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INTERACTION EFFECTS BETWEEN DISSIMILAR METALS IN HIGH VELOCITY
SODIUM AT TEMPERATURES UP TO 760°C*

I. MASS TRANSFER OF VANADIUM ONTO TYPE 321 STAINLESS STEEL

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SUMMARY

Comparative corrosion studies are being carried out with potential fuel cladding materials for advanced Liquid Metal Fast Breeder Reactors. The materials under test at temperatures as high as 760°C include refractory metal-base, cobalt-base, and iron-base alloys. Two pumped loops, made entirely of stabilized stainless steels, are used to carry out the investigations. The corrosion specimens are exposed to high velocity sodium (22 ft/sec) in a 24"-long rising temperature region (between 710° and 760°C). In the tests, the oxygen content of the sodium has been controlled over the range from <1 to 15 ppm.

Post-test examination has shown dissimilar metal mass transfer. In tests containing V-base alloys, significant amounts of V have been detected on the surfaces of type 321 stainless steel specimens. X-ray fluorescence analysis shows that about 25 times more V is present on the surface of an exposed sample than on an unexposed standard. Microprobe analysis of two type 321 SS specimens that were exposed simultaneously throughout the entire run but at opposite ends of the test section, i.e. 710° vs 760°C, showed that the difference in their corrosion behavior was the depth to which the V penetrates each sample, not the surface concentration of V. In general, increased temperature, exposure time and oxygen concentration in the sodium appeared to increase the extent of dissimilar metal reactions.

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INTRODUCTION

The objective of the BNL Corrosion program has been to evaluate alloys which would be back up fuel-cladding materials for the stainless steels presently under consideration for an LMFBR. Cobalt alloys and vanadium alloys were selected to be tested, and their corrosion behavior compared to that of stainless steels. During this test program, several observations were made with regard to interactions between dissimilar metals, as well as the transfer of carbon and nitrogen to metals. The purpose of this paper is to present some of the metal-to-metal interaction data, and in particular the transfer of V to type 321 stainless steel. Some of the other interactions observed were the transfer of Ni, Cr, and V onto Fe, Co onto stainless steels, and possibly Fe onto cobalt alloys. However, all of these appeared minor by comparison with the transfer of V onto 321 stainless steel.

TESTING TECHNIQUE

The tests were carried out in two identical loops made entirely of stabilized stainless steels. The test procedure was to place corrosion specimens into each of the loops, expose them to Na for varying increments of time and remove them after each increment to record weight changes. At various intervals other types of examination were employed, i.e. x-ray fluorescence, metallography, microprobe, chemistry, and ductility measurements. Depending on the results of examination, specimens were sometimes replaced by new ones, but in general most were returned to test. Therefore reference will be made to new and aged specimens, with the aging time and Na conditions varying from specimen to specimen.

Figure 1 shows a schematic layout of the loops. The nearly identical loops are of the figure of eight type (heat exchanger) and each contains a cold trap, a hot trap, electrochemical oxygen meters and Na samplers. The test section is located at the hottest point of loop and is connected to a dry box by a flange which permits easy access to the specimens and low contamination cleanup procedure. The test section, shown in Fig. 2, is in a rising temperature region obtained by low voltage, high current heating of the pipe, specimens, and Na. Ten mandrils, each containing 6 specimens, make up the test section. Sodium flows in an annulus created by the specimens and pipe wall. Guides on mandrils maintain the annulus. Shown in Fig. 3 is a typical mandril section of the loop in which the V-alloys were tested along with 321 stainless steel. Type 321 stainless steel was selected as the comparison alloy in both loops primarily because the loops were basically constructed of this steel, and also to study interstitial mass transfer with a stabilized steel.

Fig. 1. Sodium Corrosion Loop Flow Sheet

RESULTS

Figure 4 is a summary of runs made with the two loops that will be referred to in this paper. Loop 2 was first operated with V-alloys under hot-trapped conditions (oxygen level ~ 1 ppm O). After 2004 hours at 760°C maximum temperature, the oxygen level was changed to ~ 3 ppm and the loop was operated for an additional 787 hours. The primary objective of these two runs was to study corrosion of V-alloys; the results showed that V-alloys gain weight under hot-trapped conditions but lose weight at 3 ppm O (1). A third run was made at low temperature to determine the temperature dependence of V-alloy weight losses. A run in Loop 1, at 4 ppm O in Na, can be used as a base line corrosion rate for 321 stainless steel since no V was present in this loop.

The results from Run 2 of Loop 2 are plotted vs type 321 stainless steel specimen position in Fig. 5. From specimen position No. 1 to No. 8, the temperature rises from 710° to 760°C , and from there to the end of the test section the temperature remains constant. This was the high O run in which the V-alloys underwent high weight losses. The plot shows the general trend

Fig. 2. Schematic Layout of Test Section

and scatter of the actual data. The line drawn through the data for the aged specimens shows an unusual temperature dependence, i.e. lower weight losses at higher temperature. The new specimens do not show the effect yet because of the high initial weight losses due to leaching of Ni and Cr. Weight losses in the last interval however showed the trend was reversing even for the new specimens.

These results are summarized in Fig. 6 as corrosion rate of 321 stainless steel (calculated from weight loss measurement) vs reciprocal temperature, and compared to results of previous runs. The corrosion rates of 321 stainless steel in the base line test (FCL-1) are in good agreement with published data. (2,3) The results of the hot-trapped loop run are also in fair agreement. However, results from the high oxygen run in this loop are completely opposite in temperature dependence. Interestingly, the corrosion rate at the test section inlet compares well with that of previous runs which suggests that the unusual effect seems to be most pronounced within the test section region itself, and that by the time the Na re-enters the test section, the Na chemistry is similar to that of previous runs (no V present).

Fig. 3. Typical Mandril Section From Loop 2

X-ray fluorescence examination of the type 321 stainless steel specimens positively identified V as the species which had transferred onto their surface. The type 321 stainless steel used in fabricating the specimens contained ~ 600 ppm V before test. Fig. 7 shows plots correlating weight loss from the V specimens and x-ray fluorescence analysis of 321 stainless steel as a function of time. At the end of the hot-trapped run, approximately $2\frac{1}{2}$ times as much V was present on surfaces of 321 stainless steel as before the run. After oxygen was added to loop and the V alloys experienced high weight losses, V ratios on stainless steel increased to ~ 25 times. The ratios of surface V seemed to be independent of temperature. This contradiction was explained by microprobe analysis as will be shown later. It is pointed out here that in the last test increment, at 500°C maximum temperature, the V alloys lost about as much weight as they did in

Summary of Tests

Loop & Run No.	Time; Hrs.	Oxygen, P.P.M.	Test Section Materials	Velocity in T/S	Temp. Grad in T/S, °C
FCL 2-1	2004	Hot Trap (~1)	Vanadium Alloys 321 S S Nb-1 Zr TZM	22 fps	760-710
FCL 2-2	787	Cold Trap (~3)	Same as Run 1 Plus Iron	"	"
FCL 2-3	190	Cold Trap (~3)	Same as Run 2	"	505-475
FCL 1-1	1655	Cold Trap (~4)	Cobalt Alloys Stainless Steels Moly.	22 fps	760-710

Fig. 4. Summary of Corrosion Test Runs

Fig. 5. Loop 2, Run 2, Weight Change Data

Fig. 6. Comparison of Corrosion Rate Measurements of Type Stainless Steel

previous increments at 760°C maximum. However, the 321 stainless steel specimens experienced essentially no weight changes indicating a temperature dependence rather than a solute dependence.

Shown in Fig. 8 are microprobe traces of Ni, Cr and V for two 321 stainless steel specimens having been exposed simultaneously throughout the entire operation of Loop 2 but at opposite ends of the test section, i.e. 710° vs 760°C. The trace shows the difference between the two is the depth to which the V penetrates each sample, namely ~14 μ at 710°C and ~28 μ at 760°C. The ratio of counts at the surface are about the same for each. Also of interest to note is that the reaction layer created by leaching of Ni and Cr coincides with the depth of penetration of V.

Fig. 7. X-Ray Fluorescence Analysis of Type 321
Stainless Steel Specimen Compared With Weight
Change of Typical V Alloy Specimen

In general, metallographic examination of all the specimens seem to verify the results of the microprobe, as shown typically in Fig. 9. Shown here are photomicrographs of the two specimens of which traces were shown in Fig. 8, and superimposed is the depth of penetration of V according to the microprobe examination. Note that the reaction layers differ with temperature. The outer layer of each specimen is rich in V and Fe. The amount of V and Fe decreases uniformly from the outer edge of this layer to the inner edge. The black appearing areas are also high in V and Fe as compared to the matrix, which appears as white areas, but the V is proportionally less than in the outer layer. It appears as though the V reaches some equilibrium

MICRO PROBE TRACES OF 321 S S SPECIMENS
BOTH SPECIMENS EXPOSED IN HOT
TRAPPED AND COLD TRAPPED RUNS

Fig. 8. Microprobe Analysis Results of Type 321
Stainless Steel Specimens Exposed in
Hot-Trapped and Cold-Trapped Na at
710°C and 760°C

concentration on the surface, which is independent of temperature, and then diffuses into the steel at rates depending on the temperature.

The stainless steel specimens were evaluated by means of a mechanical test to determine whether the V penetration had an effect on ductility. The test procedure consisted of placing some lead into one of the cylindrical specimens and compressing the lead by means of two end plugs in a tensile tester. Fig. 10 shows the apparatus with a specimen before and after test. The axial load is transformed to a radial load and applied until

Fig. 9. Metallographic Results of Type 321 Stainless Steel Specimens Shown in Fig. 8

rupture. The results showed there had been essentially no effect of V penetration on the ductility of the 321 stainless steel specimens.

SUMMARY AND CONCLUSIONS

We have shown that in a mixed vanadium-321 stainless steel system, as may be encountered in an advanced LMFBR, at temperatures of about 700°C, V will migrate to the surface of the steel. The rate of uptake of V by 321 stainless steel seems to be a function of oxygen in Na and increases with time and temperature, but the surface composition appears to reach a steady

Fig. 10. Ductility Measurement Testing Apparatus

state condition and penetration proceeds by diffusion into the stainless steel. Although the mechanical properties do not appear to be seriously affected after short exposures, the effects of exposures of several years, as may be encountered in an LMFBR, may be better predicted with longer test periods, i.e. several thousand hours.

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