re	W-3Re/W-25Re
Configuration	Bare wires in ceramic insulator	
Insulator	Recrystallized Al_2O_3, 99.5 percent pure	
Wire diameter, in.	0.020	
Vacuum environment, torr	10^{-6} to 10^{-8}	10^{-8}

TABLE VII-5. - ANALYSIS FOR OXYGEN IN POTASSIUM

[Results from three independent methods corrected for systematic errors.]

Potassium batch	Analytical method	Number of determinations	Mean amount of oxygen, ppm	Standard deviation
1	Vacuum distillation	14	6.1	4.7
	Vacuum amalgamation	7	7.2	2.7
2	Vacuum distillation	7	8.7	2.7
	Vacuum amalgamation	3	6.9	2.5
3	Vacuum distillation	5	16.1	4.8
	Vacuum amalgamation	4	15.6	4.1
	Neutron activation	3	16.1	8.4

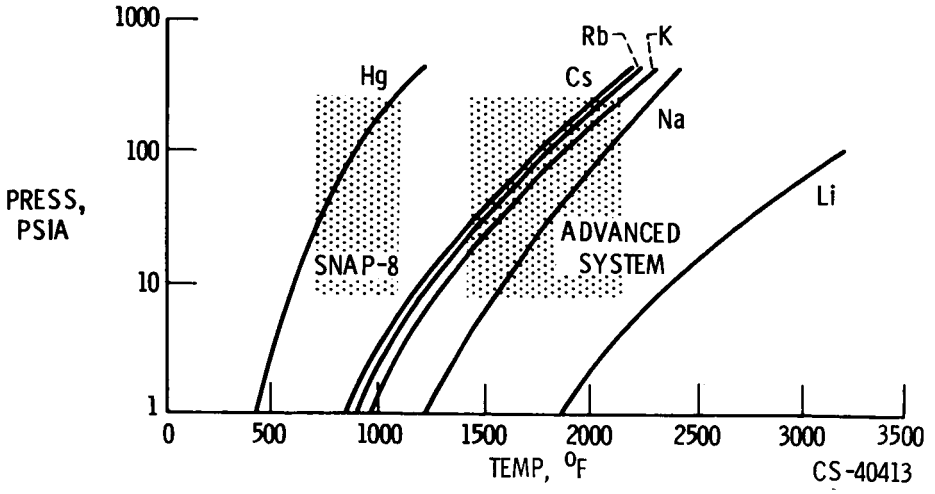


Figure VII-1. - Operational regimes for selected Rankine cycle systems.

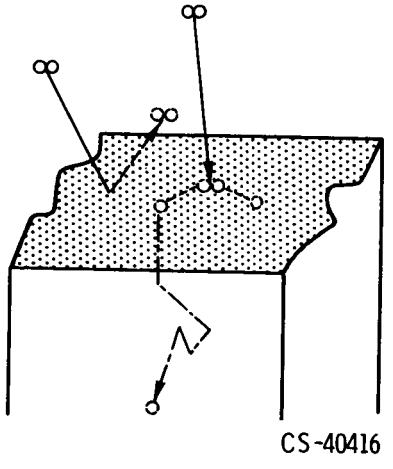


Figure VII-2. - Low-pressure oxidation model for columbium, tantalum, and their alloys.

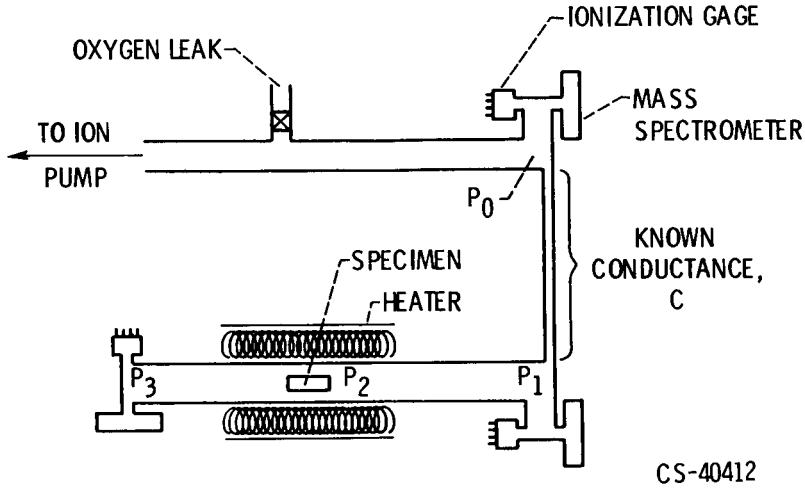


Figure VII-3. - Vacuum pressure-drop oxidation apparatus.

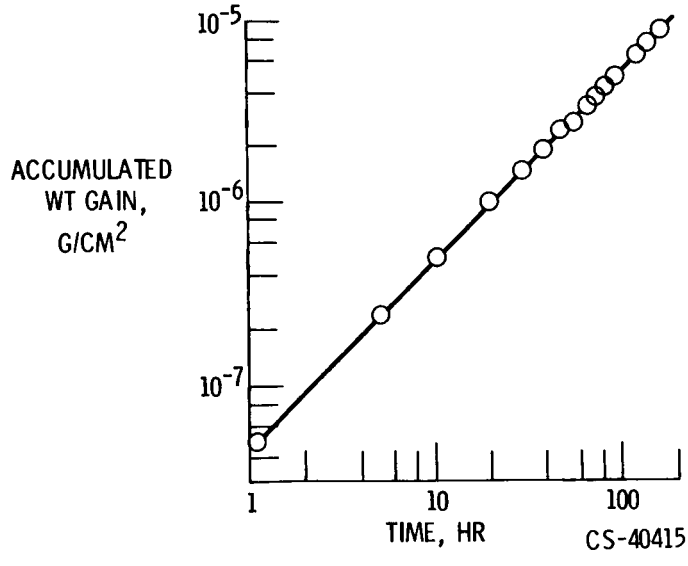


Figure VII-4. - Oxidation rate for columbium. Temperature, 1800^{0} F; oxygen pressure, 3×10^{-8} torr.

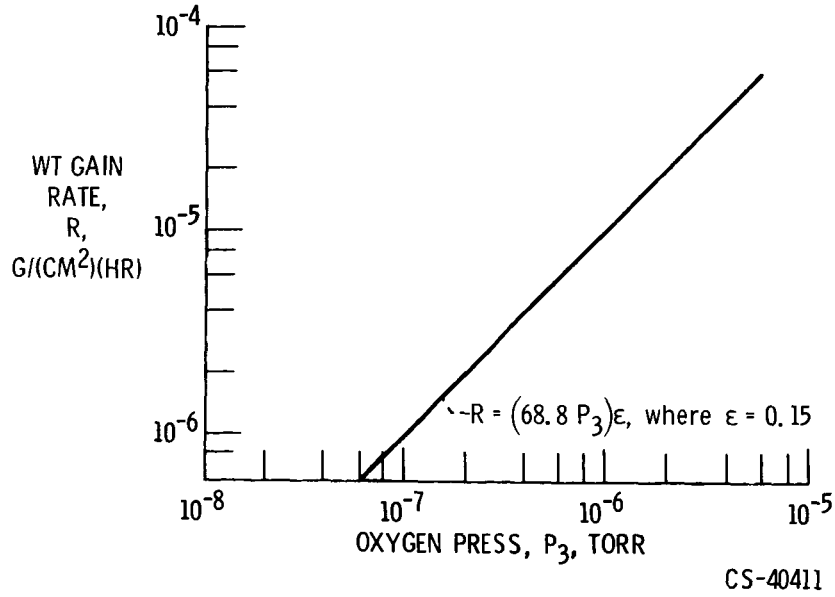


Figure VII-5. - Oxidation rate for columbium - 1-percent-zirconium alloy as function of oxygen pressure at 1600^0 to 2000^0 F.

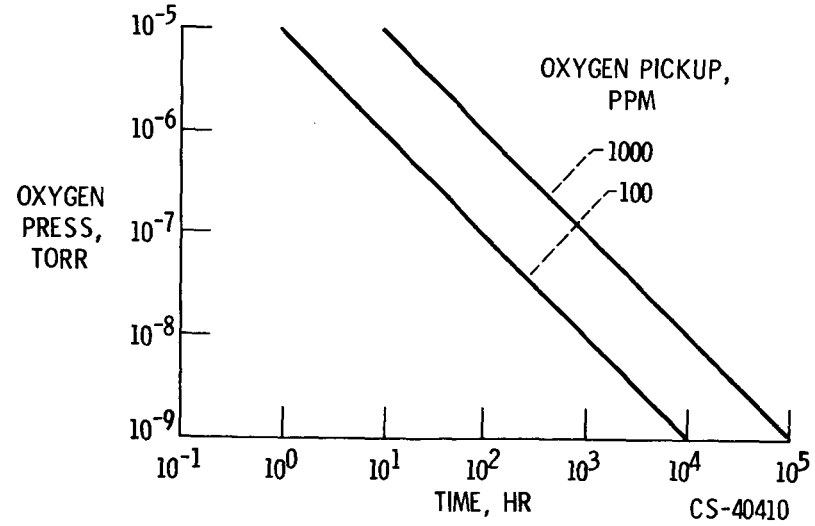


Figure VII-6. - Contamination of T-111 alloy. Temperature, 2000^0 F; 20-mil-wall tube; exposed on one side to vacuum environment.

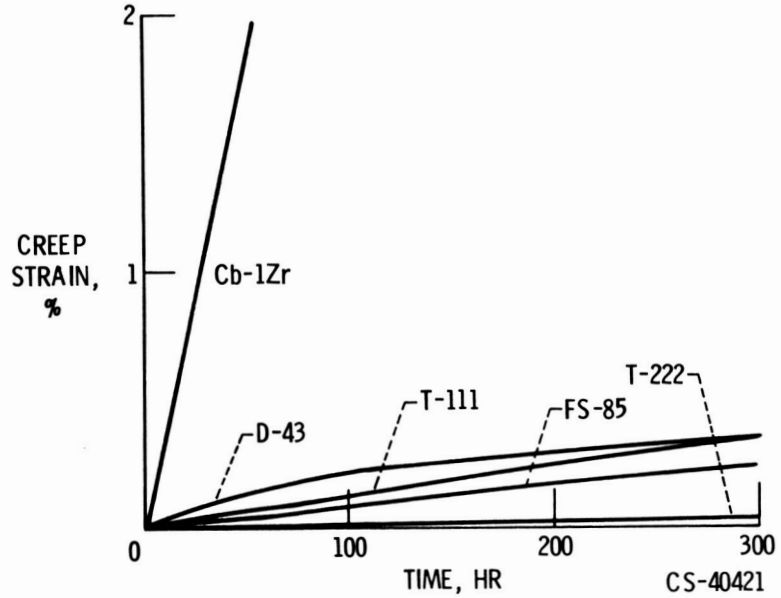


Figure VII-7. - Creep of columbium and tantalum alloys. Temperature, 2200^{0} F; stress, 4000 psi; pressure, 10^{-6} torr.

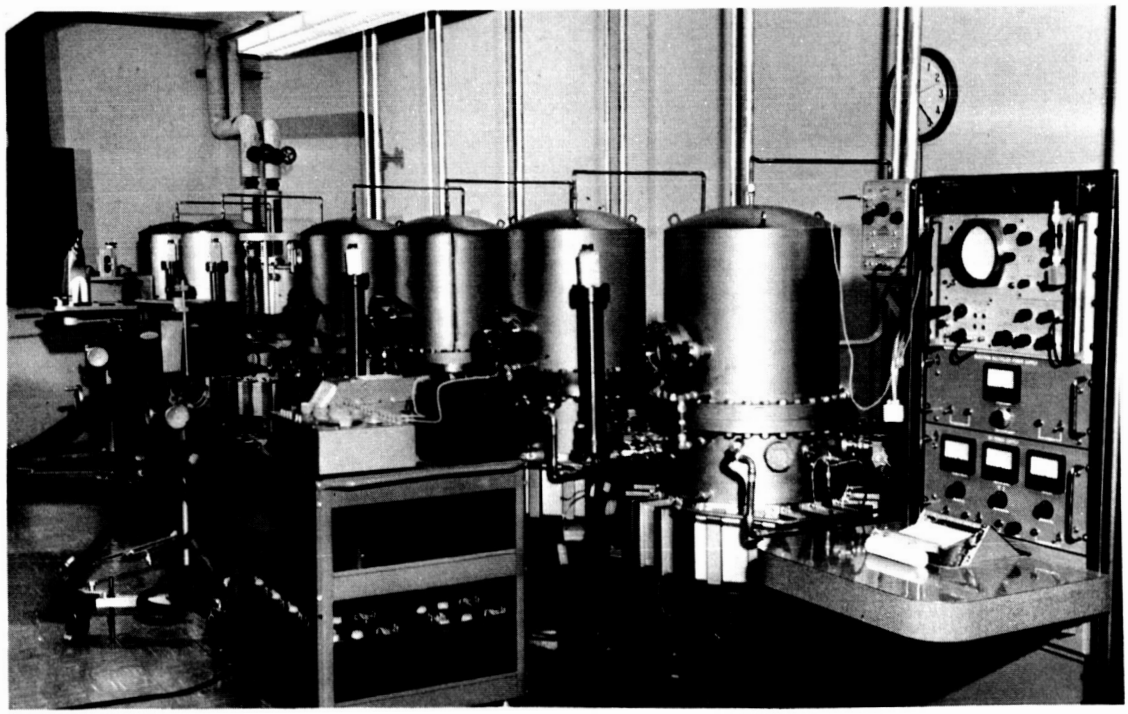


Figure VII-8. - Ultrahigh-vacuum creep units.

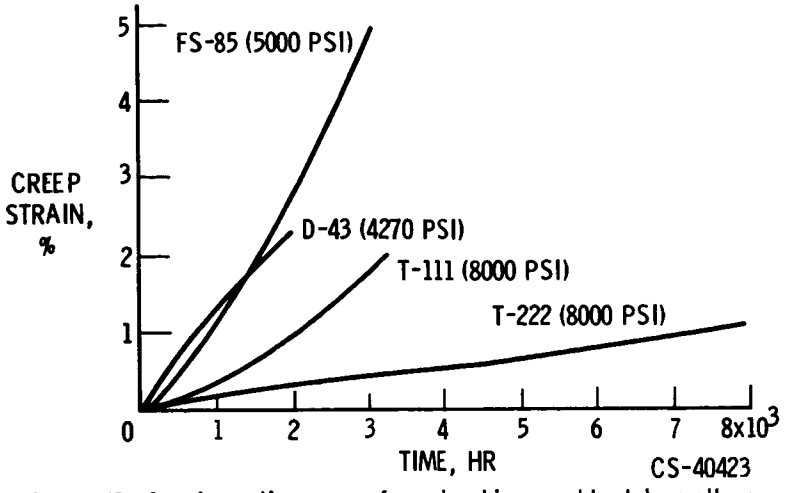


Figure VII-9. - Long-time creep for columbium and tantalum alloys. Temperature, 2200° F; pressure, 10^{-8} torr; constant ratio of stress to density.

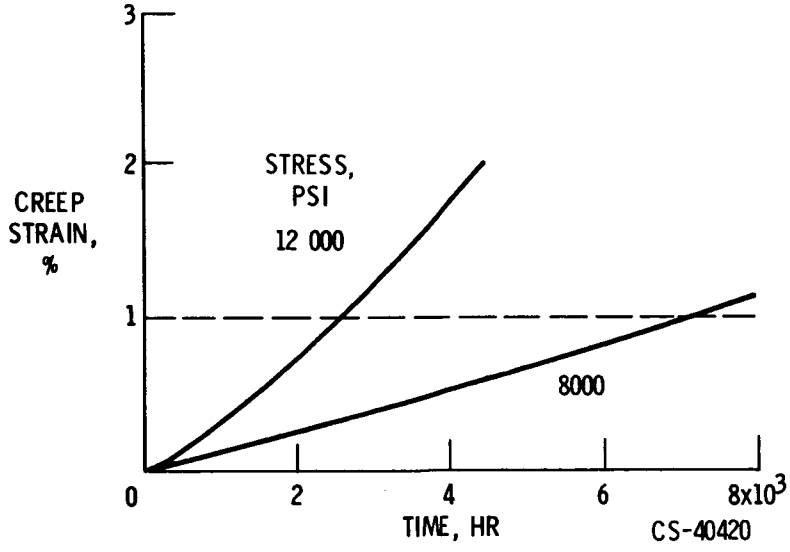


Figure VII-10. - Effect of stress on creep. Alloy, T-222; temperature, 2200° F.

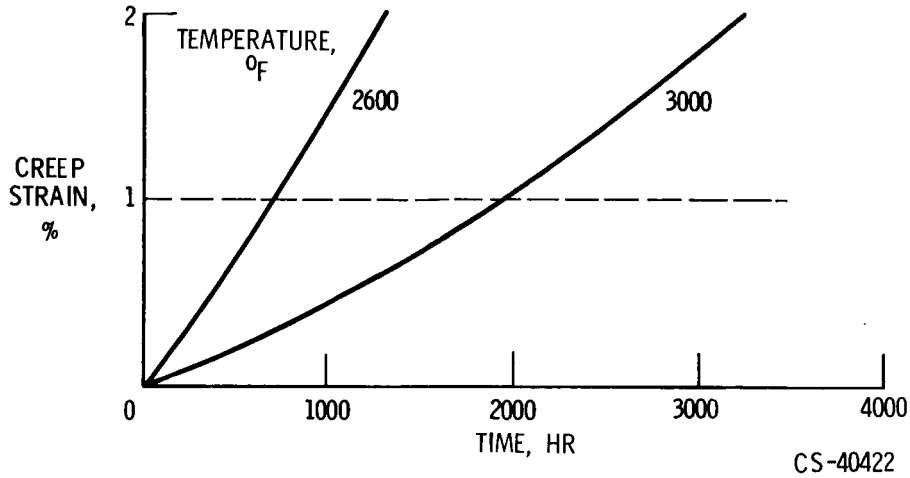


Figure VII-11. - Effect of annealing temperature on creep. Alloy, T-111; temperature, 2200° F; stress, 8000 psi; annealing time, 1 hour.

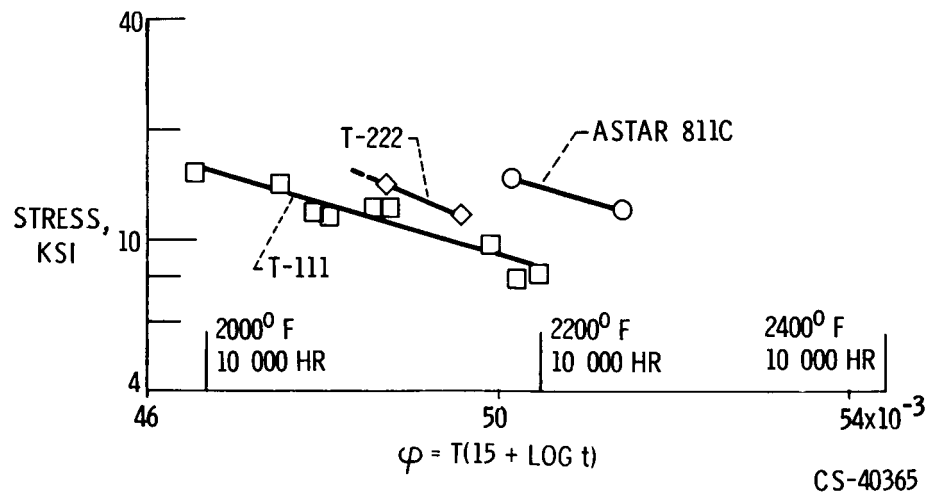


Figure VII-12. - Stress for 1 percent creep in tantalum alloys. Temperature, 3000° F; annealing time, 1 hour.

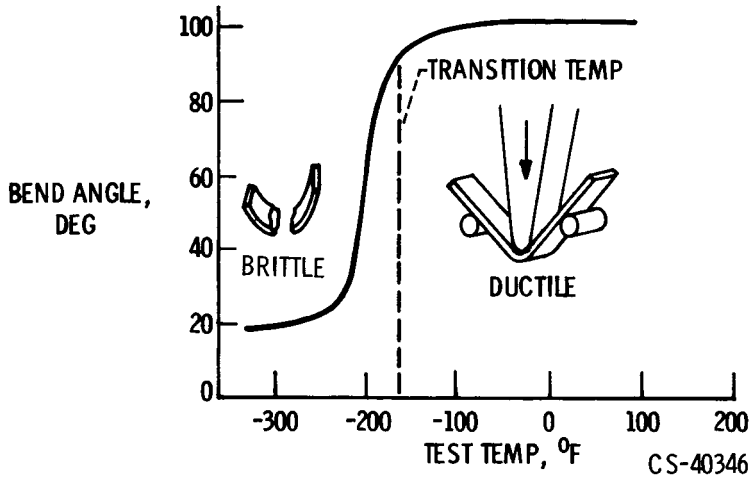


Figure VII-13. - Determination of ductile to brittle bend transition temperature.

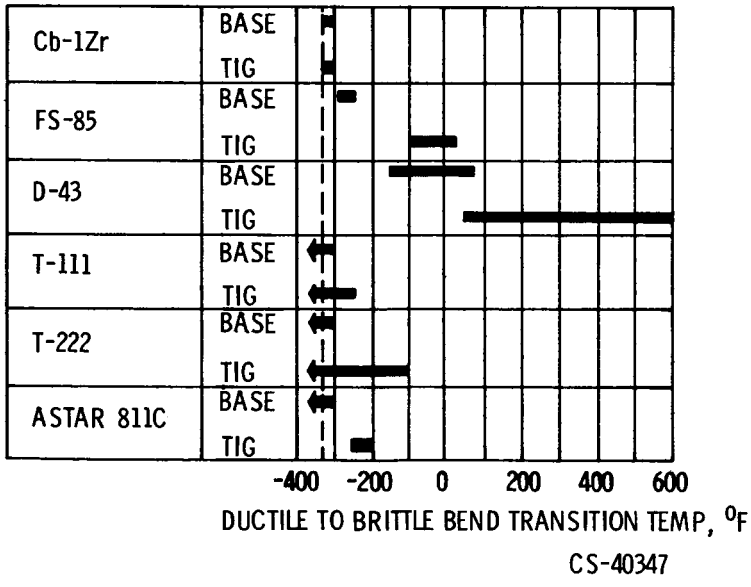


Figure VII-14. - Weld bend ductility for 0.035-inch refractory-alloy sheet with 1t bend radius.

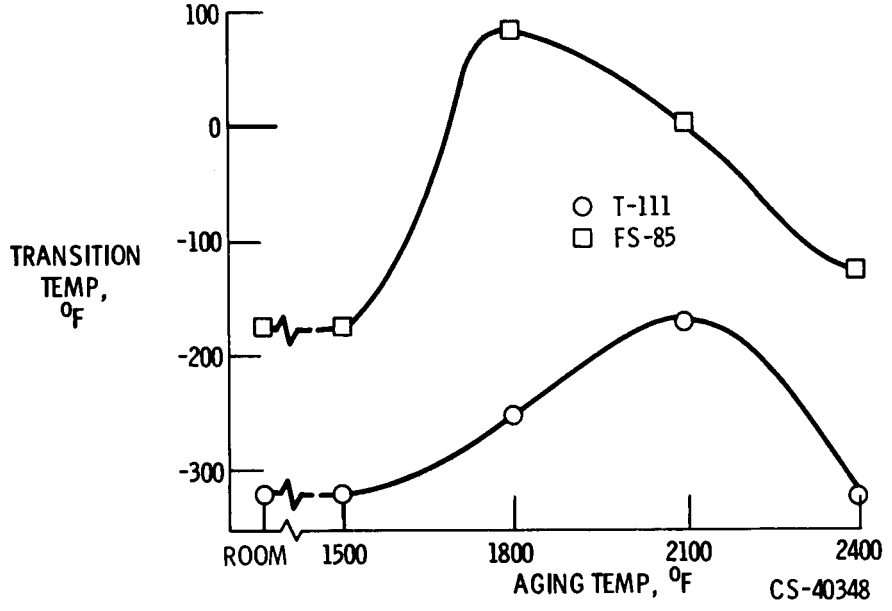


Figure VII-15. - 1000-Hour aging of welded alloys. Tungsten - inert-gas weld; temperature, 2400° F; annealing time, 1 hour.

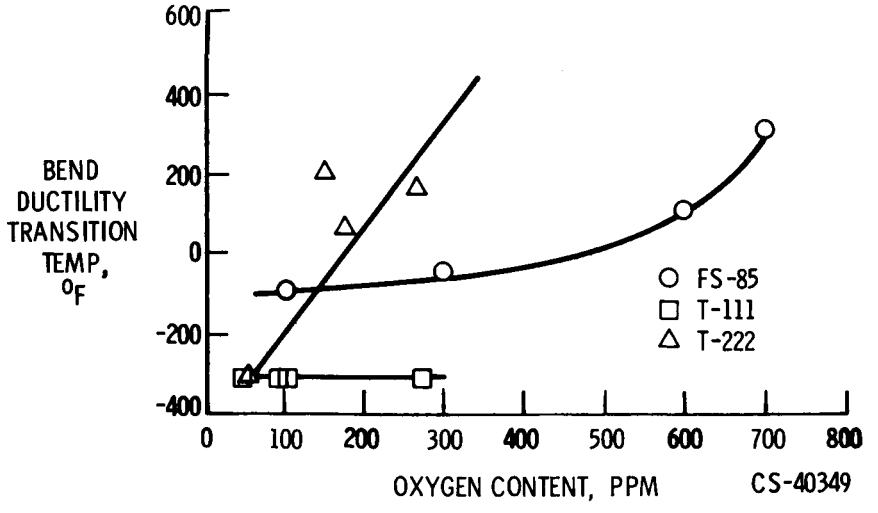
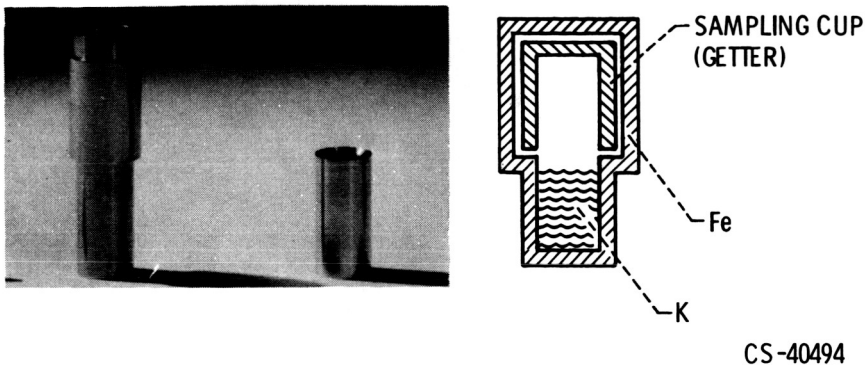


Figure VII-16. - Effect of preweld oxygen content on as-welded transition temperature.



(a) Body. (b) Sampling cup. (c) Assembled capsule.

Figure VII-17. - Solubility capsule.

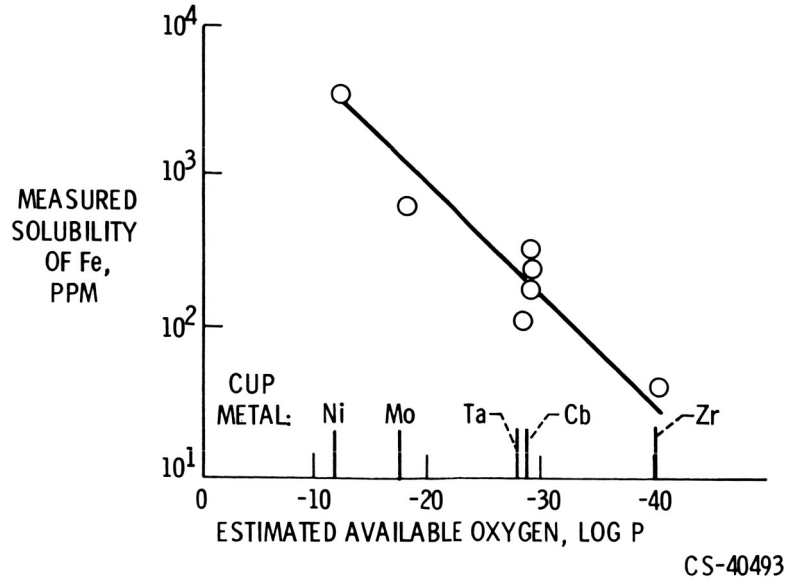
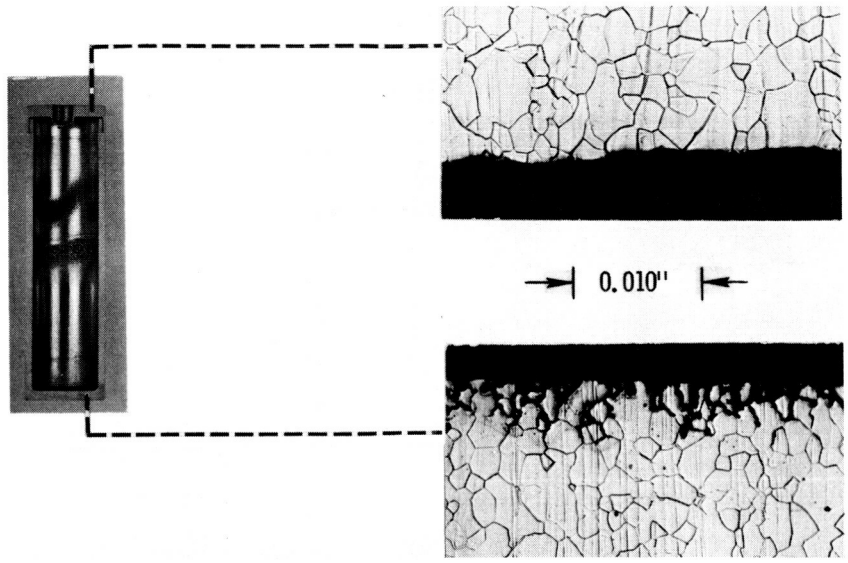
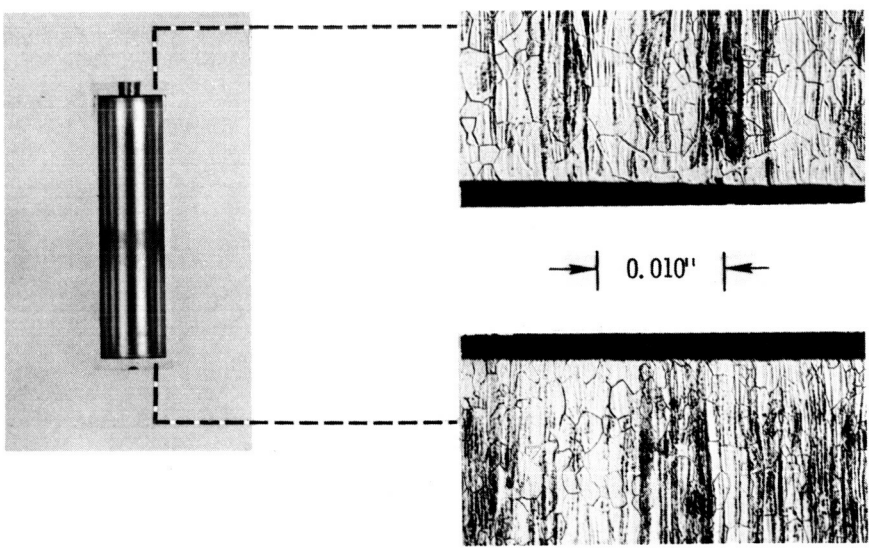


Figure VII-18. - Effect of sampling cup metal on measured solubility of iron in potassium at 1600^0 F.



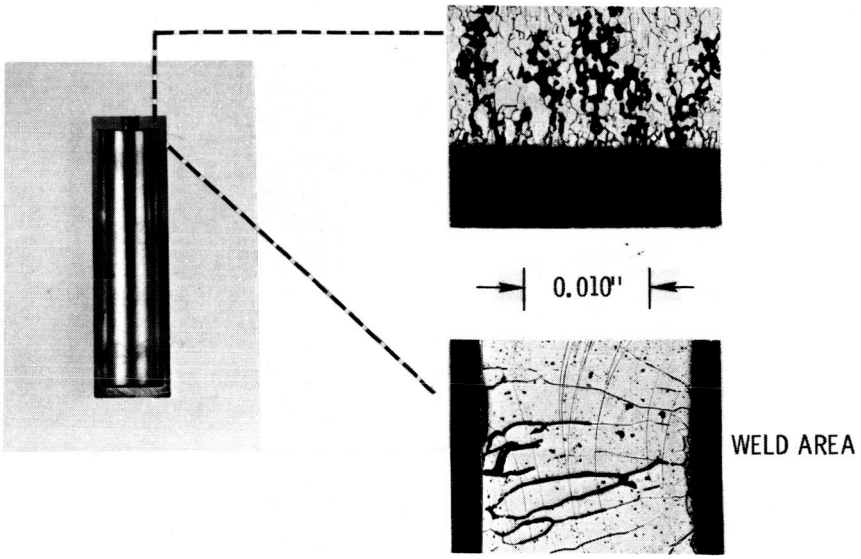
CS-40459

Figure VII-19. - Corrosion of ungettered alloy SCb-291 by potassium. Temperature, 2200° F; time, 1000 hours.



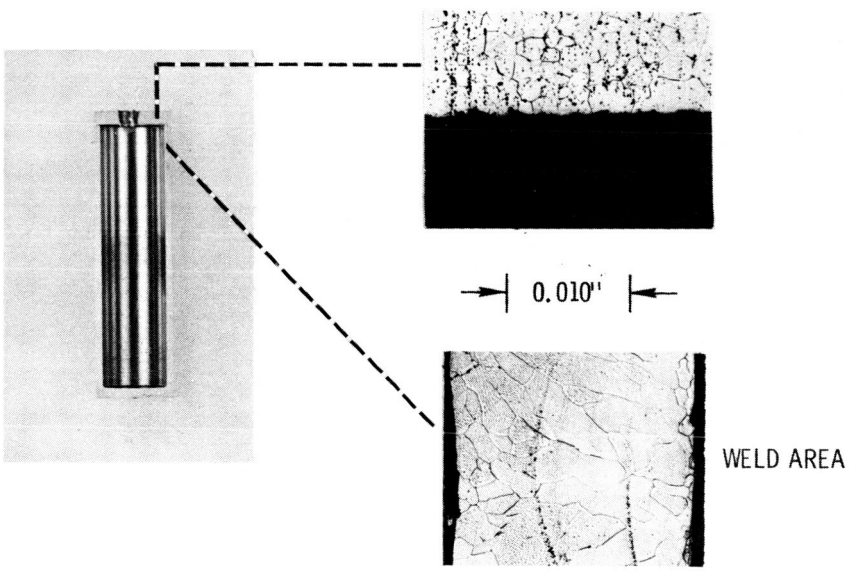
CS-40458

Figure VII-20. - Corrosion of gettered alloy FS-85 by potassium. Temperature, 2300° F; time, 2000 hours.



CS-40461

Figure VII-21. - Corrosion of ungettered alloy Ta-10W by potassium. Temperature, 1800° F; time, 128 hours.



CS-40462

Figure VII-22. - Corrosion of gettered alloy T-111 by potassium. Temperature, 2400° F; time, 2000 hours.

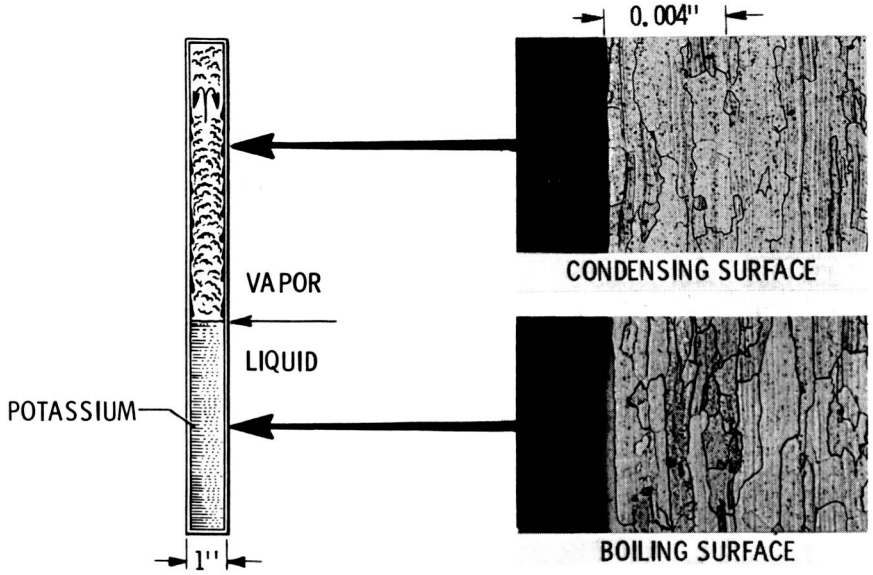
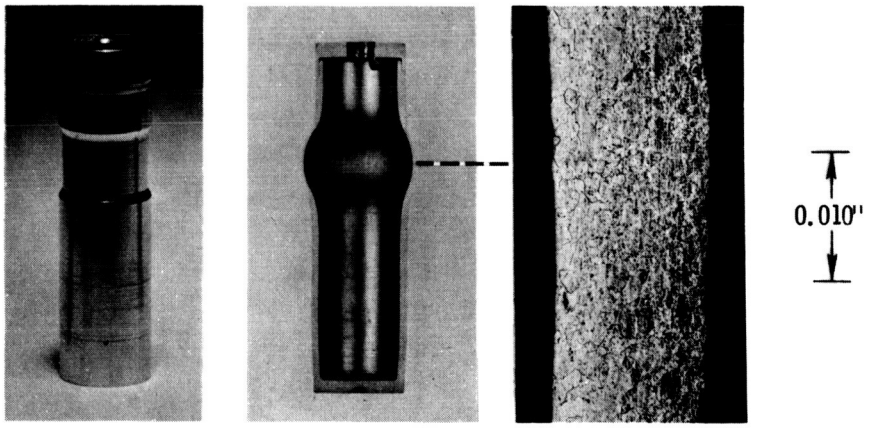


Figure VII-23. - Alloy D-43 after 10 000-hour exposure to refluxing potassium at 2000° F.



(a) Before test. (b) Sectioned capsule after test. (c) Highly stressed area after test.

Figure VII-24. - Test for stress corrosion in D-43 alloy. Temperature, 2300° F; time, 1000 hours.

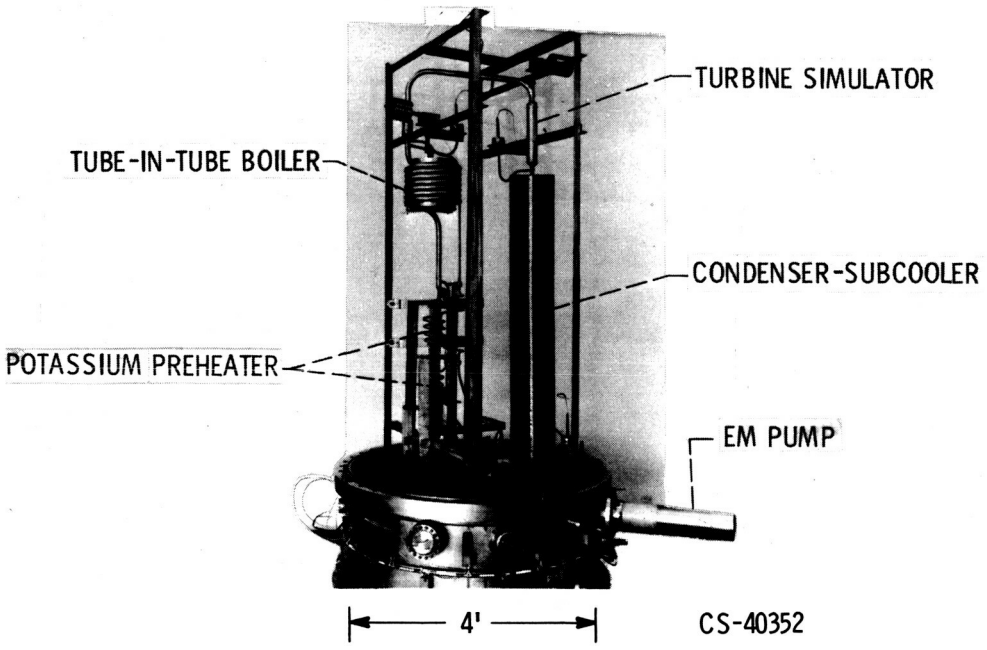


Figure VII-25. - Corrosion loop of Cb-1 Zr.

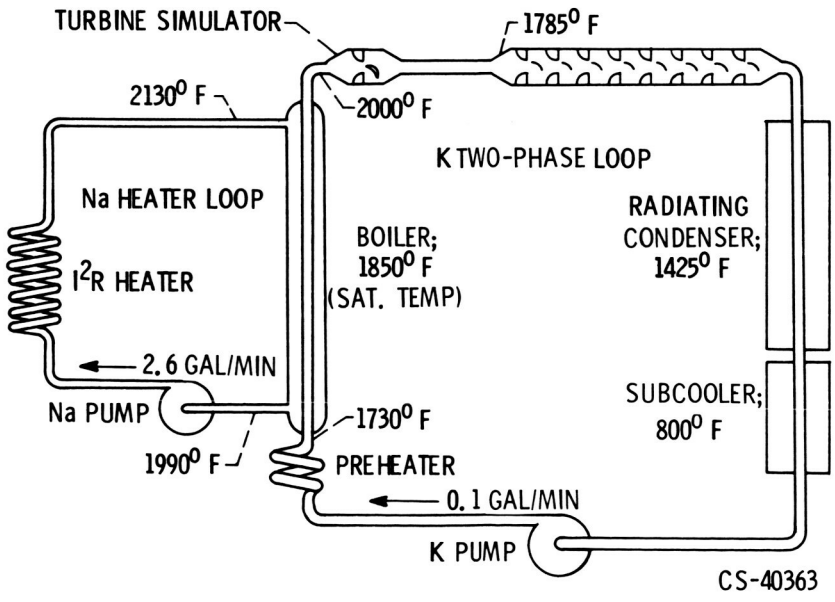


Figure VII-26. - Schematic diagram of Cb-1Zr corrosion loop.

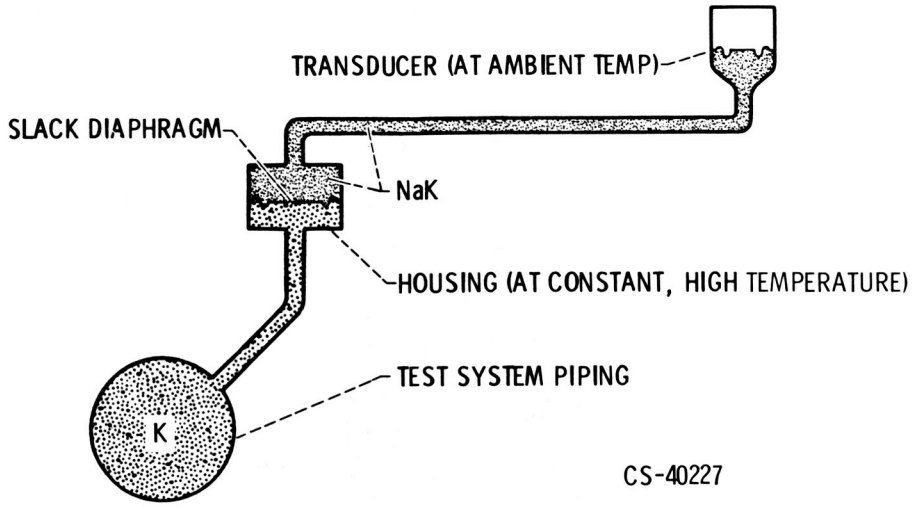


Figure VII-27. - Slack-diaphragm pressure transmitter.

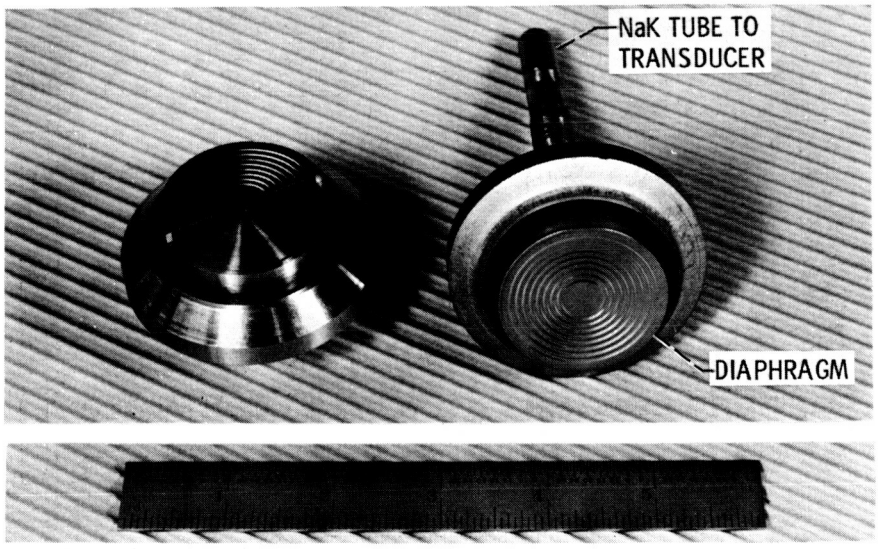


Figure VII-28. - Slack-diaphragm pressure transmitter of Cb-1Zr alloy.

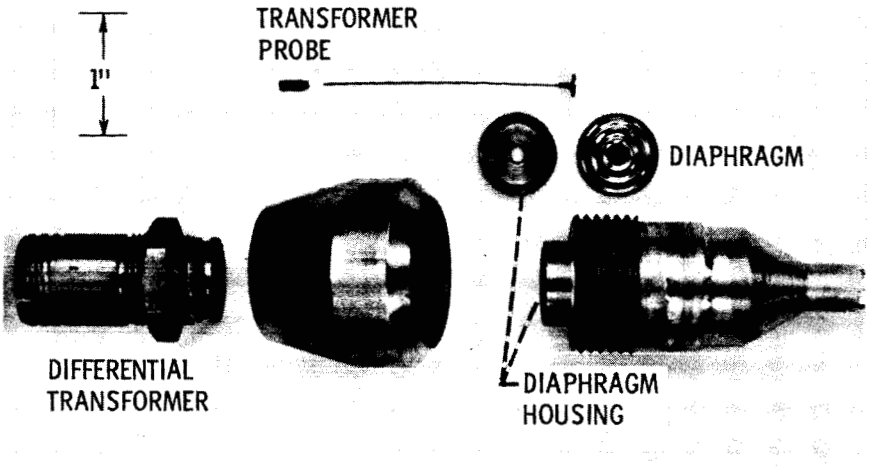


Figure VII-29. - 900° F pressure transducer.

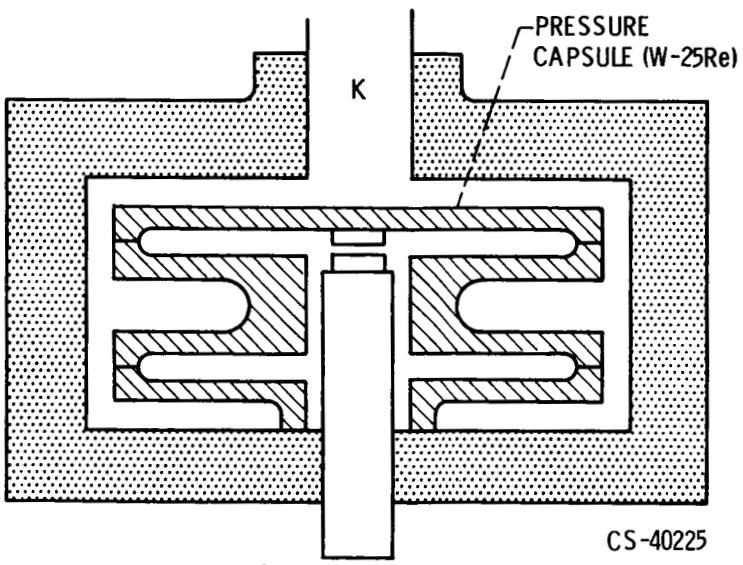


Figure VII-30. - 1800° F vacuum-diode pressure transducer.