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UNITED STATES ATOMIC ENERGY COMMISSION

**DYNAMIC CORROSION AND MASS TRANSFER OF
CHROME STEEL BY BISMUTH**

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CALIFORNIA RESEARCH CORPORATION
SAN PABLO, CALIF.

DYNAMIC CORROSION AND MASS
TRANSFER OF CHROME STEEL
BY BISMUTH

NO. -

SPL-51:34
FILE 280.50
DECEMBER 14, 1951

I Introduction

On the experimental side, the pumpability of bismuth at 700 - 750° F. has been demonstrated. No evidence of corrosion of the 5% Cr - 0.5% Mo steel pipe was observed; however, the loop was operated isothermally with a linear velocity of bismuth of about 9 ft./sec.

This report summarizes the experimental data obtained at the San Pablo Laboratory on the corrosion of 5% Cr - 0.5% Mo steel by bismuth under conditions that allow mass transfer to occur. The bismuth is circulated through a temperature gradient by means of a thermosiphon loop.

Report SPL-51:30 entitled "Literature Review and Proposed Research Program on Mass Transfer" by Mr. E. O. Lindstrom, dated October 8, 1951, summarizes other information pertinent to this problem.

II Summary and Conclusions

At 890° F., the dynamic corrosion rate of 5% Cr - 0.5% Mo steel by bismuth is 22 mils/year. At 1290° F., the rate is 2600 mils/year. Formation of a diffusion barrier by preoxidation lowered the latter value to about 100 mils/year.

The present corrosion rates are severe, and penetrations of less than 1 mil/year at 900° F. should be achieved in order to assure safe operation.

Three possible methods of reducing corrosion are:

- (1) Use of another alloy steel, such as Sicrome 53. From Brookhaven Laboratory static corrosion measurements this would probably reduce the attack by a factor of 6.

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- (2) Formation of a diffusion barrier by preoxidation or similar treatment.

- (3) Use of additives to the bismuth. The additives reduce corrosion by combining with any dissolved iron and forming a compound that prevents further attack.

Work on this problem is being continued at Livermore with emphasis on methods (1) and (3).

III Description of Equipment

Figure 1 shows a typical thermosiphon loop with heaters and thermocouples, but no insulation. A parallelogram shaped loop was chosen in order to be able to introduce all the heat into the bismuth before the bismuth rises very far in the loop. To obtain a high velocity in the loop it is desirable to have the height of the loop considerably greater than the horizontal dimension. In the present case, however, the test specimen is a metal strip which extends from the bottom of the left side of the loop to the 2 in. pipe at the top. In order to avoid the need for strips longer than 20 inches, the present loop dimensions were selected.

Ceramic heaters are installed on the hot sides of the loop. The cold sides and reservoir are wrapped with beaded No. 20 Nichrome wire.

The horizontal section of 2 in. pipe at the top of the loop serves as a reservoir for the bismuth. This reservoir can be filled by rotation of the loop around a pin welded to the reservoir.

Thermocouples are peened into blocks that are welded on each corner of the parallelogram and on the bismuth reservoir.

Figure 2 shows another loop that is insulated and attached to the supporting stand.

Chart SPD-51034-1 is a drawing of a parallelogram loop fabricated from 1/2 in., schedule 80 alloy steel pipe (5% Cr - 0.5% Mo). The flange at the top of the reservoir is connected to a pipe manifold by means of a steel gasket. The piping manifold connects to a vacuum pump, a supply of helium, and a rubber tube through which the sample may be introduced and withdrawn.

After fabrication the loop is descaled by treatment with 10% HCl for 2 hours at about 150° F.

IV Procedure

At the start of a run, lumps of oxide-free bismuth are charged

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to the reservoir, the loop being in a horizontal position. The test strip (usually 0.1 x 0.3 x 20 in. and made of the same material as the loop) is put in place, and the loop is evacuated overnight to about 80 microns pressure. The loop and reservoir are then heated to 700° F. under vacuum. The run is started when the loop is rotated clockwise 90° and the bismuth fills the loop. During the run most of the heat is introduced in the bottom side. The temperature at the upper end of the bottom heater is maintained constant to within 10° F. by attachment of the thermocouple to a Celestray Controller. The temperature at the four corners of the parallelogram and at the reservoir are recorded on a Brown Electronik Recorder.

With loop temperatures of 900° F., a vacuum is maintained over the bismuth in the reservoir. At 1300° F., the space above the bismuth is filled with helium in order to prevent distillation.

At the end of a run the temperature is lowered to 700° F., and the loop is rotated to a horizontal position. After the reservoir is filled with bismuth, the loop is filled with helium gas to above 1 atm. pressure, and the specimen strip is slowly withdrawn through the rubber tubing in the presence of an effluent stream of helium.

If the run is to be continued, a 1/4 in. sample is sawed off the end of the strip, and the strip is replaced.

V Metallographic Examination

Metallographic examination of the samples were made at the Materials Laboratory of the Richmond Refinery under the direction of Mr. J. R. Cunningham. The strip samples are mounted in plastic cylinders and then polished. The penetrations are measured with a metallograph. The distance between the bismuth-steel interface on each side of the strip is measured, and compared with either the previously measured interface distance, or the original strip thickness.

In the event that the corrosion is intergranular, the interface distance is taken between points of deepest penetration. Because of the irregularity in the attack, no attempt is made to measure penetrations to an accuracy better than 1 mil.

VI Results

Table 1 summarizes the experimental data obtained on the test strips. The linear velocity of bismuth past the strip is estimated from the power input, corrected for heat leak. Calculated Reynolds numbers are in the range of 3000 to 4000, and indicate the flow is turbulent.

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TABLE I

Dynamic Corrosion Rates of 5% Cr - 0.5% Mo Steel By Bismuth

Run Number	1	2	3	4
Condition of Strip at Start	Preset during previous 120 hours	Preset during run 1	Preoxidized*	Continuation of run no 3.
Total hours at end of run	621	31	233	478
Total hours at start of run	120	0	0	0
Observed penetration, mils	1.0	9.2	0.8	5.0
Corrosion rate, mils/year	22	2600	30	91
Pipe temp. at bottom of hot side, °F	890	1290	1290	1290
Pipe temp. at top of hot side, °F	870	1260	1260	1250
Pipe temp. at top of cold side, °F	824	1170	1230	1225
Pipe temp. at bottom of cold side, °F	810	1120	1180	1180
Power put in bottom side, watts	320	590	500	510
Measured heat leak with no circulation, watts	80	120	130	130
Net power consumed in circulation, watts	240	470	370	380
Total amount of metal circulated, tons	56	3.8	36	75
Veloc. of Bi passing strip, ft/sec	0.09	0.06	0.1	0.1

* By heating in air for 4 hours at 1350° F.

VII Discussion

Figures 3 and 4 show the increase in grain boundary penetration during Run 1 at 890° F.

The 1290° F temperature of Run 2 was selected to simulate that expected in the thermosiphon tubes of the pilot molecular still. This run was terminated because the loop became completely plugged. Figures 5 and 6 are a photograph and a photomicrograph of the strip after Run 2. Figure 7 shows the loop after being sawed apart. A spongy metal deposit had plugged the bottom 3 inches of the cold part of the loop. Spectrographic analysis indicates this material is 12% Fe, 1% Cr, 0.25% Mo and 0.05% Bi, the remainder being bismuth.

The loop was then sectioned as shown in Figure 7. The bismuth had wet the steel pipe on the hot side of the loop. Figures 8 and 9 show the attack at these points. The measured corrosion rate on the pipe is about 11 mils/year, which is somewhat greater than the 21 mils/year measured for the strip. There was no evidence of wetting in the cold leg. Figures 10 and 11 show the form of the iron in the sponge that plugged the pipe at this point.

In Runs 3 and 4 the effect of preoxidation of the steel was determined. In addition to preoxidizing the strip, the loop was also preoxidized by heating in air at 1350° F. for 4 hours. The air in the loop was replaced several times during the heating period.

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Preliminary observations of the strip after 478 hours, and of the pipe after 820 hours of operation indicated that the oxide layer was still intact and that no apparent wetting had occurred. However, Figures 12 and 13 reveal that the bismuth diffuses through the oxide layer and wets the steel. In the pipe, essentially no corrosion is evident beyond a thin wetted layer. This is considerably less than the observed corrosion rate on the preoxidized strip, and is probably explained by the different conditions involved in the preoxidation.

Two serious consequences of severe corrosion in the 20 mil wall target tubes are:

- (1) Weakening of the tubes with subsequent rupture
- (2) Plugging of the pipes in the circulation system.

Some estimate as to when condition (2) may develop can be gained from experience in the operation of mercury boilers. Under conditions having a penetration of 4 mils/year, the system plugged and became inoperable in about 1 year.

Chart SPD-51082 shows that the corrosion of 5% chrome steel by bismuth is more severe than the corrosion of mild steel by mercury. By maintaining a minimum concentration of 50 ppm of magnesium and 0.75 ppm of titanium in their mercury boilers, the General Electric Company³ has reduced the corrosion by a factor of 100.

VIII References

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- (2) Report SPL-51:28 "Design, Construction and Operation of Molten Bismuth Test Pump" - October 9, 1951
  - (3) R. C. Reid, Paper 51-S-13 - presented at the Spring Meeting of The American Society of Mechanical Engineers, April, 1951.

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Figure 1
THERMOSIPHON LOOP BEFORE BEING INSULATED

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Figure 2

THERMO SIPHON LOOP AFTER INSULATION

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Bismuth

Steel

Figure 3 (Magnification 450X)
Photomicrograph of strip at start of run 1. Note penetration of molten metal along grain boundaries after 120 hours of circulation at 890° F.

Bismuth

Steel

Figure 4 (Magnification 450X)
Photomicrograph of strip at end of run 1. Note increased grain boundary penetration due to additional 421 hours at 890° F.

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Figure 5 - Photograph showing
lower part of wetted strip at
end of run 2.

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Bismuth

Steel

Figure 6 (Magnification 110X)

Photomicrograph of section of strip 8 in. from the bottom at the end of run 2. Note spotty attack. Appears to be no wetting or attack in center but pitting at each edge.

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Figure 7 - Photograph of loop sawed
apart. Shows location of sections
shown in Figures 8, 9, 10 and 11.

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Bismuth

Steel

Figure 8 (Magnification 110X)

Photomicrograph in pitted area of pipe on hot side of loop. Note roughness of attached surface.

Bismuth

Steel

Figure 9 (Magnification 450X)

Photomicrograph of same area as Figure 8, but at a higher magnification. Note penetration of molten metal into steel, and iron particles being removed.

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Figure 10 (Magnification 110X)

Photomicrograph of iron sponge in cold leg of loop

Figure 11 (Magnification 110X) Nitral etch

Photomicrograph showing dendritic form of recrystallized iron in sponge.

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Bismuth

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Oxide Film

Bismuth

Steel

Figure 12 (Magnification 450X)
Photomicrograph of section of preoxidized strip at end of run 3. Note penetration of bismuth into oxide layer, and the layer of bismuth that has wetted the steel inside of the oxide film.

Bismuth

Oxide Film

Bismuth

Steel

Figure 13 (Magnification 110X)

Photomicrograph of strip at end of run 4. Note broad band of molten metal under the oxide layer, and the roughness of the steel where it has been attacked. Note also porosity of oxide layer, with molten metal penetration in from outer surface of oxide.

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DYNAMIC CORROSION RATE OF ALLOY STEEL BY BISMUTH

Penetration,
Mils/Year

5% Cr - 0.5% Mo

100

5% Cr - 0.5% Mo
Preoxidized

0 - 553 hrs

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Corrosion Rate of
Iron by Mercury
(for reference)

0.1

400

1000

1100

1200

1300

1400

100-015

t, °F.

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Chart SPB-51082

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