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AD863593

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AFSC ltr dtd 2 Mar 1972

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SODIUM CORROSION REVIEWS

A book published in Moscow in 1967, *Liquid Metals*, is now available from CFPST in English translation. It is a collection of Soviet papers on heat transfer and component technology related to sodium-cooled fast reactors. A single paper on corrosion of structural materials reviews the general theories of corrosion by alkali metals and the role of oxygen impurities in the corrosion process. Evidence is presented that oxygen in liquid sodium at elevated temperatures exists in the very active ionic form, which the investigators suggest is the basis for the accelerating influence of oxygen on the corrosion of steels by sodium.

The results of Soviet loop tests on a large assortment of ferritic and austenitic steels, six nickel-base alloys, and two refractory metals are similar to those obtained from comparable studies in the United States and other countries. Representative observations are:

1. Unless a ferritic-pearlitic steel contains enough of the carbide-forming elements to tie up all its carbon as stable carbides, it will be decarburized in the high-temperature zones of a dynamic sodium system and may suffer a significant reduction in strength.

2. Pearlitic steels show very low rates of weight loss in flowing sodium up to 12 m/sec, 700 C (1290 F), and 50 ppm of oxygen.

3. Austenitic steels are readily carburized (with consequent loss of ductility) if carbon steels or pearlitic steels are present in the same sodium system. They are also nitrided if a source of nitrogen is available.

4. Austenitic steels are more prone to mass transfer in sodium systems than ferritic steels, the tendency increasing sharply with peak temperature above 600 C (1110 F).

5. Sodium attacks austenitic steels intergranularly with increasing severity as the temperature and oxygen levels are increased. However, most austenitic steels are sufficiently corrosion resistant up to 700 C if the sodium contains less than 50 ppm oxygen. American investigators would set the oxygen limit closer to 10 ppm.

6. Nickel-base alloys are more prone to dissolution and mass transfer in flowing sodium than are steels. Mass-transfer rates increase with temperature, time, and nickel content of the alloy.

7. Molybdenum is highly resistant to flowing sodium containing 20 ppm oxygen at temperatures to at least 1050 C (1920 F) and flow velocity seems to have no effect.

8. Columbium is severely attacked by sodium at 120 C unless the oxygen content of the sodium is kept below 10 ppm. The corrosion rate increases with increasing flow velocity.

Thorley and Bardsley have drawn on the results of numerous past sodium-corrosion studies to explain some of the structural changes that occur when the various materials are exposed to flowing sodium. Some of their observations follow:

- **Columbium** - Loses weight by formation and spalling of Na2Cb205 at a rate depending on temperature, oxygen content, and velocity of the sodium.

- **Zirconium** - Forms a black, adherent ZrO2 film and gains weight at a rate which is independent of oxygen content (to 50 ppm) and velocity (to 25 ft/sec) of the sodium.

- **Stainless Steel** - Loses nickel and chromium from surface, resulting in the formation of an iron-rich ferritic layer which corrodes at a rate governed by temperature and oxygen content of the sodium; also it may be carburized and form Fe3C and NiC in 650 C (1200 F) sodium containing carbon impurities.

- **Ferritic Steel** - Becomes decarburized under the driving force of high-activity carbides such as Fe3C, especially when stainless steels are present in the same circuit, resulting in increased ductility and grain size and decreased strength.

- **Brazing Alloys** - Undergo selective leaching (e.g., Microbras 50 loses phosphorus and Microbras 30 loses silicon).
General Electric's updated evaluation of potential fuel-cladding materials for the LWR contains a chapter on the corrosion of selected materials by liquid sodium. (3) This chapter constitutes a comprehensive state-of-the-art review of the general corrosion picture as well as specific information on steels and alloys based on nickel, cobalt, tantalum, and tungsten. Alloys ranked as having "good" corrosion resistance are ferritic steels, austenitic/stainless steels, iron-chromium-nickel-cobalt alloys, cobalt alloys, and molybdenum. "Intermediate" ratings were given to vanadium and columbium alloys as well as to nickel-base alloys with less than 50 weight percent nickel. Alloys with over 50 weight percent nickel were rated as "poor".

CORROSION IN RANKINE-CYCLE SPACE POWER SYSTEMS

Alkali Metal Systems

The Proceedings of a 1968 symposium on refractory metal alloys contains several papers dealing with their application as structural materials for liquid-metal Rankine-cycle space electric power systems. (4) The review by Hoffman and Harrison points out that refractory metals generally have excellent compatibility with liquid metals, but only if strict controls are exercised over impurities. Their discussion includes information from tests of refractory metals in contact with liquid sodium, cesium, potassium, sodium, and lithium. It also describes the compatibility results obtained in a 500-hour test of a two-loop Cb-I2r facility in which sodium was circulated in the heater circuit and potassium was boiled and circulated in a two-phase secondary loop containing turbine-simulator test sections of Mo-TiZm alloy.

A paper by Semmel reviews the status of refractory-alloy applications to alkali-metal Rankine-cycle systems for future power requirements above 100 kw. (4b) Columbium and tantalum alloys are considered for containment for over 10,000 hours at temperatures near 1100 C (2000 F). Molybdenum alloys are considered for alkali-metal-vapor turbine-wheel and -blade applications where weldability is not essential.

The 5000-hour test mentioned above was conducted by General Electric. (5) The secondary loop was designed to simulate a Rankine-cycle space power system. Maximum and minimum temperatures in the sodium circuit were 2150 F and 1960 F, respectively, while temperatures in the two-phase potassium loop ranged from 2000 F for superheated vapor at the boiler outlet to 600 F liquid.

The system was operated in a vacuum chamber at 2 x 10^-6 torr with no significant contamination of the components by the vacuum-chamber environment. Extensive chemical, metallurgical, weight-change, and dimensional examinations indicated that the Cb-I2r structural alloy and the Mo-TiZm turbine alloy have excellent compatibility with the alkali metals. No significant corrosion was found, and the substantial oxygen migration noted from the hotter to cooler regions of the sodium circuit had no detectable effect on the strength or the ductility of the Cb-I2r alloy.

Mercury Systems

Workers at NASA-Lewis operated a two-phase, forced-convection mercury loop constructed of the cobalt-base alloy HS-75 (L-605) for 1147 hours with a liquid velocity of about 8 ft/sec. The peak temperature in the boiler was 1072 F and the vapor reached 1300 F in the superheater. Severe corrosion to a depth of about 10 mils was found near the boiler inlet where two-phase flow began. This penetration was much greater than had been expected from lower velocity capsule and loop tests, indicating that liquid velocity is an important corrosion parameter.

A U.S. patent has been granted on a technique for inhibiting the corrosion of an alloy containing cobalt, tungsten, chromium, and nickel (which includes most cobalt-base superalloys) by hot lithium and mercury. This involves soaking the alloy in high-temperature mercury long enough to leach chromium and nickel from the first several mils on the surface layer. The next step is to anneal the alloy in hydrogen to convert the surface layer to the intermetallic compound Co3W, which presumably is highly resistant to attack by the molten mercury.

Capsule tests were run for 1000 hours at General Electric to evaluate the resistance of Cb-I2r and T-111 (Ta-8W-2Hf) alloys to corrosion by 1200 F liquid mercury. These alloys are being considered as possible replacements for the lower strength unalloyed tantalum tubing presently specified for the Na-heated mercury boiler in the SNAP-8 Rankine-cycle space power system. Specimens of tantalum and the two alloys were strained 5 and 20 percent by bending and tested in the as-bent and as-bent-and-annealed (8 hours at 1600 F, 2 hours at 1900 F, or 2 hours at 2100 F) conditions. Through stress-corrosion cracking of these alloys under similar conditions had previously been reported by Brookhaven, neither cracking nor changes in weight or metallographic structure could be detected in any of the General Electric specimens.

CORROSION BY LITHIUM

The Soviets conducted a study to determine the effect of molten lithium on the corrosion resistance and strength of welded joints in 1Kh18N10T (18Cr, 10Ni, 0.8Ti, 0.8Si, 0.12C) and 2Kh13 (17Cr, 0.25C) steels. Parameters were weld atmosphere (spectrographically pure argon and commercial argon), lithium purity (pure lithium and lithium contaminated with oxygen, nitrogen, or both), and exposure temperature (700, 800, and 900 C).

Results for the 1Kh18N10T steel, shown in Table 1, indicate that neither lithium purity nor welding-atmosphere purity has a dramatic effect on short-time tensile properties within the range studied. However, the specimens were slightly weaker and less ductile when tested in pure lithium than when tested in argon and also when welded in commercial argon than when welded in spectrographically pure argon. These effects are attributed to intergranular penetration of the steel by the lithium. The penetration was noted to be shallower in the welds than in the base metal, suggesting that the welded material has better corrosion resistance to lithium than does the base metal.
The as-welded ferritic steel 2Kh13 showed a marked loss of strength and ductility as a result of similar lithium exposures in the range of 250 to 450 °C (480 to 840 °F) but between 450 and 800 °C (840 and 1470 °F), the properties of the lithium-exposed and argon-exposed specimens were the same. However, if the specimens were given a postweld heat treatment prior to their exposure, their mechanical properties were unaffected by either the lithium or the purity of the welding atmosphere.

The heats of solution of molybdenum and tungsten in potassium are 6.7 and 17.6 kcal/mole, respectively. The authors believe that interstitial impurities may affect the tungsten solubility data much more than they do the molybdenum data.

**CORROSION BY LEAD-BISMUTH ALLOYS**

Ferritic steels are promising container materials for molten bismuth-lead alloys, although their use above about 450 °C (840 °F) requires the addition of corrosion inhibitors (magnesium plus zirconium or titanium). Weeks and Romano made detailed studies of the solubilities of iron and the inhibitors in bismuth-lead alloys in an attempt to estimate the relative aggressiveness of bismuth-lead alloys toward ferritic steels. At a given temperature, the solubility of iron in liquid bismuth-lead alloys increases with the bismuth content of the alloy, as shown in Figure 1. The 20-fold greater solubility of iron in bismuth than in lead is reflected in a comparable ratio of corrosion rates of steel loops in which pure bismuth and pure lead were circulated at 700 to 800 °C (1290 to 1470 °F). The corrosiveness of a bismuth-lead alloy is predicted to be proportional to its bismuth content.

**SOLUBILITY OF STRUCTURAL METALS IN POTASSIUM**

The solubilities of several refractory metals in molten potassium containing less than 20 ppm oxygen, as reported by NASA-Lewis, are given by the following equations:

<table>
<thead>
<tr>
<th>Metal</th>
<th>Equation</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>$\log S = \frac{-4500}{T_k}$ from 1012 to 1541 K</td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>$\log S = 2.21 - \frac{1742}{T_k}$ from 1040 to 1516 K</td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>$\log S = 5.02 - \frac{3851}{T_k}$ from 1055 to 1328 K</td>
<td></td>
</tr>
</tbody>
</table>

The optical-spectrographic and wet-chemical methods used were not sensitive enough to measure the solubilities of titanium and zirconium, though indications are that they are both below 10 ppm up to 1339 K. The heats of solution of molybdenum and tungsten in potassium are 6.7 and 17.6 kcal/mole, respectively.
The solubilities of titanium and zirconium in the eutectic alloy (55.5 weight percent bismuth) are given by

\[
\log_{10}(\text{ppm Ti}) = 4.99 - 2.160/T_f \text{ from } 285 \text{ to } 700 \text{ C}
\]
\[
\log_{10}(\text{ppm Zr}) = 6.15 - 3.172/T_f \text{ from } 350 \text{ to } 750 \text{ C}.
\]

As with iron, pure bismuth will dissolve substantially more titanium or zirconium than the bismuth-lead alloys will. However, the solubility of these inhibitors in even high-lead alloys appears to be adequate for the effective retardation of the corrosion of steels.

Tests carried out on various steels submerged in molten lead-bismuth alloy indicate that the liquid metal causes a substantial reduction in the fatigue limit of the steel, providing wetting of the specimen is insured (by pretinning) before testing. This effect has been related to the stability and strength of oxide films, which presumably can inhibit the corrosive actions that weaken the steel.

A study by the Soviets confirms these observations and sheds further light on them.\(^{14}\) The results of their fatigue tests on a 13 weight percent chromium steel, 4K3 Cr, at 500 and 600 C (930 and 1110 F) in air and in molten lead-bismuth eutectic are shown in Figure 2. Note that the fatigue strength at 500 C in the liquid metal is much lower than in air, while at 600 C, the specimen had to be pretinned before the fatigue-strength reduction became significant. This is because the scale formed on the steel at 500 C is a brittle, oxygen-rich FeOCr, that is readily wet by the lead-bismuth. Raising the temperature to 600 C leads to the appearance of a chromium spinel FeO-CrO\(_3\), which inhibits wetting by the molten alloy and its diffusion into the steel surface.

An isothermal dynamic-testing technique was used at Ames Laboratory to investigate the corrosion of 2.25Cr-1Mo steel by molten lead-bismuth eutectic with and without additives.\(^{15}\) With the eutectic alone, the steel was highly resistant to attack up to 500 C (1290 F). Above 700 C, the degree of attack increased with temperature until, at 900 C (1650 F), only long fingers of ferrite remained at the metal surface in place of the original material. With a mixture simulating a liquid-metal reactor fuel contaminated with fission products (lead-bismuth plus zirconium, uranium, magnesium, molybdenum, cerium, neodymium, and lanthanum), corrosion was not detected until 800 C (1470 F) was reached. Above 800 C, attack increased the same as with the pure eutectic.

Liquid-metal corrosion mechanisms

An interesting concept presented by Nikitin is that the reduction in stress-rupture life of solid metals as a result of exposure to liquid metals can have various physical bases, depending on the materials involved.\(^{16}\) For example, the weakening effect of molten bismuth on copper (Figure 3) is attributed to adsorption of the bismuth on the copper surface. This causes a reduction in the activation energy for fracture of the copper, as indicated by the slope of the Arrhenius line for the bismuth environment, which is lower than for air in Figure 3.

Diffusion is another possible cause for reduced stress-rupture life, exemplified by the sharply reduced time to rupture of Arco iron in liquid zinc, as compared with the time in air (Figure 4). Nikitin attributes the nonlinearity of the zinc-atmosphere curve to the predominant weakening role played by diffusion. A third mechanism for reducing stress-rupture life is corrosion, as illustrated by the deleterious effect of molten sodium on the nickel-base alloy E1872 (Figure 5) at temperatures above 600 C. Unlike the other two phenomena, corrosion produces effects which get worse (relative to results in air) with increasing temperature, as a result of the faster dissolution rates on the specimen surface and at the tips of cracks.

![Figure 2. Effect of environment on fatigue of 4K3Cr13 (13 wt % chromium) steel in rotating bending.](image)

**Figure 3. Effect of environment on rupture life of copper at 4 kg/cm² stress.**

**Cavitation by liquid metals**

At several sites, studies have been in progress to define the conditions necessary for cavitation to occur in liquid-metal systems as a basis for designing cavitation-free pumps, turbines, vapor separators, etc. At NASA-Lewis, for example,
In air, 100-hr life

In molten zinc 1000-hr CL life

CL in molten zinc W

Temperature, C

FIGURE 4. EFFECT OF ENVIRONMENT ON RUPTURE LIFE OF ARMCO IRON AT 7 kg/mm² STRESS(16)

with the aid of a vibratory apparatus, cavitation damage by sodium to Type 316 stainless steel, Stellite 6B, and L-605 alloy at 800°F was found to increase exponentially with increasing pressure of the argon cover gas.(17)

Subsequent parametric studies on the L-605 cobalt-base alloy showed that the damage rate was greater at 800°F than at either 400°F or 1200°F for all cover-gas pressures tested (to 4 atm).(18) The combined effects of ambient pressure and sodium temperature are shown in Figure 6 along with the saturation lines, which mark the theoretical limits for zero cavitation-damage rate. The quantitative values of damage indicated in Figure 6 would be different for different test facilities, vibration amplitudes, and frequencies.

In a program to investigate cavitation in an actual axial-flow pump the NASA-Lewis investigators conducted a 200-hour cavitation test in 1500°F sodium on a test rotor containing blades of Types 316 and 318 stainless steel and René 41 (a Ni-Cr-base superalloy).(19) At a constant tip speed of 75.5 ft/sec (3450 rpm) and a constant suction specific speed of 6500, the cavitation damage was concentrated near the tip leading edge of the suction surface. The René 41 blades sustained less cavitation damage than the stainless steel blades, with the Type 316 stainless steel suffering more than the Type 318. Roughening of the surfaces of all three materials was attributed to corrosive attack by the sodium.

A similar rotor, pumping 1500°F sodium at about the same suction specific speed (6100) but more than double the rpm (7200), showed more severe damage to all three blade materials.(20) Additional tests demonstrated that the noncavitation performance (dimensionless head-discharge relationship) is essentially independent of temperatures between 1000°F and 1500°F. However, under cavitating conditions, sodium temperature has an increasing effect on performance with increasing flow coefficient.

To aid in comparing cesium with sodium as the working fluid for space power plants, Oak Ridge investigators reviewed all previous experience concerning erosion in mercury-vapor and potassium-vapor turbines.(21) Analytical and experimental studies of turbine-bucket erosion and cavitation damage are described and summarized in tables and curves.
REFERENCES


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