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UNUSUAL DIFFUSION AND CORROSION PHENOMENA OBSERVED IN LIQUID METAL AND MOLTEN CAUSTIC CORROSION TESTS

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TO: W. D. Manly DATE: August 21, 1952

FROM: Anton deS. Brasunas and L. S. Richardson

SUBJECT: Unusual Diffusion and Corrosion Phenomena Observed in Liquid Metal and Molten Caustic Corrosion Tests

In the course of making numerous liquid metal corrosion tests at temperatures of approximately 1000°C, there have been definite indications in certain instances of the inward penetration of the low melting metal into the higher melting point metal. Among others, sodium and lead, both of which are supposedly insoluble in certain metals, have shown evidence of such penetration.

Sodium, for instance, has completely penetrated a 0.25 inch thick copper wall section and appears to have penetrated about 0.006 inch into stainless steel.

Sodium atoms are appreciably larger than copper, iron, chromium, or nickel atoms and hence their diffusion rates might be expected to be quite small in the lattice network of smaller atoms. Nevertheless, there is ample evidence that it does occur. This phenomena can have an appreciable effect on the mechanical properties of certain alloys whose stability may be affected by the presence of these atoms.

Corrosion Tests with Sodium

(1) An evacuated copper capsule which was filled with sodium was heated to 1000°C for a period of 100 hours. Upon opening this capsule, no sodium remained. On standing in air for several weeks, the sectioned copper capsule became stained in the manner shown in Figure 1. Analysis of the deposit indicated that it was Na_2CO_3.

(2) A similar test was made with a copper-plated (0.010 inch) stainless steel (Type 304) specimen placed in a copper capsule. The surrounding bath in this experiment was NaOH. The copper capsule was placed in an evacuated stainless steel jacket and heated for 100 hours at 1500°F.

The copper capsule, when opened, contained only a partially oxidized specimen. However, the interior surfaces of the stainless steel jacket were coated with metallic sodium.

This has been interpreted as follows: The sodium hydroxide was reduced by the stainless steel to metallic sodium. Sodium then penetrated through the copper capsule and condensed in the cooler portions of the system.

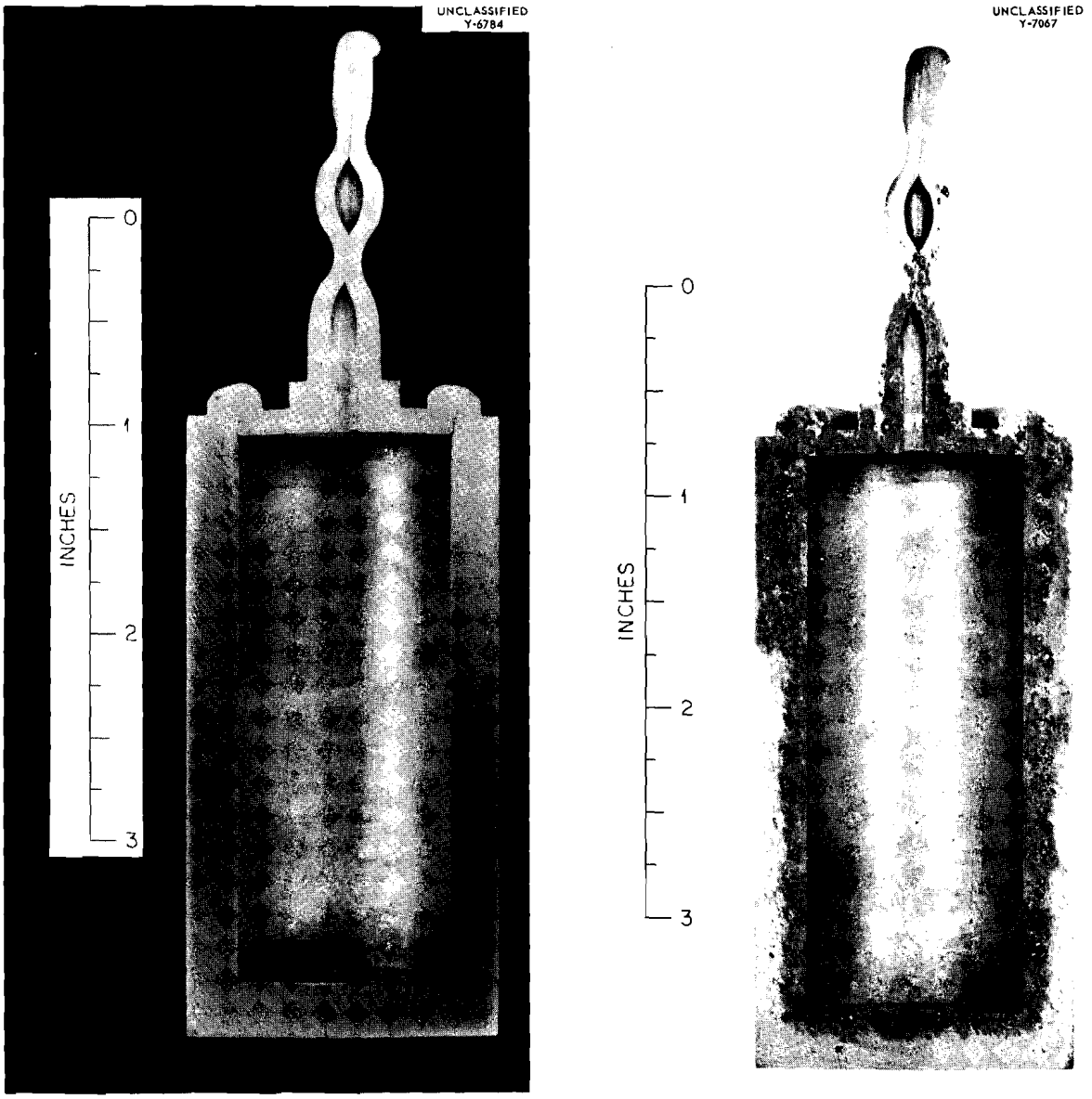

Figure 1. A sectioned view of an OFHC copper capsule which contained sodium and was heated to 1800°F for 100 hours. Specimen at left is as polished; specimen at right, one month later.

The reaction is as follows (M being the stainless steel):

$$M + NaOH \rightleftharpoons MO + Na + 1/2\ H_2$$

If Na and H_2 were to diffuse through the capsule wall, the reaction would tend to favor complete reaction forming metal oxide. (When Zr was used instead of 304 stainless steel using a nickel capsule, ZrO_2 formed and Na was retained in the capsule.) The formation of Na_2CO_3 was also noted on the sectioned surface of this copper capsule.

(3) When a 316 stainless steel specimen was exposed to sodium for 100 hours at 1800°F, the weight change and metallographic examination indicated very little if any corrosion. However, precipitation was noted in the surface region as is shown in Figure 2, which could not be explained unless one were to assume that some sodium diffused into the steel precipitating sigma particles. It would seem to indicate that sodium is a sigma promoter, since weight change indicates very little sodium pickup.

On standing in air for a year, a white deposit of Na_2CO_3 slowly formed. This is shown in Figure 3.

Calculation of Diffusion Coefficients

If the test where sodium completely penetrated a copper capsule is considered, an estimate of the size of the diffusion coefficient required can be made. If it is assumed (1) that sodium diffused through copper as a soluble substance, and (2) that diffusion is sufficiently rapid to establish steady state diffusion,

then $D = \dfrac{M - \delta}{At \cdot \Delta c}$, where δ is the thickness of the copper sample (1/4 inch), M is the weight of material lost (20 g), t is the length of the test (110 hours), A is the surface area of the container (40 cm^2), and Δc is the difference in concentration at the inner and outer surfaces. The largest possible value for this would be the solubility of sodium in copper. This has been reported as less than 0.1% by weight. Using these values, D was calculated to be 8×10^{-3} $cm^2/sec.$ or larger. This is an enormous value, far greater than that observed in any other metallic systems. It was therefore concluded that sodium has penetrated the polycrystalline copper capsule not by the ordinary diffusion process, but essentially via grain boundaries, since a Cu-Na phase has been found as a grain boundary constituent throughout the capsule wall. This is shown as Figure 4.

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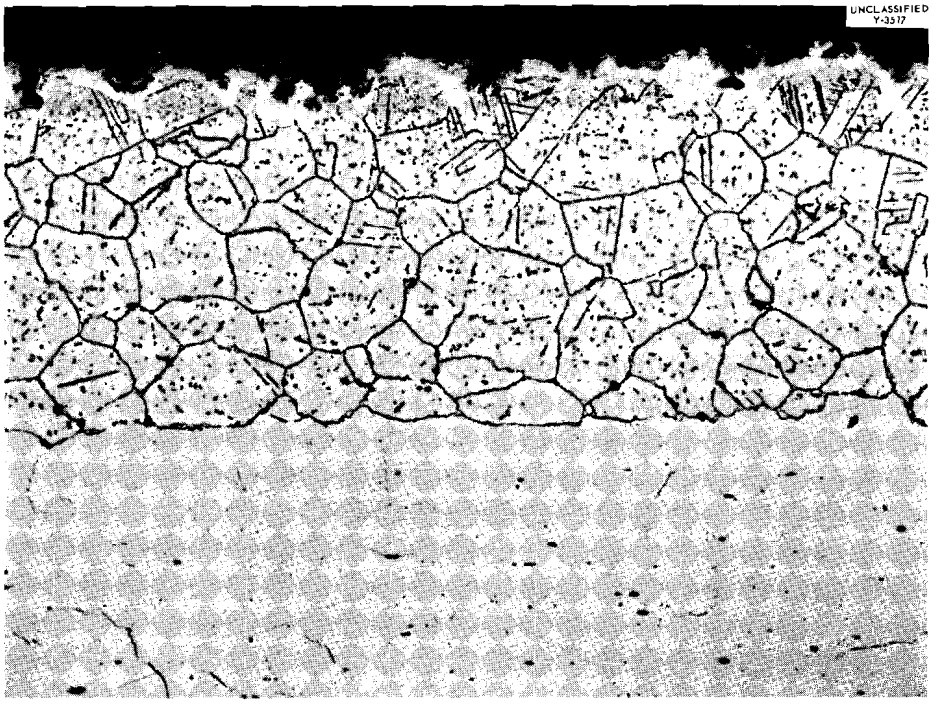

Figure 2. Surface region of 316 stainless steel exposed to sodium at 1800°C for 100 hours. Note shallow surface irregularities and precipitation of unknown phase believed to be sigma. 250X.

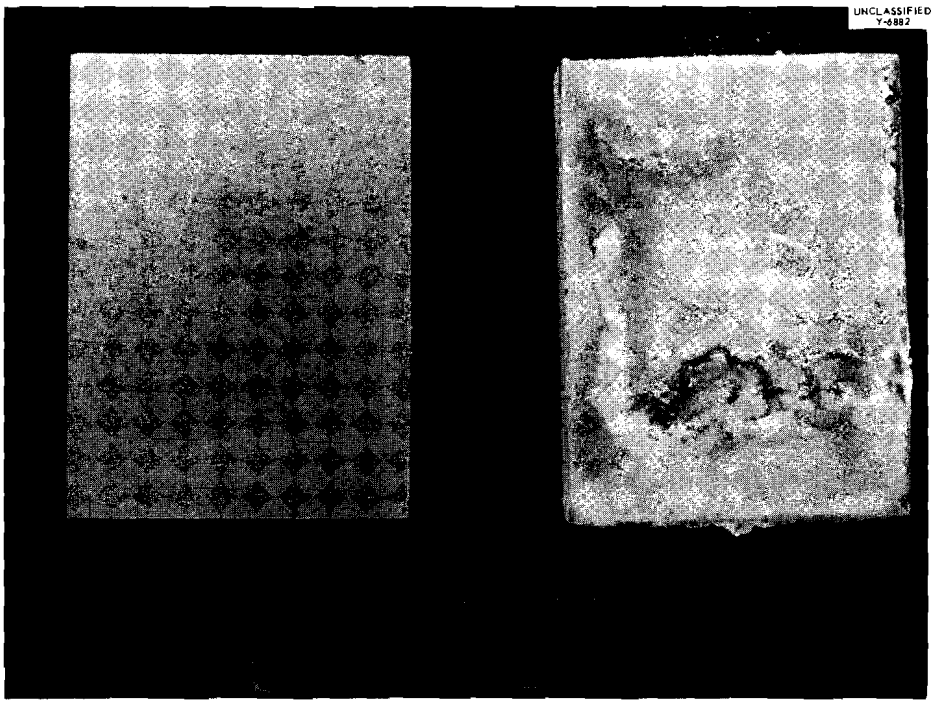

Figure 3. Corrosion test specimen (type 316) after 100-hour exposure to sodium at 1800°F. Specimen at left is appearance after removal from test; specimen at right is similar specimen one year later.

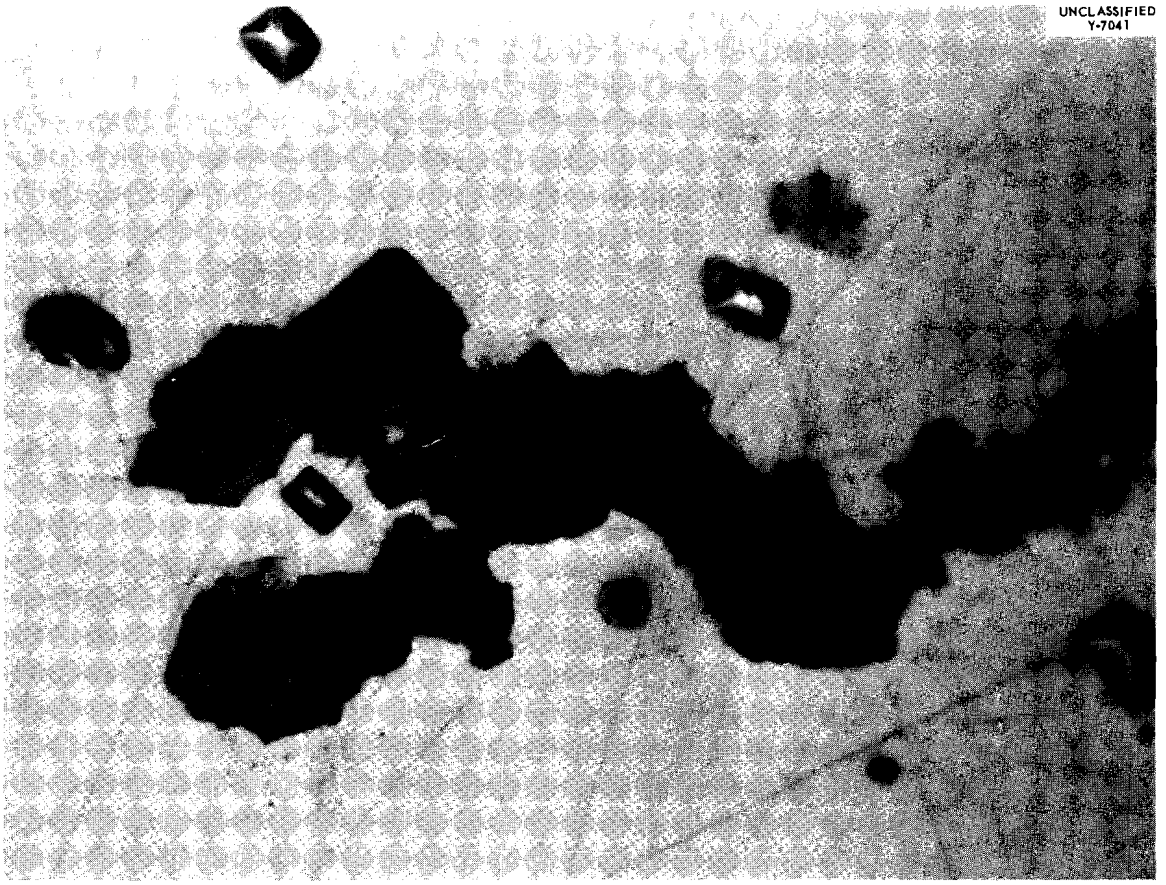

Figure 4. Evidence of sodium penetration shown by precipitation of Cu-Na grain-boundary phase in OFHC copper after 100-hour exposure to sodium at 1000°C. 500X.

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