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CORROSION IN LIQUID METAL SYSTEMS

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D. H. Gurinsky, J. R. Weeks, C. J. Klamut
Brookhaven National Laboratory, Upton, New York
L. Rosenblum, Lewis Research Center, Cleveland, Ohio
J. H. DeVan, Oak Ridge National Laboratory, Oak Ridge, Tennessee

1. Introduction

Liquid metal corrosion investigations have been stimulated recently by the increased interest in fast reactors [1]. Also, space power systems require liquid metals both for coolants and for working fluids in Rankine cycle power conversion systems [2]. The scope of liquid metal investigations has therefore been expanded to include Na, K, Rb, Cs and Hg for high temperature boiling systems.

This paper will review the current theories of liquid metal corrosion, the methods employed in liquid metal testing and analysis, and the state of the art of each of the alkali metals, Hg, and liquid alloys containing Pu.

2. Mechanisms

Liquid metal corrosion arises from a thermodynamic imbalance at the interfaces between liquid and solid metal. Several types have been observed [3]: dissolution and precipitation under a temperature differential, migration under an activity gradient, or penetration of the solid by the liquid.

DISSOLUTION CORROSION is primarily a function of the solubility of the solid in the liquid and its change with temperature. In nearly all cases the rate of solution is velocity dependent. A possible explanation is that the transfer of atoms of the solid into the immediately adjacent liquid is more rapid than their subsequent migration through the liquid.

At any point x in a corroding system the solution rate R depends on the solubility S_o, the concentration of the dissolved species in solution S, and a solution rate (mass-transfer) coefficient α: $R_x = \alpha_x(S_o - S)_x$. When liquid diffusion is controlling the solution rate in a flowing system, α is a function of the diffusivity of the dissolving species, the physical properties of the liquid, the system geometry, and the velocity v; $(S_o - S)_x$ is a function of the temperature differential ΔT. One therefore predicts $(R)_{T,\Delta T} = kv^{0.8}$. The same $v^{0.8}$ dependence has also been observed in systems which do not appear

[redacted]

to be primarily diffusion limited. Estimation of the dependence of R with T or ΔT requires knowledge of the temperature dependence of both α and S_o.

Equations now used to describe mass transfer kinetics assuming uniform dissolution are generally based on a heat transfer analogy. The early Epstein-Weber-Brooks [4] equation for the maximum corrosion rate in a closed loop is limited to small ΔT's; Epstein [5] has recently proposed an equation applicable to systems with larger ΔT's and large, essentially isothermal areas at both the hot and cold sections of a loop. Other general equations have been given by Bonilla et al. [5,6] for liquid diffusion, by Keyes [7] for both liquid and solid-state diffusion and by Gill et al. [8] for part liquid and part solid-liquid controlled reactions. These treatments require knowledge of the flow parameters, α (obtained from dissolution rate experiments), S_o, and their changes with temperature. When S_o increases rapidly with temperature, most corrosion occurs locally near the maximum temperature; the integrated mass transfer M can be estimated [9] from the equation $M = \alpha_{T\ max} A\ \Delta S_o$, where $\Delta S_o = (S_{oT\ max} - S_{oT\ min})$ and A is the small hot area. It has been observed that in loops with large, nearly isothermal areas dissolution or deposition may decrease along this region (downstream effect) [10].

The presentation to this point largely ignores precipitation. If the high and low temperature reactions are the exact reverse of each other, the low temperature reaction will control the overall mass transfer rate, since the rates of reversible reactions usually increase with temperature. This exact reversibility, implicit in many formulations which include the low-temperature dissolution rate constant α_c, has been demonstrated in high temperature Na by Holman [10a]. However, when the solute reaches saturation in the liquid at the minimum temperature, precipitation occurs which often is not the reverse of the dissolution: heat flows through the boundary layer more rapidly than solute atoms [5] so that the solute may not have to diffuse through the surface boundary layer to nucleate. Also, the precipitate, once formed, causes a flow discontinuity which effectively reduces the diffusion distance for solute precipitation.

Solid-state diffusion controls dissolution at temperatures at which the more soluble (minor) constituent of the alloy diffuses to the solid-liquid interface more rapidly than the less-soluble (major) constituent dissolves. Keyes [7], and Harrison and Wagner [11] have treated this case; the latter predicted a sine-wave shape of the solid-liquid interface. When the solute is removed from solution primarily by diffusion into the solid metal, the low temperature diffusion rate may control mass transfer.

In boiling systems solution attack by the fresh condensate is expected to be rapid since $S \approx 0$. Precipitation may occur at the boiling interface where the liquid locally becomes supersaturated by evaporation, or on the superheater surface where entrained liquid droplets are vaporized.

Radiation has not been found to enhance liquid-metal corrosion either in Na systems [11a] or Zr inhibited Bi. Changes in composition of the liquid metal due to nuclear transformations may make it more corrosive.

ACTIVITY GRADIENT MIGRATION, which can be independent of ΔT, arises when a metallic or non-metallic constituent exhibits a different activity in two solid alloys contacting the liquid, or in a liquid-solid couple.

Migration of metallic constituents includes: (1) isothermal mass transfer of a pure metal resulting in etching of high-energy boundaries and crystallite deposition [12], (2) transfer between two solid metals or alloys to equalize activity of constituents in contact with the liquid [3], or (3) surface deposition of a dissolved metal inhibitor [13].

Migration of non-metallic constituents often controls the selection of materials for alkali metal containment. O in Na is known to accelerate mass transfer [14]. The effect of O on steels is probably due to the formation of a soluble mixed oxide such as $(Na_2O)_2FeO$ [12,15]. Weeks and Klamut [9] attributed the increase in the solubility of Fe in O-saturated Na [16] to formation of this compound, and used these data to estimate its free energy of formation. Mottley [17], using these same data, formulated mass transfer equations for steels in O-contaminated Na, assuming the rate-controlling step to be migration of FeO (or the mixed oxide) through the liquid.

The effect on corrosion of alkali-refractory metal mixed oxides appears to increase with the atomic weight of the alkali metal. The activity of O in Li and Na has been calculated from an ideal solution law approximation; O-exchange with refractory metals calculated on this basis compares favorably with experiment [9]. O-exchange calculations in K, however, do not agree well with experiment [18], possibly due to the formation of mixed oxides. Studies with Rb and Cs suggest that mixed oxides also play an important role in corrosion by them.

Carbon transfers through alkali metals when there is a C activity difference between alloys [19]. Although CO, Na_2CO_3 etc. should be reduced to free C by Na, corrosion results suggest that C and O may be associated in Na containing more than 50 ppm O [19,20].

Nitrogen is an especially serious contaminant in Li [21]. N may migrate through Na and embrittle the surface of steels or refractory metals. N can be introduced into Na from a cover gas impurity through association with dissolved metallic impurities, notably Ca.

Hydrogen [22] migration through alkali metals is usually not serious except during reactor shutdowns, since hydrides which can cause embrittlement do not precipitate in most solid alloys above 400°C.

PENETRATION by a liquid metal into the grain boundaries of a solid metal occurs when the grain boundary interfacial energy γ_B is greater than twice the solid-liquid interfacial energy γ_{SL} [23]. Penetration under stress may occur when the liquid lowers the surface energy of the solid and therefore the energy required to separate atoms of the solid metal [24]. Weeks [25] has suggested an empirical method of estimating the interfacial surface energy from solubility data.

3. Liquid Metal Impurity Analysis and Monitoring

The analysis of impurities in liquid metals continues to be difficult The validity of an analytical method is based on the analyses of samples containing known impurities. In actual practice the form of the impurity may not be known. Calibration for accuracy and precision are also handicapped by lack of standard samples, poor techniques for replicate sampling, and inattention to environmental contamination.

OXYGEN amalgamation analysis [26] remains the most widely used method for O in Na and K. Excellent precision is claimed for low concentrations of O in Na using vacuum amalgamation [27]. For O levels <100 ppm, good precision was found for O in K [28,29]. Amalgamation has been used for O in Rb [30] and Cs [31], although it may not be quantitative in Cs.

Vacuum distillation, popular in Europe for determining O in Na [32, 33], has recently been reactivated in the U.S. as a method for O in Na [34] and K [35]. Agreement has been found between vacuum distillation and vacuum amalgamation at O levels <50 ppm in K. The effect of residual gas as manifest by system pressure was found to be marked. Using a replicate sample of K the following was obtained [35]: (1) amalgamation in vacuum, 19±3 ppm (6 samples); (2) distillation at 2×10^{-6} torr, 18±1.2 ppm (3 samples); (3) distillation at 5×10^{-5} torr, 52±19 ppm (4 samples).

The alkyl halide method [36] coupled with infra-red analysis has yielded good precision e.g. 20±4 ppm for O in Na [38]. However it has been judged by some to be poor because it is difficult to remove water from the reagents [30,35] or because the results suggest that oxides react with the reagent [31,37].

The methanol method [39] has been tested for the determination of O in Li [40] and Na [41]. In the latter excellent precision was obtained: 3±1.5 ppm. (Subsequently a blank of 3 ppm was uncovered [42].)

The gettering-vacuum fusion method [43] is lengthy and expensive but specific for O; the precision is not known. It has been used for O in Na and K [35,37].

The liquid ammonia method has been tested for O in Li, Na, K and Cs; the precision to date is of the order of ±10 to 20% at the 100 ppm level in Na and at the 300 to 2000 ppm level in Li [44].

The fluorination method [45,46] is hazardous, but is specific for O;

it has been used for O in Li [47] and K [48].

An activation method which uses thermal neutrons has been tried for high ppm O in Li [49]. Activation methods based on fast [35,50] and thermal [50] neutrons are currently being studied for O in K. These O-specific methods should give acceptable precision if low O-bearing containers can be found.

Other methods for O in alkali metals are covered in recent reviews [34].

CARBON analyses in the alkali metals are performed by either of two oxidation methods: wet [51,52] or dry combustion [53-55], followed by measurement of the CO_2 evolved. Good recovery and good precision with known samples have been reported. However in two recent round robin analyses for C in Na among a dozen laboratories, the data were highly scattered [56,57]. In these instances the deviation appeared to be the result of sample heterogeneity.

NITROGEN has been determined in Li by hydrolysis [58,59] or fluorination [47]. In Na and K the Kjeldahl method [60,61] has been used.

HYDROGEN has been determined by isotope dilution with deuterium in Na and NaK [62] and by isotope dilution with tritium in Na [63].

MONITORING DEVICES for O in Na include plugging, resistivity, and electrochemical meters. The plugging meter is widely used in Na loops [64]. Lately refinements have been made to improve the ease and speed of operation [65]. A precision of ±5 to ±10 ppm at <100 ppm O is indicated from recent data [34,65]; however, accuracy is dependent on the much questioned Na_2O solubility-temperature curve and the presence of precipitates other than Na_2O.

The Blake resistivity meter [66] is claimed to have a sensitivity of the order of a few ppm O in Na. Small changes in temperature and the presence of impurities have a large effect on the measurements. A current evaluation has found it to be useful in the 10 to 80 ppm O range in Na [67].

The electrochemical meter proposed by Horsley [68] for O in Na is now under development [69]. A 44 day run was made using $Na-Na_2O$ and Cu-CuO electrodes and a $ThO_2-Y_2O_3$ solid electrolyte at 375°C. Reproducibility was good; however, several hours were needed for equilibration when O changes occurred. The effect of mixed oxides has not been evaluated.

4. Corrosion Test Methods

Test methods in all-liquid systems have remained essentially unchanged over the last decade. However, with the interest in liquid metals as working fluids for a Rankine cycle power system [2], reflux capsule tests and natural and forced-convection two-phase loops have been developed [5].

Reflux capsule tests least simulate service conditions; their value lies in screening materials. Natural-convection loops, which have well defined boiling and condensing areas, can be better instrumented and are easier to interpret; however, the liquid boils and condenses at the same temperature. Only in forced-convection loops can service conditions be simulated.

Two-phase tests often suffer from boiling instability manifested by slugging and reverse flow with concomitant thermal and mechanical shock and disruption of concentration gradients. Consequently the corrosion data from these tests should be interpreted with caution. Mitigation of boiling instability in corrosion tests is discussed in recent reports [5,69a].

Since it has been recognized [5,70] that corrosion testing of refractory metals requires a very low concentration of impurities in the test environment, high vacuum test facilities (10^{-7} to 10^{-9} torr) are currently used in most of the programs testing these metals. Inert gas environments are not considered feasible for refractory metal testing because the low O contamination level required ($<10^{-4}$ ppm) is difficult to monitor.

5. Lithium

Corrosion studies of Fe, Co and Ni base alloys* in Li have shown that these materials are not satisfactory for prolonged use at 600-800°C [71]. In recent years, however, studies have shifted to refractory metals, since these metals combine exceptional corrosion resistance to Li and high temperature strength. Many refractory metal capsule tests conducted with Li at temperatures up to 925°C have demonstrated that, at low contamination levels, the solubilities in Li of Ti, Mo, and Nb, measured in refractory metal capsules, lie near the limits of detection (about 10 ppm) up to 925°C [72-74]. No serious temperature gradient mass transfer of refractory metals by Li has been detected in dynamic tests [71,75].

Although the pure refractory metals demonstrate excellent resistance to pure Li, impurities in either Li or the refractory metal, particularly O and N, accelerate corrosion. Because O has a relatively low chemical activity in Li, it is less harmful than N. N contamination in Li markedly increases the apparent solubilities of Fe, Cr, Ni, Nb, and Ti [74]. The apparent solubility of Mo at 1320°C has been shown to be independent of O contamination in Li up to 5000 ppm [76], and similar behavior would be expected for Nb, Ta, W, and V.

The presence of O as an interstitial impurity in Nb or Ta results in rapid penetration of these metals by Li [77]. A threshold O concentration of 200-500 ppm is required to initiate corrosion, the depth of attack increasing with increasing O in the solid metal. The corrosion process involves the formation of an oxide phase, as yet unidentified, which is found along grain boundaries or {110} crystallographic planes. The addition of a strong oxide former such as Zr markedly increases the O threshold needed to produce Li penetration. The increased tolerance imparted by Zr is equal to the amount of O which it can tie up as ZrO_2. Resistance to penetration, however, depends on the form that O takes in Nb-Zr alloys. Thus, alloys in which O exists in a metastable solid solution form are very susceptible to Li penetration. After

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*Compositions of materials discussed can be found in Table I.

heat treating to precipitate ZrO_2 these same alloys completely resist penetration by Li [77,78].

The concentration of O in Zr, Ti, or V does not measurably affect the corrosion resistance of these metals in Li; the effect of O in Mo and W on Li corrosion has not been evaluated.

Numerous tests have been conducted to determine the compatibility of dissimilar alloys in Li [71]. Combinations of alloys in Li which individually resist corrosion may seriously interact. For example the properties of Be and Fe individually are not modified in Li. When combined Be and Fe are embrittled by interalloying. Systems in which both of the components are refractory metals interact less than mixed Fe, Ni, and Co base systems.

6. Sodium

Corrosion of austenitic stainless and low Cr steels by Na at 650°C is being studied in forced circulation loops as part of the AEC Na Components Development Program. Variables are maximum temperature, temperature differential, O content of the Na, and the alloys (316 SS, 2 1/4Cr-1Mo, 5Cr-1/2Mo-1/2Ti) [10]. Preliminary measurements indicate that the average corrosion rate of 316 SS is 0.04 mm/yr at 650°C in 150°C cold-trapped Na [79]. Low-Cr steels under the same condition corrode somewhat less. Microprobe analysis of corroded austenitic stainless steel surfaces show that, in the low O (~10 ppm) systems, the surface layer is depleted in Ni and Cr, whereas x-ray fluorescent analysis of surfaces exposed to Na containing higher O (~50 ppm) show preferential depletion of Fe [10]. These results suggest that both a solution (Ni and Cr) and a soluble mixed oxide (Fe) corrosion process are simultaneously acting in this temperature range. A downstream effect was observed in these loop tests which has been analyzed by Epstein [5] and Mottley [17].

Nickel-base alloys and austenitic stainless steels were tested in Na at temperatures up to 815°C at ORNL in the aircraft reactor program [80]. Very little transfer or corrosion was detected below 700°C. Above 700°C, mass transfer of Ni-base alloys was observed which increased rapidly with temperature and linearly with ΔT and v. The cold leg deposits were rich in Ni. Fe-base alloys exhibited much less transfer in the 700-815°C range probably due to their lower Ni content. O in Na up to 500 ppm had little effect on mass transfer in the Ni-base systems, whereas 1500 ppm O had a significant effect.

Carbon transport by Na in austenitic stainless steel systems occurs if a C activity difference exists between alloys used in the same system or if a source of C is accidentally introduced into the system. Carburization of austenitic stainless steels results in some modification of the mechanical properties [19]; possible effects on reactor components have not been evaluated. The mechanical property changes of austenitic stainless steel in C-saturated Na are being studied by Andrews and Baker [81]. At 650°C, negligible C transfer was encountered if type 316 SS or 5Cr-1/2Mo-1/2Ti steel was used separately or in combination [10]. A 0.13 mm carburized surface layer was found on 316 SS in a 316 SS and 2 1/4Cr-1Mo composite system [10]. In a 304 SS loop operating at 560°C, tabs of 1 1/4Cr-1/2Mo, 2 1/4Cr-1Mo and 5Cr-1/2Mo were decarburized, whereas decarburization of 5Cr-1/2Mo-1/2Ti, 7Cr-1/2Mo, and 9Cr-1Mo steels was negligible [82]. C transfer from the hot to the cold leg was observed in an all 2 1/4Cr-1Mo system [10]. O up to 50 ppm appears to have little effect on carbon transfer. However, higher O concentrations may accelerate C transfer [19,20]. A start has been made on the development of compatible alloys for Na systems which are designed to minimize C transfer [83].

The behavior of Ta, Zr, V and Nb alloys in static and flowing Na at temperatures near 650°C are being studied in the U.S.A. [84-86] and U.K. [87] for fuel element claddings for fast reactors. Ta in cold and in hot-trapped Na at 660°C [86] lost about 0.2 mm/yr and 0.012 mm/yr, respectively, in static tests, whereas Zr gained weight in cold-trapped systems. In flowing Na (50 day tests), Ta lost 0.0025 mm/yr in hot trapped (<10 ppm O) Na, and 0.075 mm/yr in cold trapped (40 ppm) Na. Apparently, Ta oxides spall, whereas Zr absorbs O. Intergranular attack of arc-cast Ta exposed to 650°C Na containing 80 ppm O is associated with platelets present in the weld zones.

Niobium and V-base alloys containing additions of Zr, Mo, Ti, V, Nb, Cr and W were tested as inserts in dynamic systems operating at 650°C [84]. In 7 and 9 day tests in which the Na contained 120-200 ppm O and operated at a flow of 0.15 m/sec, corrosion of V-base alloys (weight loss) was about an order of magnitude less than that apparently typical of Nb-base alloys. Most promising were the V-10Ti and V-20Ti alloys which exhibited the least weight loss and the thinnest hard surface layers [85].

The behavior of refractory metal alloys is also being studied in boiling Na [5]. Nb-1Zr in capsules refluxing at 1205°C and in a natural circulation boiling loop operated at 1090°C was not attacked by Na after 5000 hours. Mo and Ta tabs in Nb-1Zr capsules also resisted attack by Na under these same conditions, whereas a Nb tab was attacked intergranularly to a depth of 0.15mm. In capsule tests in which alloy composition, O additions, and "getters" were studied, corrosion was correlated with higher than normal N content in the alloy. The excellent corrosion behavior of Nb-1Zr was unexpected in view of the high solubilities measured in preliminary experiments [88].

7. NaK

The containment of NaK was studied in the temperature range 540°C to 815°C in low and high velocity loops [80,87]. Tabs of Ni-, Fe-, and Co-base alloys and Mo and Nb metals were tested in cold trapped-natural circulation loops containing eutectic NaK (22 w/o Na-78 w/o K) [89] at temperatures up to 816°C and test times up to 5000 hours. None of the materials was attacked more than 0.08mm; Mo and Nb were the most resistant. The amount mass transferred was halved when NaK (56 w/o Na-44 w/o K) was substituted for Na in inconel forced-circulation loops (815°C for 1000 hour) operated under similar conditions [80].

8. Potassium

The corrosion behavior of liquid K is similar to NaK and Na. McKee [5] has compared the mass transfer rates in liquid Na and K in identical 316 SS thermal convection loops operated at a maximum temperature of 870°C. Although the rate of material transport by K in a 5000 hour test was a factor of three lower, corrosion in both systems was manifested by selective removal of Ni from hot-leg regions and formation of a thin ferritic surface layer. The mechanical properties of Haynes 25, aside from normal aging, were not affected by 1000 hour contact with K at 1010°C in capsule and loop tests [90].

Studies of boiling K contained in Ni, Fe, and Co alloys have been made at maximum liquid-vapor temperatures ranging to 870°C [90,91]. Tests for 1500-3000 hours in boiling K show that type 316 SS and Haynes 25 are equally resistant to attack. At equivalent temperatures and mass flows the corrosion rates of both alloys were higher locally in the condenser area than in the above all-liquid systems. In contrast to all-liquid K systems, corroded areas in these boiling loops were not preferentially leached of any metallic constituent. However, a deposit of $Cr_{23}C_6$ was found in the subcooler of the 316 SS loop [91,92]. Transfer of C from the condenser to the subcooler was also observed in inconel and Haynes 25 boiling K loops.

Niobium and Ta alloys are considerably more resistant than conventional alloys to attack by K above 900°C as determined from preliminary data. The corrosion resistance of Nb-1%Zr has been evaluated in refluxing capsules containing K at 900-1200°C for periods up to 3000 hours [93-95]. Capsules and tab inserts have generally been negligibly corroded. However, metallic deposits at the vapor-liquid interface were observed in small screening test capsules [93]; these deposits were found only in capsules which had deformed during test. Nb alloys containing W, Zr and/or Y have been tested in both refluxing capsules and natural circulation loops which operated up to 1200°C. The corrosion behavior of these alloys was similar to that of Nb-1%Zr [93,94]. It is significant that carbides in all of the refractory alloys tested to date have been unaffected by long term exposures to high temperature K. However activity gradient migration of interstitials has occurred in K loops containing dissimilar alloys. Nb and its alloys tend to getter both N and C from austenitic stainless steels or Co-base alloys, lowering their ductility [96], whereas Mo-½ Ti tabs in Haynes 25 loops getter only C in the presence of Zr tabs [90].

Oxygen in K reacts with refractory metals such as Nb and Ta to produce surface oxide layers at low temperatures and to increase the O content of the solid metal at higher temperatures. Solubility studies of Mo and Nb in K have shown a strong effect of O in the solvent. The apparent solubility of Mo in K at 1095°C increases linearly with O additions from 200 to 5000 ppm [76]. This behavior was attributed to the formation of a mixed oxide identified by x-ray diffraction as K_2MoO_4. The apparent solubility of Nb in K at 400 and 600°C likewise increases with the amount of O added to K [97].

9. Rubidium and Cesium

The data available on corrosion of materials by Rb and Cs are less extensive than the data on the other alkali metals and are primarily qualitative.

Rubidium corrosion has been studied up to 1100°C. In Ta and Haynes 25 reflux capsules containing Ti-Zr gettered Rb, the Ta capsules were attacked whereas inserted tabs of Be, V, Nb-1Zr, Mo-1/2Ti and Haynes 25 resisted corrosion at 1100°C [30]. Solubility experiments performed in Ta crucibles were inconclusive. A Nb-1Zr test conducted at 1000°C [98] in a forced-convection boiling loop containing Ti-Zr gettered Rb, has not shown corrosion after 700 hours.

Cesium corrosion has been studied up to 1700°C. Below 1000°C, most of the common engineering alloys [99-102] and the unalloyed refractory metals [99,101,103] were moderately corrosion resistant; TD Ni was attacked at 1000°C [31,100]. In a series of reflux capsule tests certain ceramics (Al_2O_3, MgO and BeO) were corrosion resistant up to 1100°C [99,104-5]. Nb-1Zr [100,101] and Ta-8W-2Hf [106] appeared to resist attack at 1370°C in non-gettered Cs; Mo [100, 103] alloys were attacked at this temperature and Nb-1Zr showed intergranular penetration at 1000°C [105]. W-25 Re was satisfactory up to 1700°C [103] in non-gettered Cs.

10. Mercury

The corrosion resistance of containment materials for Hg liquid and vapor is being reexamined because of its planned use as a working fluid in space power systems. Reflux capsule tests [107-109] have confirmed that corrosive attack by Hg is a function of the solubility of the constituents of an alloy. Owens and Nejedlik [107] arrange the relative solubilities of elements in Hg in the following order, Mn>Ni>Ti>Cr>Be>Si>Co>Fe>V>Mo>W>Nb>Ta based on corrosion data at 480°C. Weeks and Fleitman [110] measured solubilities (in ppm) at 650°C: Ti 215, Zr 195, Ni 120, Cr 27, Co 1.1, Fe 0.75, Nb 0.04 and Ta <0.002.

Corrosion tests have demonstrated that the relative resistance to attack is ferritic steels >Co-base alloys >austenitic stainless steels, which order is expected on the basis of the solubility of constituents. The effect of the inhibitors Ti and Zr have been evaluated on carbon steel, low Cr steels and Haynes 25 [111]. Corrosion resistance of the above is markedly improved by additions of both Ti or Zr; Zr is the more effective inhibitor in capsules, all liquid, and boiling loops. Wang [112] has studied inhibition of corrosion of Ti by Zr and Ni additions to Hg. Inhibitors do not completely eliminate corrosion, however, particularly in the boiling systems.

No attack or weight loss was found in reflux capsule tests (liquid 590°C, vapor 700°C) containing W, Mo, Ta and Nb-1Zr tabs [107]. Scheuermann et al. [108] obtained the same result in 5000 hour 700°C tests with Ta and Nb-1Zr. Nejedlik's observations also agreed with the above. When Nb-1Zr was tested in a boiling convection loop (boiler and condenser at 650°C, superheater at 760°C), no mass transfer was noted; however, cracks developed after 7700 hours in the bend of the superheater section [109]. Subsequent tests [110] demonstrated that cracking occurs in Nb-Zr alloys at 600-760°C in bend areas; some leaching of Zr accompanied cracking. The long-term behavior of Ta [109] in a boiling convection loop (boiler and condenser at 650°C, superheater at 760°C) is being determined. A gamma graph taken after 11,000 hours shows no corrosion or mechanical failure.

Several vapor impingement tests conducted by Bleil [113] (velocity 305 m/sec, Hg vapor 88% quality) gave high weight losses of Mo alloys and showed good resistance of Dynacut and Stellite 6B.

11. Plutonium Fuels

Plutonium 2.5 w/o Fe [114-117] was used in the first two cores of the Los Alamos Molten Plutonium Reactor. The fuel was contained in pure and low alloy Ta casings. Intergranular penetration of Ta by Pu, similar to the attack of O-contaminated Nb by Li resulted in Pu contamination of the Na coolant.

The penetration mechanism [118] was studied in capsules (2/3 full of the Pu 2.5 w/o Fe alloy) fabricated from unalloyed Ta, Ta-W alloys, Ta + interstitials and welded Ta over the temperature range 500-700°C in Zr hot-trapped convectively-circulated Na loops.

The resistance to penetration of the materials tested was determined by the percentage of capsules failing after fixed times; in the temperature range 600-700°C the number of failures increased as follows: (1) double arc melted unalloyed Ta (highest C content), (2) electron-beam melted unalloyed Ta, (3) Ta + 0.75% W + Y, (4) Ta + 0.1% W. Failures in welds were independent of method of the process used (electron beam or W inert gas).

The study of the effect of interstitials, aside from demonstrating that increasing N content increased brittleness, proved that high O alone resulted in an abnormal increase in penetration. Heat treatment of unalloyed Ta specimens containing 60 ppm C showed conclusively that a one hour heat treatment between 1450-1600°C markedly improved the resistance to penetration. This heat treatment results in increased grain-boundary precipitate (probably Ta_2C) and an increased hardness. This grain boundary precipitate is believed to change the inequality of the surface tension relation from $\gamma_B > 2\gamma_{SL}$ (Pu penetrates non-heat treated Ta) to $\gamma_B < 2\gamma_{SL}$ (Pu does not penetrate heat treated Ta) by interposing the precipitated phase between adjacent Ta grains [118].

In the new core in addition to the Pu 2.5 w/o Fe, a fuel composition 34 w/o Pu, 10 w/o Co, 56 w/o Ce will be used. The latter fuel in the preliminary experiments is less corrosive to Ta than Pu-2.5 w/o Fe.

12. Conclusions

Since 1958 the U.S. Liquid Metals Program has been primarily directed at the development and testing of materials for higher temperature applications. In the Sodium Components Program the engineering tests to determine the long term behavior of containment alloys have shown that the 650°C temperature range is feasible.

In the nuclear auxiliary power program refractory alloys show promise for containment of liquid Li. Refractory alloys also appear suitable for power conversion systems using boiling K, Na, Rb, Cs and Hg.

The confirmation of the importance of impurities (in the liquid metals and the containment alloys) on the corrosion process has resulted in advances in testing and analytical techniques. Although the precision of impurity analyses and the monitoring techniques of the liquid have been improved, accuracy remains uncertain because of the lack of calibration standards. Use of x-ray fluorescence and microprobe techniques have delineated the subtle surface effects due to corrosion.

From this review the authors conclude that those engineering programs which show the best progress are the ones complemented by basic studies.

13. Acknowledgements

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TABLE I - NOMINAL COMPOSITION OF ALLOYS DISCUSSED IN THIS PAPER

		Alloying Elements (w/o)										
Type Alloy	Alloy	C	Fe	Cr	Ni	Mo	Co	Mn	Si	Ti	Zr	Other
Austenitic Stainless Steels	316	.08*	Bal	17	12	2.5		2*	1*			
	304	.08*	Bal	19	10			2*	1*			
Nickel Base	Inconel	.04	7	15	78			.35	.20			
Fe-Base Low Cr Steels	$1\frac{1}{4}$Cr-$\frac{1}{2}$Mo	.15*	Bal	1.25		.5		.45	.75			
	$2\frac{1}{4}$Cr-1Mo	.15*	Bal	2.25		1.0		.45	.5*			
	5Cr-$\frac{1}{2}$Mo	.1*	Bal	5.0		.5		1.0*	.5*			
	5Cr-$\frac{1}{2}$Mo-$\frac{1}{2}$Ti	.12*	Bal	5.0		.5		.45	.5*	.5		
	7Cr-$\frac{1}{2}$Mo	.15*	Bal	7.0		.5		.45	.75			
	9Cr-1Mo	.15*	Bal	9.0		1.0		.45	.75			
	Dynacut	1.23	Bal	3.75		8.7	8.2				1.8	2.0V
Cobalt Base	Haynes 25	.15	2.5	20	10		Bal	1.5	.5			15W
	Stellite No. 6B	1.1	3*	30	3*		Bal	.3 to .6		4xC min .7*		4.5W 2.5

Refractory Alloys: Nb-1Zr(99%Nb+1%Zr); Mo-$\frac{1}{2}$Ti(99%Mo+$\frac{1}{2}$%Ti); W-26Re(74%W+26%Re); Ta-8W-2Hf(90%Ta+8%W+2%Hf); Ta+.75W+Y(99%Ta+.75%W+Y); Ta-10W(90%Ta+10%W); V-10Ti(90%V+10%Ti); V-20Ti(80%V+20%Ti)

*Maximum

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