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Advanced Neutron Source

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SUMMARY OF CORROSION LOOP TEST RESULTS
FOR THE INSTITUT LAUE-LANGEVIN
CLADDING MATERIAL

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February 1995

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U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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Summary of ANS Corrosion Loop Test Results for the ILL Cladding Material

The test specimen chosen for CTEST No. 43 was fabricated from the special "Al-Ni-Fe" alloy (VDM-4194) used in the cladding of the ILL reactor at Grenoble. Chemical analysis of this alloy at ORNL compared well with the supplied composition report and average values for the ILL cladding and our standard 6061 Al alloy appear in Table 1 for comparison.

For the most direct comparison with the data base of oxidation results we are accumulating for 6061 Al, moderately aggressive thermal-hydraulic conditions and a coolant pH of 5 were chosen for this test. Further, in an attempt to induce spallation (again for comparison with behavior of 6061), the power to the test section was increased twice during the duration of the test while holding other control parameters as constant as possible. A summary of the test parameters as a function of time appears in Table 2.

The pH and conductivity variations as a function of time are shown in Figure 1. Except for a divergence corrected by a recalibration early in the test and a weekend dip late in the test, control of pH (near 5.0) and conductivity (near 500 $\mu\text{S}/\text{m}$) was excellent. The excursion to lower pH is generally considered (at least for 6061 Al) to be less aggressive from a film growth standpoint, but since it occurred late in the test and was of short duration it was thought to have little effect. In addition, the pH-conductivity relationship shown in Figure 2 is in good agreement with the ideal for nitric acid additions to water, calculated on the assumption that the coolant is "pure" water with only H^+ and NO_3^- ion contributions to conductivity.

The calculated film growth at the three principal positions on the specimen as calculated from the temperature, power, and coolant flow measurements during the test is given in Figure 3. The film growth curves agree reasonably well with those derived for 6061 Al under similar exposure conditions. In some instances

for 6061 and other alloys, abrupt substantial amounts of spallation have resulted in visible changes of the calculated film growth rate curves. From the shape of the rate curves for the ILL specimen, it was not obvious, but certainly possible, that spallation had occurred at the hot end of the specimen.

When the ILL specimen was removed from the test loop for destructive examination, the test surfaces revealed a range of discoloration from gray-gold at the coolant entrance to dark brown or black at the coolant exit. Spallation like that observed on many 6061 Al specimens ("comet tail") was not observed. However, a scattered distribution of small "craters" was noted over the hottest part of the specimen; a total of 50 or so such craters was observed within several millimeters of position 6. Due to the rather shiny appearance of the material at the bottom of the craters, many appear sufficiently deep to expose substrate metal. The craters are close to round at the specimen surface with a diameter on the order of 150 μm . The craters appear to represent a very localized form of spallation.

Metallographic examination of specimen cross sections from the principal positions revealed relatively uniform film thicknesses. The film revealed characteristic boehmite features and a distribution of metallic particles. In addition, two craters were intersected and partly visible in the position 6 cross section; in this plane, neither of the craters penetrate to the metal surface. No reaction zone similar to that observed in 6061 was noted in the underlying alloy. However, unlike any previous observations in this program, the oxide/metal interface was found to have a very convoluted - almost serrated in appearance - interface when viewed at high magnification (Figure 4). The convoluted interface was not observed on the cross sections from positions 2 and 4 (Figure 5) nor on the cooler "tab" portions of the specimen at position 6.

Table 3 presents the various measurements of film thickness for the ILL specimen. The metallographic measurements (considered to be the "definitive" measurement) are noted to be in good agreement with the eddy current measurements but somewhat greater than the calculated values (based on temperature changes at each position, shown in Figure 3). Reasons for the difference are unclear, but a possible factor is the presence of the metallic particles in the ILL alloy oxide that would tend to increase film

conductivity above that used in the calculation procedure (same as that for boehmite on 6061 Al, 2.25 W/m*K). This would have proportionately increased the calculated thickness. It is probable that the larger difference between calculated and measured film thickness noted at specimen position 6 is due to the local temperature perturbation caused by the advent of the spallation craters. The thickness reported for position 6 in Table 3 represents the unspalled film, whereas the calculated value, based on temperature measurements, must of necessity include the averaging effect of the locally thin film segments associated with the craters.

A cross section of the specimen from position 6 (hot end) of the specimen was examined in the electron microprobe to investigate the presence and distribution of iron in the outer layer of the oxide film. Figure 6 identifies the Fe-rich layer at its usual location on the outermost micron or two of the boehmite layer. Although some error is introduced due to the fact that the probe sampling diameter is roughly equal to the thickness of the iron layer, the iron in the outer layer approached 7.5 at%, which is relatively high among similar measurements in this program. Figure 7 illustrates in greater detail the distribution of minor elements in the film. Other than Al, Mg is present in the highest concentration in the film. Although too few points were examined in the base metal to make a definitive conclusion, the Mg concentration seems to be slightly depleted in the base metal. The concentration of Mg observed in the film on the ILL specimen is greater than that observed for any of the 6061 specimens examined to date (all of which have roughly equal bulk Mg). The small Ni-Fe peaks in Figure 7 are consistent with the probe diameter overlapping one of the numerous Ni-Fe-Al intermetallic particles within the oxide layer. The fact that the Fe in the Fe-rich layer is accompanied by a small Cr peak rather than a Ni peak is significant and associates this Fe with the stainless steel loop components exposed to coolant rather than the iron in the alloy. The presence of tungsten in the oxide has been consistently observed in our experiments and likely is a result of reaction products originating in a tungsten carbide seal face.

In general, the product film growth rates correlate extremely well with CORRELATION II, indicating that the general growth behavior for this alloy closely follows that of 6061 Al for this range of thermal-hydraulic conditions. The rate constants

calculated for film growth at the three principal specimen positions for parts A and B of CTEST No.43 are given in Figure 8 where they are compared to the given ANS 6061 Al data correlation. This behavior is consistent with our test results on several other aluminum alloys where no measurable differences in the pre-spallation film growth rates were found. Rate constants were not calculated for part 43C because of the short time span and the probability that spallation had affected the apparent rates.

It appears from the rates curves shown in Figure 3 that cratering may have been in progress for about 100 h before the test was terminated. Even so, as was pointed out above, no internal reactions were observed beneath the spallation craters in the post-test examination, as might have been expected for a 6061 Al alloy. This behavior resembles that of the 8001 Al alloy. It was estimated that the cratering in the ILL alloy began when the temperature drop across the oxide film was about 150°C, less than that observed for spallation on 8001 Al, but a little above that for typical 6061 Al film spallation.

Table 1. Composition (weight percent) of the ILL cladding alloy and that of our "standard" 6061 Al material.

<u>alloy</u>	<u>Mg</u>	<u>Si</u>	<u>Fe</u>	<u>Ni</u>	<u>Cr</u>	<u>Cu</u>	<u>Zn</u>	<u>Mn</u>	<u>Al</u>
6061	0.96	0.51	0.44	0.004	0.20	0.27	0.082	0.096	bal
ILL	0.92	0.09	0.85	0.95	0.33	0.01	-na-	0.30	bal

Table 2. Effective test parameters for CTEST No. 43. 43A is the initial portion of the test, while 43B and 43C represent subsequent power increases.

<u>parameter</u>	<u>43A</u>	<u>43B</u>	<u>43C</u>
duration, h	0-384	385-669	670-747
power to test section, kW	45.2	50.4	52.7
average heat flux, MW/m ²	12.6	14.0	14.7
local heat flux, MW/m ²			
position 2	12.2	13.2	13.7
position 4	12.5	13.9	14.5
position 6	13.1	15.1	15.9
average pH	5.04	5.02	4.95
conductivity, μ S/m	510	520	600
coolant velocity, m/s	25.6	25.6	25.6
coolant temp (°C), inlet	49	50	52
local coolant temp (°C)			
position 2	54	55	56
position 4	62	64	66
position 6	70	73	75
coolant temp (°C), outlet	74	77	80
local interface ^a temp (°C)			
position 2	136	143	147
position 4	143	153	158
position 6	152	166	173

^aoxide film/coolant interface

Table 3. Film thickness measurements for CTEST No. 43 (ILL alloy).

Measurement Device	Film Thickness, μm		
	position 2	position 4	position 6
eddy current	17.5	21.8	28.4
metallography	15.6	20.3	28.1
calculation	14.4	17.9	22.7

Figure 1. Variations in pH and electrical conductivity of the coolant water during CTEST No. 43.

Figure 2. Range of coolant pH and conductivity for CTEST No. 43 compared to "ideal" values.

Figure 3. Calculated film growth at the three principal positions during CTEST No. 43.

Figure 4. As-polished cross section at channel center at position 6 of the CTEST No. 43 test specimen (ILL alloy).

Figure 5. As-polished cross section at channel center at position 4 of the CTEST No. 43 test specimen (ILL alloy).

Figure 6. Electron microprobe traces for Al, O, and Fe across the boehmite layer on specimen from CTEST No. 43 at position 6.

Figure 7. Electron microprobe traces for minor elements across the boehmite layer on specimen from CTEST No. 43 at position 6.

Figure 8. Rate constants for film growth on ILL alloy specimen during CTEST No.43 compared to ANS Correlation II.

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