UNCLASSIFIED

MASTER

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

ORNL
CENTRAL FILES NUMBER
58-10-86

"External Transmittal Authorized"

COPY NO. 21

DATE: October 23, 1958

SUBJECT: Depletion of Minor Constituents from Coast Metals No. 52
(89 Ni - 5 Si - 4 B - 2 Fe) and No. 53 (81 Ni - 8 Cr - 4 B
4 - Si - 3 Fe) Brazing Alloys During Various Exposures.

TO: W. D. Manly

FROM: D. H. Jansen

- Copies to:
1. W. D. Manly
 2. P. R. Bell, Jr.
 3. R. E. Clausing
 4. J. H. DeVan
 5. E. E. Hoffman
 6. D. H. Jansen
 7. P. Patriarca
 8. G. M. Slaughter
 9. M. J. Skinner
 10. E. Byron (Westinghouse Electric Corporation)
 11. General Corrosion Files - E. E. Hoffman
 - 12.-15. Laboratory Records
 16. ORNL-RC
 - 17.-18. Central Research Library
 19. ORNL Document Reference Library
 20. Metallurgy Library
 - 21-36. TISE, AEC

Summary

Nickel-base brazing alloys containing boron and silicon (3 to 4 wt %) become depleted of these minor constituents during exposures to fused fluoride fuels, liquid metals, or oxidizing atmospheres. Impoverished regions, the depths of which are dependent on temperature and time of exposure, contain approximately one-third the original amount of boron and silicon that is present before test.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory.

UNCLASSIFIED

The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Introduction - Procedure

During some initial corrosion tests on the Coast Metals No. 52 (89 Ni - 5 Si - 4 B - 2 Fe) brazing alloy, (Fig. 1, Y-18354), it was found that an impoverished region was always present at the surface which had been exposed to the corroding media, (Figs. 2, Y-14502 and 3, Y-18080).

This same impoverished region was found on the Coast Metals No. 52 brazing alloy after oxidation tests in air,¹ but did not appear when annealed in vacuum or in helium.

Due to the presence of boron in some fuel baths used to evaluate the corrosion resistance of boron containing brazing alloys, a series of seesaw corrosion tests was conducted on two boron bearing alloys to determine if this characteristic removal of minor constituents was time and/or temperature dependent. Therefore, two brazing alloys, Coast Metals No. 52 and Coast Metals No. 53 (81 Ni - 8 Cr - 4 Si - 4 B - 3 Fe), were corrosion tested in both NaF-ZrF₄-UF₄ (53.5 - 40.0 - 6.5 mole %, fuel 44) and NaK (56-44 wt %) at 1400°F for 100-hr, at 1500°F for 100, 500, and 1000-hr, and at 1600°F for 100-hr. Due to the relative inertness of nickel to the fuel 44 and NaK, this was used as a container material for these tests. Pure alloy buttons (arc melted under vacuum) were used for test specimens. With these materials it was possible to approach an ideal 2-component test system, that is, the alloy and the fuel.

Results

From the series of tests on Coast Metals No. 52 and No. 53 it was found that depletion of boron and silicon from the edge of the alloy was both time and temperature dependent. The depth of the depleted regions were successively greater the higher the test temperature and the longer the test duration at the same temperature. (Table I) Metallographic examination shows more impoverishment on the Coast Metals No. 52 alloy the longer the test duration at one given temperature (Fig. 4, Y-20134 and Y-21485) or the higher the test temperature for the same test duration, (Fig. 4, Y-19824 and Y-20133).

-
1. Oxidation tests conducted by:
G. M. Slaughter, Welding and Brazing Group.

A spectrographic traverse across the sample in Fig. 3 shows that the boron in the specimen is $\leq 1\%$ from the surface down to a depth of 8 mils. Nominal boron content was 4 wt %. The concentration of boron then rose abruptly to its normal value (4%) and remained there for the remainder of the traverse. The silicon concentration dropped to one-third of its normal concentration (or less) in the depleted region. The iron concentration appeared to decrease little, if any, in this region.

In general, all the samples after test showed this type of analysis. Only in depth of depletion, dependent on time and temperature of exposure, did the results differ. No boron was detected on the nickel test containers during microspark analyses. Microspark tests on the Coast Metals No. 53 samples after test failed to show any depletion of chromium.

The depletion of these minor constituents leaves a nickel-rich matrix that is relatively much softer than the original alloy. Fig 6 (Y-22613) shows a Coast Metals No. 52 alloy after testing in NaK; the depleted region has a Diamond Pyramid Hardness of 174 (100 gram load) while the interior portion of the specimen showed a much harder material.

The same type of depletion occurred on Coast Metals No. 52 alloy samples when exposed to 1500°F air for 100- and 500-hr periods during oxidation tests. Microspark analyses on these oxidation samples indicated, as in the case of corrosion tests, that boron and silicon had been depleted from the surface.² Depletion amounted to 6 mils in a 500-hr oxidation test in 1500°F air.

Depletion of Coast Metals Alloy in Heat Exchangers

Only the results of depletion as found in corrosion tests have been reported above thus far; the same type of removal of minor constituents occurred in the operation of a NaK-to-fuel heat exchanger but on a gross scale. In Fig. 7 (Y-21220) is shown a Coast Metals No. 52 fillet from an Inconel tube-to-header joint from the NaK inlet header of one of the tube bundles from an operated

2. Slaughter, op. cit.

heat exchanger. The braze fillet shown was exposed to the $\text{NaF-ZrF}_4\text{-UF}_4$ (50-46-4 mole %) mixture of 1400°F for approximately 1400-hr. As can be seen in the figure, gross depletion has occurred at the braze-fuel (fillet surface) interface. Depletion of the minor constituents also occurs by a diffusion mechanism into the Inconel base materials (header plate and tube wall) where the fuel is not in contact with the alloy. As shown in Fig. 8 (Y-23076) this diffusion into the header plate (shown by the depleted alloy at the braze fillet-header interface and the heavy precipitate) causes an increase in hardness which diminishes as the distance from the alloy increases.

In Fig. 9 (Y-20297) is shown a macrophotograph of the configuration of the braze fillets used for Figs. 7 and 8.

Another heat exchanger operating under conditions slightly more severe than the one just described was also examined, some fillets from which are shown in Fig. 10 (Y-22049 and Y-22050). Depletion of the minor constituents of the alloy to a depth as great as 50 mils can be seen in (b). In Fig. 10 (a) can be seen a twin structure which has developed in the nickel-rich depleted region, while in (b) a grain boundary (bottom, center) has grown from the Inconel base material into the nickel-rich matrix remaining. No hardness measurements or spectrographic results were obtained on these braze fillets.

Operational conditions on this heat exchanger were as follows: 503-hr at 1700°F and an additional 44-hr at 1600°F . During the test period, the heat exchanger was above 1150°F for a total of 911-hr.

Conclusions

The depletion of boron and silicon from the exposed surface (whether exposed to fused fluoride base fuels, liquid metals, or high temperature air) of nickel-base brazing alloys is detectable by spectrographic, visual, and hardness analyses. If these depleted amounts of minor constituents can be tolerated in the bath involved, this condition can possibly be advantageous, since an extremely nickel-rich material is left which is ductile³ and very corrosion resistant.

3. A ductility test was conducted by G. M. Slaughter of the Welding and Brazing Group at ORNL as follows: Coast Metals No. 52 brazed to an Inconel bend test specimen was oxidized and then subjected to bending. The specimen showed the nondepleted region of the alloy to crack while the depleted region remained intact during the bend test.

Table I

Depth of Depleted Region (Mils) of Coast Metals
Brazing Alloys after Corrosion Testing

Alloy & Bath	Depth (Mils) of Depleted Region at Temperature and Test Time Indicated:				
	1400°F	1500°F			1600°F
	100-Hr	100-Hr	500-Hr	1000-Hr	100-Hr
Coast Metals No. 52 in Fuel 44	1	2.5	4	5	2.5
Coast Metals No. 52 in NaK	1.5	2	5	-	3
Coast Metals No. 53 in Fuel 44	0.5	1.5	4.5	6.5	1.5
Coast Metals No. 53 in NaK	1	2.5	5	6.5	2.5

Fig. 1. Coast Metals No. 52 (89 Ni - 5 Si - 4 B - 2 Fe) brazing alloy button in the as cast (before exposure) condition. Etchant: 10% oxalic acid (electrolytic).

Fig. 2. Coast Metals No. 52 brazing alloy on a nickel T-joint after a static corrosion test in sodium for 100-hr at 1500°F. Note the depletion of the second phase at the surface of the braze fillet that was exposed to the bath. Etchant: 10% oxalic acid (electrolytic).

Fig. 3. Coast Metals No. 52 alloy button after static test in fluoride base fuel No. 44 at 1500°F for 500 hr. Note depleted region at exposed edge. Etchant: 10% oxalic acid (electrolytic).

Fig. 4. Coast Metals No. 52 brazing alloy buttons after seesaw corrosion testing in NaK at 1500°F hot zone temperature for (a) 100 hr and (b) 500 hr. Etchant: 10% oxalic acid (electrolytic)

Fig. 5. Coast Metals No. 52 brazing alloy buttons after seesaw corrosion testing in fuel 44 at (a) 1400°F and (b) 1500°F hot zone temperature for 100 hr each. Etchant: 10% oxalic acid (electrolytic)

Fig. 6. Coast Metals No. 52 brazing alloy button after seesaw corrosion test in NaK for 500 hr at 1500°F hot zone temperature. Note the difference in hardness of the interior of the specimen and the relatively soft surface which has been depleted of boron and silicon. Etchant: 10% oxalic acid (electrolytic).

Fig. 7. Coast Metals No. 52 brazing alloy fillet from operated NaK-to-fuel heat exchanger. Fillet has been exposed to fuel 30 ($\text{NaF-ZrF}_4\text{-UF}_4$, 50-46-4 mole %) for 1400 hr at 1400°F . Note deep depletion zone and subsurface voids in the body of the fillet and the depletion into the base metals at the tube wall-header plate interface. Etchant: 10% oxalic acid.

Fig. 8. Portion of Coast Metals No. 52 braze fillet showing the increase in hardness of the Inconel header plate due to diffusion of minor constituents from the alloy.

Fig. 9. Macrograph showing configuration of braze fillets, tube walls, and header plate as used in Figs. 6 and 7. Picture is reverse of microphotographs because of lens reversed. Nickel plate is for edge retention during metallographic polishing operation. Etchant: 10% oxalic acid (electrolytic). 13 1/2X.

Fig. 10. Coast Metals No. 52 braze fillets from tube-to-header joints taken from an operated heat exchanger operated for 900 hr at 1700°F. Fillet surfaces were exposed to the NaF-ZrF₄-UF₄ (56-40-4 mole %, fuel 30) mixture. Etchant: 10% oxalic acid (electrolytic).