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REMOVAL OF SUPERFICIAL BLEMISHES
FROM TYPE 316
STAINLESS STEEL FUEL CLADDING

October 1969

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REMOVAL OF SUPERFICIAL BLEMISHES
FROM TYPE 316 STAINLESS STEEL FUEL CLADDING

By

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Cladding Development Sub-Department

October 1969

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REMOVAL OF SUPERFICIAL BLEMISHES
FROM TYPE 316 STAINLESS STEEL FUEL CLADDING

R. R. Studer

INTRODUCTION

Late in March of 1969, during visual examination of an end cap weld on a fuel pin subassembly made for PNL-6, an engineer in FFTF Fuels Department noted a small discolored area on the cladding. Similar blemishes were soon discovered on other cladding tubes of the same manufacture. Because replacements for the affected cladding tubes were not available, an investigation of the nature of the discoloration phenomenon and its effect on the integrity of the cladding was begun immediately.

SUMMARY

The discolorations were found, in about equal profusion, on all of three lots of Type 316 stainless steel fuel clad tubes produced by one manufacturer, but were absent on process scrap which had not been centerless ground on the outer surface. Tube bores were unaffected. Several conjectures as to the origin of the discolorations are presented in the discussion.

Affected tubes retained normal mechanical properties. Cleaning procedures were revised so that blemishes could be removed without compromising the integrity of the fuel pins.

CONCLUSIONS

The discolored spots on cladding tube purchased for PNL 6, 7 and 8 Irradiation Test Subassemblies resulted from operations performed in the vendor's plant subsequent to the final drawing operation. They are completely superficial and are readily removed by the usual nitric acid passivating treatment. Passivated specimens show no intergranular attack.

The origin of the discoloration is not certainly known. A likely cause is the use of a grinding coolant contaminated by carbon steel particles when the tube was given a final surface finishing operation.

The observed condition did not affect the tubes functionally. The aggregate of affected areas was certainly less than $1/4 \text{ in.}^2$, probably not more than $1/10 \text{ in.}^2$, and so would have had an undetectable effect on the irradiation environment even had they not been discovered.

DISCUSSION

PROCUREMENT HISTORY

Fuel clad tubing for Irradiation Test Subassemblies PNL 6, 7 and 8 was ordered late in 1967. The total amount of tubing (Type 316 stainless steel, seamless 0.250 in. OD $\times$ 0.218 in. ID) was divided in three categories, all of which were produced by the same tubing manufacturer to essentially the same specifications. The parts of the specifications pertinent to surface conditions of the finished tubes are given in Appendix A.

t

The smallest increment of tubing was produced from redraw stock, Allegheny Ludlum Heat No. 68505, obtained by Battelle-Northwest (BNW) from Atomics International (AI) inventory and furnished to the tubing manufacturer for conversion to finished tubing per Purchase Order B8S-777-40107. Because of the origin of this starting material, the manufacturer was not required to perform chemical analyses.

The other two lots of tubing were made of identical starting material furnished by the manufacturer. The difference between the two lots was mainly the extent of dimensional correction, care in handling, and nondestructive testing applicable at the tube hollow stage of manufacture.

The tubing made from the AI redraw stock was not amenable to ultrasonic detection of small defects because of the prevalence of spurious signals, "noise". The tubing manufactured from vendor-furnished stock was less noisy, and ultrasonic testing was performed in the vendor's plant according to the purchase specification.

The finished tubing, plus process scrap from AI redraw stock increment, was received at BNW in October, 1968. All finished tubing was shipped in individual paper sleeves and packed in wooden boxes. The two lots originating from vendor-furnished raw material, herein called "G" and "H" lots, were released to process after local testing and inspection. The lot made from the BNW-furnished redraw stock, plus the process scrap, was left in the original shipping containers and placed in storage.

Details of the tube manufacturing processes which might provide information on the sources of surface defects are not available. The vendor chooses to consider all aspects of his manufacturing process as proprietary; however, the surface texture of the finished tubes is characteristic of centerless grinding.

BNW PROCESSING HISTORY

INSPECTION AND CLEANING

Both eddy current and ultrasonic methods were used to test for structural discontinuities. Tubing acceptable on the basis of ultrasonic test results was cut to length, and the ends were faced and deburred on a lathe. After the inside and outside diameters were measured by air gauging, the tubes were processed through an alkaline cleaning solution (Appendix B).

ASSEMBLY

The final processing operation pertinent to this discussion is the welding of end caps into the tube. This operation is performed by chucking both end cap and tube in an assembly fixture, the chucks serving as the grounding contacts for the welding current. The chucks, and therefore work pieces, are stationary during the welding operation. The circumferential weld is produced by a conventional TIG torch mounted in a rotating carrier.

DEFECT DETECTION

WELDING

Visual examination of an uncompleted fuel pin (one end cap welded in place) revealed a small discolored area on the tube surface, approximately 1 3/8 in. from the weld, (Figure 1). Under low-power magnification this area appeared to be an arc burn resulting from poor contact between the work piece and the collet. Examination of corresponding areas of other pin assemblies revealed similar discolorations with the iridescent "Newton's Rings" appearance characteristic of scale resulting from very localized overheating. More thorough examination of the pins found the discoloration existing in locations which could not possibly be affected by the welding operation and, later, on tubes which had not been welded.

CLEANING

All tubes from lots "G" and "H" had gone through the cleaning process before the discolorations were first observed. Welding could not have caused the majority of the discolorations; therefore, the cleaning system was suspected as the prime source.

Four tubes were examined visually at 10X magnification, and all discolored areas identified by scribing, with a carbide stylus, a short circumferential mark about 3/16 in. to either

side of the discoloration. One tube, which under similar examination was found to be free of defects, was used as a control. Some of the defects found during this examination appeared to be spots of red rust, although most had the heat scale appearance mentioned earlier.

The five tubes were cleaned simultaneously, according to the specified procedure. The next day the five tubes were again examined at 10X magnification.

The control tube still had no discolored areas; all of the spots on the other four tubes were unaffected by the cleaning operation. No new spots developed in unmarked areas, but slight discoloration was evident around several of the scribe marks. The cleaning process was obviously incapable of removing either type of discoloration; it was also unlikely to produce either type of defect on a tube surface having no mechanical impediments to clean rinsing.

The four tubes having defect indications were later cut to short lengths for use in laboratory development of an effective cleaning procedure.

EXAMINATION OF AS-RECEIVED TUBING

Tubing Lot "J" had not been removed from its shipping container, where the finished tubes were packed together with associated process scrap.

The finished tubes, which had been packaged in individual paper sleeves, were now inspected for discoloration. An estimated 40% of the finished tubes had one or more spots of either the rusty or iridescent blemishes. A similar incidence was found on that portion of the process scrap which had been processed through a degreasing operation and, judging from the surface texture of all lots of finished tubes, a centerless grinding operation. Scrap which was still coated with drawing

lubricant had no discoloration blemishes. At this point it is worth noting that the blemishes were confined to the outer surface of the tubes. More than 100 ft of affected tubes were sectioned to facilitate microscopic examination of the bores, which were found uniformly free of any discoloration.

IDENTIFICATION AND ORIGIN

CHEMISTRY

Conventional wet analytical methods were not attempted. Electron microprobe analyses made on several of the indications were inconclusive, as were X-ray diffraction studies.

VISUAL APPEARANCE

One type of blemish was visually identified as common rust (red iron oxide, Fe_2O_3) by color, visible texture, and degree of adherence (Figure 2). Chemical behavior with the several cleaning agents used confirmed this identification. It has long been known that the austenitic stainless steels can develop rust under certain conditions of processing and handling.⁽¹⁾ Many of these spots were associated with a slight surface depression resembling a dent rather than a pit. The probable cause is the use, during the centerless grinding operation, of grinding coolant contaminated with minute particles of carbon steel. Dry grinding with contaminated abrasive is capable of the same results. The other type of discoloration, represented by Figure 3, was less readily identified; the investigators do not yet agree on its origin. The first hypothesis, of heat scale produced by welding current arcing between workpiece and collet, was soon discredited. Another, that of localized overheating of hard inclusions during centerless grinding, was given some support by the X-ray diffraction patterns of the discolored areas as

compared to those of the base metal. However, metallographic examination did not confirm the existence of the hard inclusions. A third tentative explanation took into account the non-free-rinsing character of certain formulations of alkaline cleaning solutions. A residue of alkaline silicate may cling to surface burrs or galls left by a "wild grit" on the centerless grinder belt. Exposure to atmospheric carbon dioxide yields a mixed reaction product of silica plus sodium carbonate which is neither soluble in strong alkaline solutions nor completely removed in water rinses. Such a deposit, varying in thickness from center to edge, could be the source of the "Newton's Rings" pattern mentioned earlier.

Still another theory has been proposed that both types of spots are but differing manifestations of the same oxidation or rusting phenomenon. In any event, nature and cause are likely to remain moot for lack of sufficient authentic specimens for experimental work. They have also been made irrelevant by the absence of similar blemishes on tubing from other sources

EFFECT ON MECHANICAL PROPERTIES

Mechanical properties testing, at room temperature and at 1000 °F, performed on specimens having discoloration blemishes shows no deterioration of short-term properties as compared with normal tubing. (Table 1)

CLEANING AND SALVAGE

As mentioned in earlier paragraphs, the discolorations were unaffected by the existing cleaning methods. Both types were removed in warm 10% nitric acid, always within a matter of seconds after immersion. Complete removal of both the blemish and its cause was demonstrated by:

- (1) Holding cleaned specimens 48 hr in distilled H₂O
- (2) Holding cleaned specimens 72 hr in air saturated with H₂O at 170 °F
- (3) Holding cleaned specimens 11 weeks in office and laboratory environments.

In no case has any discoloration developed on specimens cleaned in nitric acid. The safety of HNO_3 cleaning is demonstrated by Figures 4 and 5. No evidence of intergranular attack was found on specimens exposed to 10% HNO_3 at 140 °F for 30 min, even in the region of end-cap welds. It should be noted that the nitric acid treatment is specific for removal of soils from stainless steel. (1,2)

REFERENCES

1. *Metals Handbook, 8th Edition Vol. 2, American Society for Metals, Metals Park, Ohio, 1964.*
2. *Recommended Practice for Descaling and Cleaning Stainless Steel Surfaces; ASTM Spec No. A380-57, American Society for Testing and Materials, Philadelphia, Pa.*

TABLE I. Mechanical Properties

20% Cold-Worked (83263)					
Test Temp.	0.2% Yield Strength, psi	Ultimate Tensile Strength, psi	Uniform Elongation, %	Total Elongation, %	Total Elongation by Scribe Marks, %
Room Temp.	81,680	116,830	17.9	25.4	20.3
	72,480	114,460	18.5	23.6	18.2
	76,730	115,840	15.7	22.2	17.0
1000 °F	68,320	89,110	10.6	14.6	11.6
	71,290	90,990	9.3	13.3	10.3
	69,310	89,500	8.5	11.9	9.2
Annealed (83260)					
Room Temp.	40,500	85,050	71.6	82.8	65.9
	42,080	86,630	64.0	83.3	67.0
1000 °F	25,940	66,930	38.9	43.8	34.6
	25,840	67,620	37.3	43.3	33.0

20X

FIGURE 1. *Spot Originally Suspected of Resulting from an Arc Burn*

100X

FIGURE 2. *Rust Spot on Tube Surface; Dark Spot at Left of Photo is Marking Ink*

FIGURE 3. Unidentifiable Material on Tube Surface 100X

FIGURE 4. Transverse Section at Inner Surface of Tube After 30 min in Warm 10% HNO_3 , Unetched 500X

500X

FIGURE 5. Transverse Section at Outer Surface of Tube After 30 min in Warm 10% HNO_3 , Unetched

500X

FIGURE 6. Transverse Section at Outer Surface of Tube, As-Received

APPENDIX A

SPECIFICATIONS FOR FINISHED TUBESSURFACE CONDITION

The tubes shall be bright annealed and the internal and external surfaces free of all scale and oxide. Surfaces shall exhibit a maximum roughness equivalent to 32 rms. (ASA Designation 32) Finished tubes shall be free from grease, oil, residual lubricants, and other extraneous materials. Representative tubes selected on the basis of procedures to be established by the Buyer shall have a clean white cloth drawn through the bore. The presence of metallic flakes or particles on the cloth shall be cause for rejection. Discoloration of the cloth, without the presence of flakes or grit, shall not be cause for rejection.

CLEANING

The use of cleaning agents containing chlorine is undesirable. If the supplier uses such cleaning agents, he shall so state in his bid for fabrication under this specification and in his test reports on tubing fabrication. The supplier shall demonstrate that the total residual chloride on the surface of the delivered tubing is less than 0.0005 mg of chlorine per square inch of inner surface. The method employed for such demonstration shall be described in any bid for fabrication of tubing under this specification.

HANDLING

The tubing shall be handled in a manner necessary to minimize the formation of surface defects. This may require more than usual care during fabrication to ensure complete cleanliness prior to annealing operations; surveillance of drawing and tube reducing operations to prevent foreign

material contamination of the tubing during size reduction; and prevention of mechanical defects during handling operations prior to delivery to the Buyer.

APPENDIX B

CLEANING PROCEDURE

STAINLESS STEEL TUBING AND CAPSULE COMPONENTS

FABRICATION PROCEDURE 16

PURPOSE

To remove all traces of machining lubricants, dirt and finger prints which are detrimental to weld integrity and to performance in the reactor.

PROCEDURE

1. Fill cleaning tank to desired level with deionized water.
2. Before heating water, add "Oakite 90" in the ratio of 12 oz of Oakite powder to 1 gal of water. (Use caution in handling the Oakite which is a strong alkali. Never add to hot water.)
3. Heat bath to ~90 °C and immerse parts to be cleaned.
4. Use a long handled bottle brush to clean the inside of tubing and/or long cylindrical parts. Allow parts to remain in cleaning solution for 20 to 30 min.
5. Remove parts from cleaning solution and rinse with hot tap water followed by a second rinse in deionized water at room temperature. Be careful to rinse thoroughly the inside of tubing and long cylindrical parts.

NOTE: Do not handle clean parts with bare hands at anytime before, during or after the rinsing operation. Wear clean cotton, nylon or rubber gloves.

6. Following the deionized water rinse, dry the parts with an electric flameless heat gun.
7. Place the clean parts in dust-tight plastic bags until ready for assembly.

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