Reformer Manifold Cracking

Unusual cracking of manifold tubing welds in ammonia plant reformer may alert operators to possible malfunctions in other units.

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SYNTHESIS GAS FOR AMMONIA MANufacture is made in a direct natural gas fired furnace by reforming a steam/methane mixture over nickel catalyst. The preheated mixture enters centrifugally cast HK-40 alloy catalyst tubes through pigtails, flows down through each tube and is collected in Incoloy 800 alloy tubing manifolds on both sides of an HK-40 riser. Partially reformed synthesis gas flows up through the risers into a transfer line and on to the secondary reformer. This primary reforming furnace contains eight rows of 42 catalyst tubes each. A schematic of the furnace arrangement is shown in Figure 1.

Each catalyst tube is joined to manifold tubing with forged Incoloy "Weld-O-Lets". The riser connection is made with a forged Incoloy tee. All Incoloy components were specified as Grade II—grain coarsened for high temperature service by solution annealing. Weld specifications called for a TIG root pass with Inco 82 filler metal and metal-arc weldout with Inco 182 electrodes. The manifold assemblies, which include the tees and Weld-O-Lets, are externally insulated with ceramic blanket insulation held in place with Inconel 600 alloy sheet metal jacketing.

Inspection and repairs

During routine inspection in June, 1968, after approximately 6 months' service since the previous inspection, liquid dye penetrant testing showed cracks in riser tee-to-manifold butt welds in four of eight catalyst tube rows. Rows 1, 2, 3 and 8 (No. 1 nearest the secondary reformer) were affected. Following this discovery, insulation was removed from one catalyst tube Weld-O-Let on both sides of each riser, and these welds were also dye penetrant tested. One more crack was found, on the riser side of the first Weld-O-Let-to-manifold weld north of No. 3 riser. A description of each crack, plus observations regarding surface appearance and degree of magnetism, follows, and shown in Figure 2:

- Row No. 1: Circumferential crack about 2 in. long in top of weld "B". Tubing on both sides of tee showed slight oxidation and little or no magnetism. Upper half of tee was moderately magnetic; lower half showed little or no magetism.
- Row No. 2: Circumferential crack about 2 in. long at bottom of weld "B". Tubing showed no significant oxidation. Upper half of tee was moderately magnetic; lower half showed little or no magnetism.
- Row No. 3: Circumferential cracks about 1½ in. and 3 in.

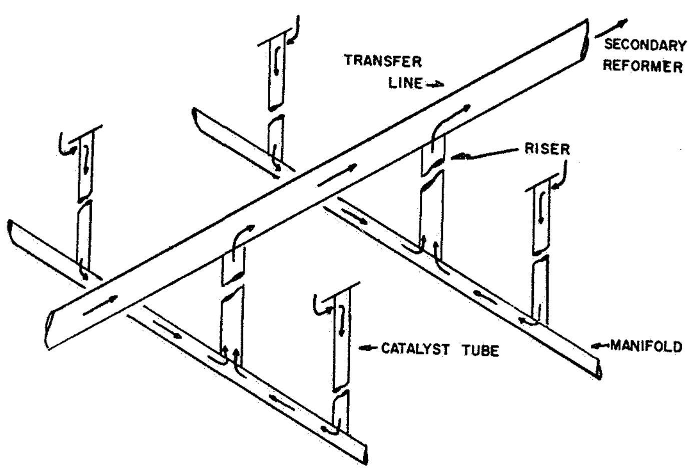

Figure 1. Schematic of primary reformer arrangement.

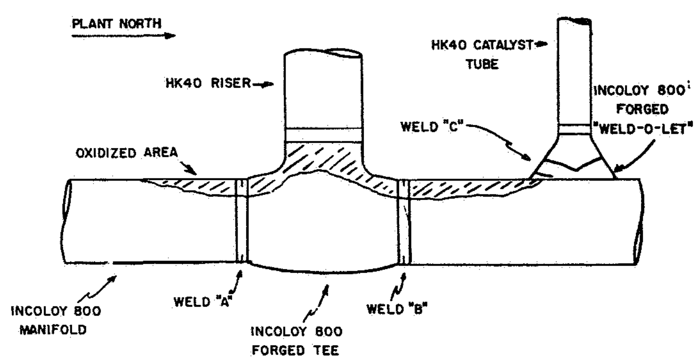

Figure 2. Manifold schematic—tee and Weld-O-Let welds.

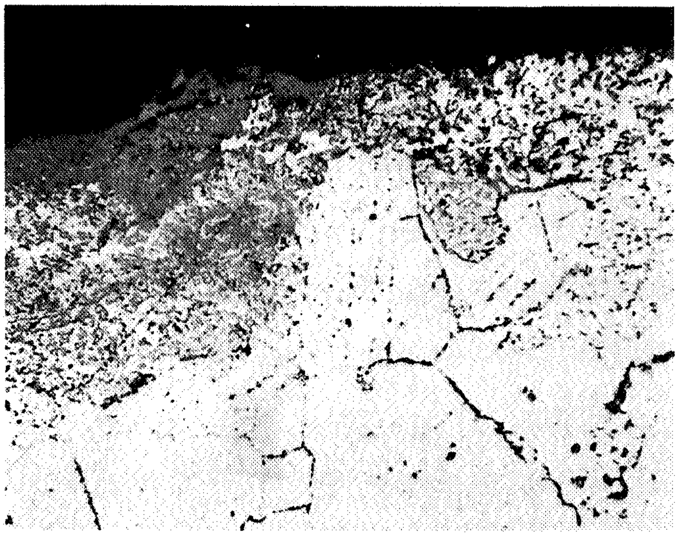

Figure 3. Microstructure at 200x.

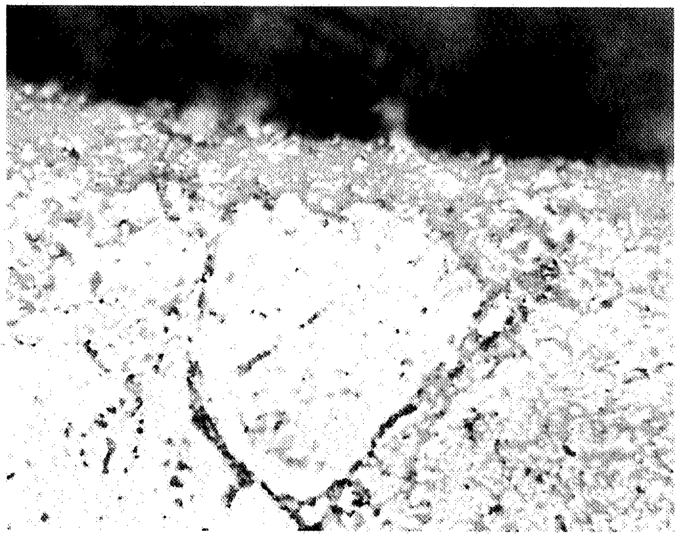

Figure 4. Surface structure at 500x.

long in top of welds "A" and "B", respectively; circumferential crack about 2 in. long at bottom of weld "A"; circumferential crack about 4 in. long in the riser side of weld "C". Upper surfaces of manifold tubing showed severe oxidation and considerable magnetism, particularly north of tee. Upper half of tee was moderately magnetic. Area around crack near weld "C" showed slight oxidation and magnetism.

- Row No. 8: Circumferential crack about 2 in. long in top of weld "A". Tubing around crack showed slight oxidation and magnetism. Upper half of tee was slightly magnetic; lower half and all non-oxidized tubing areas were nonmagnetic.
- Rows Nos. 4, 5, 6 & 7: No evidence of cracks. Little or no oxidation. Magnetism varied from very slight to essentially none.

Initially, it was decided to grind out all cracks and reweld with metal-arc and Inco 182 electrodes. Work started with the crack in No. 1 manifold-to-tee butt weld. The crack was ground until dye penetrant showed no indications. Maximum depth of the groove was about 3/32 in. The first bead of Inco 182 weld metal showed considerable porosity, as did two subsequent beads. These beads were ground out, and a trial was made with an "Inco-Weld A" coated electrode deposit, which showed no defects after slag removal. However, dye penetrant inspection showed extreme porosity in tee and manifold metal adjacent to the weld. These surfaces bled dye from minute point and linear indications even after repeated cleaning with solvent. Apparently, the heat from welding opened defects in these areas, which showed no indications prior to depositing the first bead.

Repairs to this crack were stopped and an attempt was made to repair one crack in No. 3 tee-to-manifold weld. Following grinding and deposition of the first weld bead, dye penetrant showed similar but more severe indications of gross porosity and fine linear defects adjacent to the bead.

Next, a small area on manifold tubing showing little or no oxidation or magnetism was selected for a weld test:

1. A 3 in. dia. spot was polished to bright metal (about 1/64 in. maximum was removed) and dye penetrant tested. No indications were found.
2. A single "Inco-Weld A" weld bead was deposited on the polished surface. The bead was cleaned, allowed to cool and and dye penetrant tested. There were no indications.
3. The bead was ground smooth, dye penetrant tested and found to be free of indications.

It was concluded that: (a) depth of unsound metal is a function of degree of oxidation and magnetism; and (b) rather broad areas adjacent to the weld area must be ground to sound metal to attain a satisfactory repair.

Weld repair procedure

Ultimately, all cracks were repaired successfully using the following procedure:

1. Grind out cracks and adjacent tee and manifold surfaces until dye penetrant shows no indications within 1½-2 in. of weld area.
2. Deposit "Inco-Weld A" stringer beads, one at a time, with cooling, slag removal and dye penetrant testing after each bead. Grind out weld and base metal defects to sound metal before depositing the next bead.
3. Continue one-bead-at-a-time repair until welding is complete. Grind weld smooth and flush with adjacent base metal and dye penetrant test.
4. Ultrasonically measure wall thickness at all ground areas. Weld overlay, using above procedure, all areas showing less than minimum specified allowable wall thickness.
5. Dye penetrant test and radiograph repaired and overlaid welds, and remaining unaffected tee welds.

The maximum depth of cracking and unsound metal, about ¼ in., occurred in No. 3 manifold. Final inspection showed no defects.

During repairs, a wedge-shaped sample about 2 in. long x 3/16 in. deep was hack-sawed from the top of No. 3 manifold tubing just north of the tee-to-manifold butt weld, for metallographic examination and X-ray microprobe analyses.

The manifold sample was first clamped in a vise and tapped lightly with a small hammer. It failed in a brittle manner through about 90% of its thickness. Examination of the fracture faces showed a thin, greenish layer on the external surface, and a dull gray, sugary appearance throughout its remaining thickness. Then the sample was examined metallographically. A typical microstructure is shown in Figure 3.

The outer surface is shown near the top of the photomicrograph. Note the non-uniform depth of the heterogeneous phase. There appears

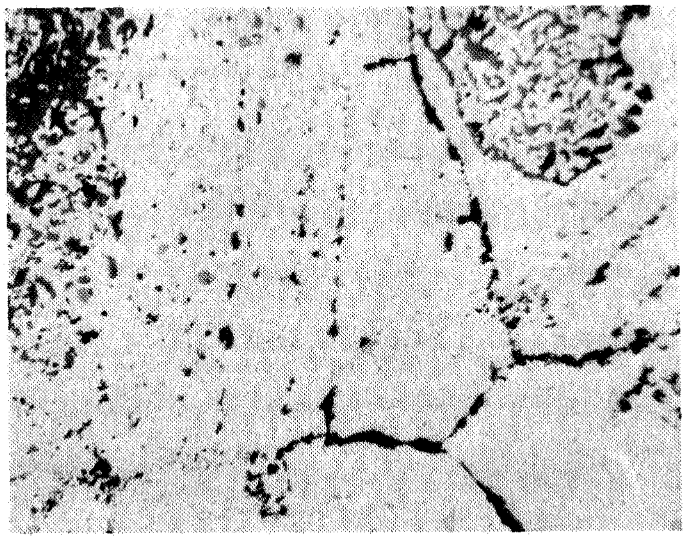

Figure 5. Internal structure at 500x.

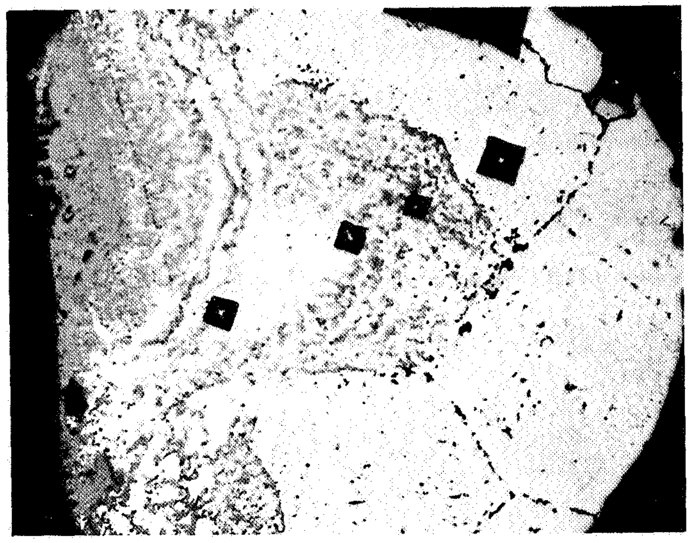

Figure 6. Microhardness impressions at 250x.

to be virtually 100% non-metallic material at the extreme outer surface, followed by a mixed metal-non-metallic layer, and then essentially 100% metallic phase. Note also, the large grain size and considerable amount of material in grain boundaries. Photomicrographs taken at higher magnification of surface and grain boundary phases are shown in Figures 4 and 5. These structures help explain the dye penetrant test indications of extreme porosity previously discussed.

A Vickers microhardness determination showed a wide variation in hardness, as seen in Figure 6. The metallic phase was in the range 100-120 VHN. However, heterogeneous areas approached 1,000 VHN, indicating a complex, refractory-like composite material.

During investigation at high magnification, an unusual, unidentified, needle-like phase was noted within some grains, seen in Figure 7. Some needles actually appeared to be micro-cracks, whereas others appeared to be some type of non-metallic inclusion.

The sample was then subjected to microprobe analyses by X-ray fluorescence.

Microprobe analyses

A photomicrograph of the target area chosen for one series of microprobe X-ray fluoresence analyses is shown in the upper left-hand corner of Figure 8. This area includes heterogeneous zones along with grain boundary constituents and inclusions within grains. In this kind of analysis, the element being determined appears as a bright area against a dark background in the photograph. Microprobe micrographs showing chromium, oxygen, silicon, titanium, sulfur, nickel and iron scans are also shown.

Note that chromium is segregated at the heterogeneous zones. Oxygen, silicon and titanium are also segregated at these zones as well as in the grain boundaries. Sulfur appears as a random dispersion of particles throughout the structure. This suggests that some of the particles shown in Figure 7 may be sulfide inclusions. Neither nickel nor iron appears segregated in heterogeneous zones or grain boundaries.

A photomicrograph of a smaller target area chosen for a second series of microprobe analyses is shown in the upper left-hand corner of Figure 9. Microprobe micrographs for all of the above elements except sulfur, which also appear in Figure 9, show similar results.

Results of the inspection, metallographic and microprobe studies indicate a type of internal oxidation of Incoloy 800 alloy base metal (and, presumably, the Inco 182 weld metal) initiated from the external or fired side of the reformer manifolds. Oxidation was non-uniform, and chromium, oxygen, silicon and titanium were segregated in heterogeneous zones at and below the external surface, and in the grain boundaries. This left an extremely

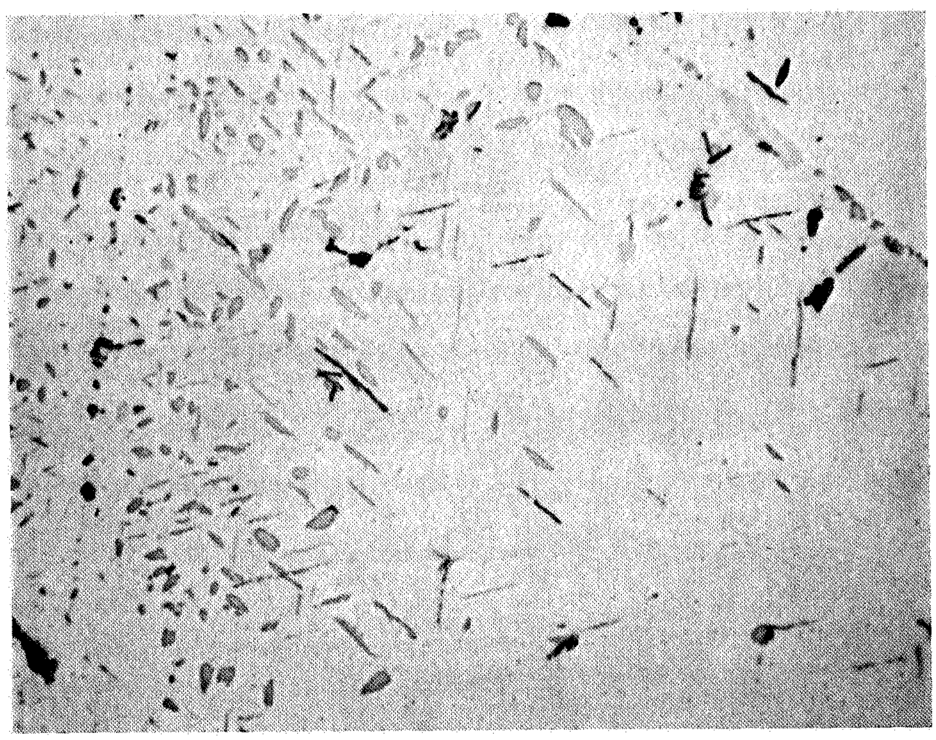

Figure 7. Needle-like inclusions at 750x.

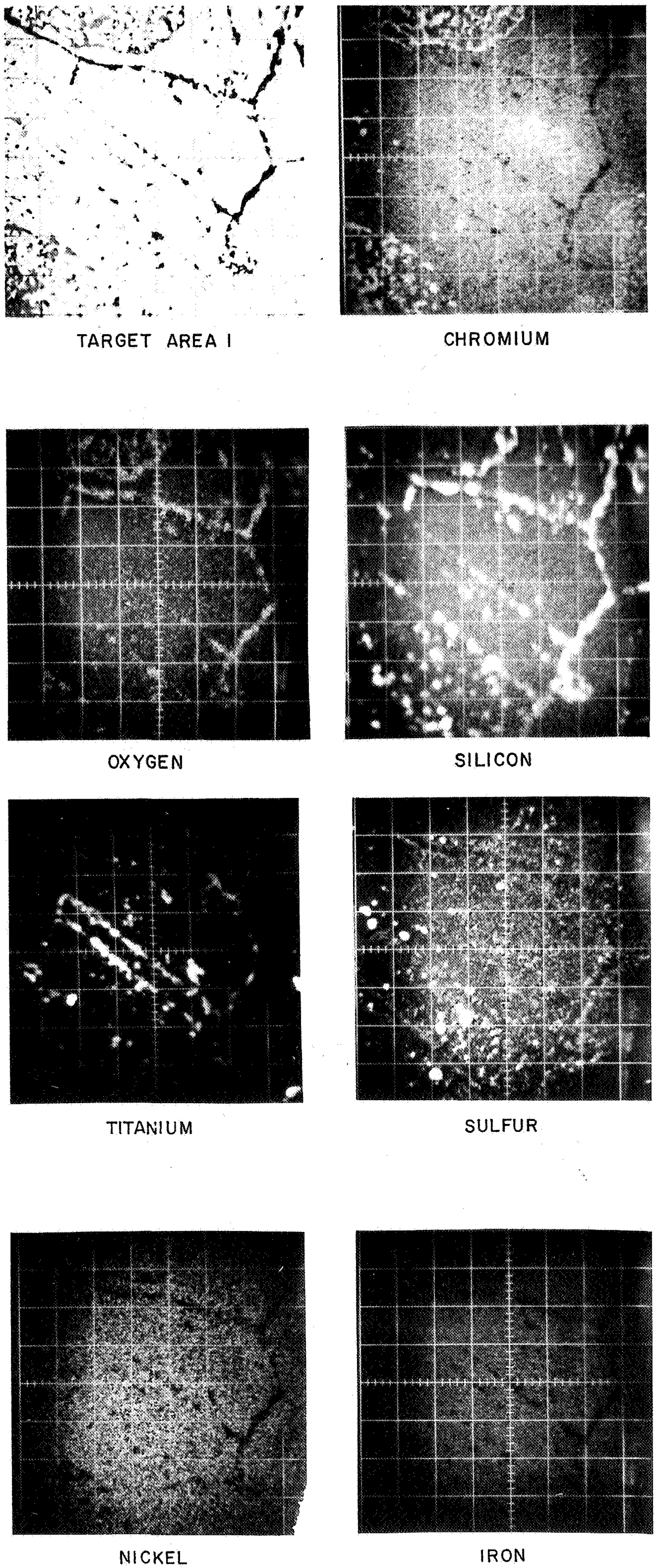

Figure 8. X-ray fluorescence microprobe micrographs of Target Area 1.

brittle, weak, porous magnetic layer on the surface, varying in depth from a few thousandths to ¼ in. All cracking appeared to be confined to this layer; underlying metal appeared sound.

Copson and Lang *(1)* described some of the characteristics of this phenomenon, based on their extensive studies on nickel-chromium alloys:

- Selective oxidation of chromium within the metal structure; remaining metal is magnetic.
- Affected metal is brittle and weak, breaks easily and shows dark green fracture surfaces.
- Microstructure shows sub-surface oxidation and oxides in grain boundaries and within grains.
- Occurs in the 1200-2100°F temperature range.

All of these conditions were found during the investigation.

Internal oxidation

It is reported that internal oxidation is rare in nickel-chromium-iron-alloys containing less than 70% nickel, more than 20% chromium and appreciable iron. This may explain why cracking occurred in weld metal, nominal 65% Ni and 15% Cr, rather than base metal, nominal 33% Ni and 21% Cr (despite columbium, which was assumed to be present in the weld, and which reportedly helps resist internal oxidation).

The exact cause of internal oxidation in the reformer manifolds is unknown. This phenomenon generally occurs in atmospheres which are oxidizing to chromium but reducing to nickel. The burner fuel gas mixture is adjusted to provide about 3% excess oxygen. This should be sufficient to resist internal oxidation, providing there is no local oxygen depletion. It is possible that free flue gas circulation was impaired by the external insulation around the manifolds. Replacing the tight-fitting blanket insulation around the tees with a loose radiant metal heat shield for improved flue gas circulation is being considered. Other possible causes may be pinholes or tight cracks in the manifolds through which process gas could leak and keep oxygen from the metal surfaces. The manifolds were not pressure tested after repairs.

Atmospheres which also cause carburization and sulfidation are said to accelerate internal oxidation of nickel-chromium alloys. Although the manifold sample was not analyzed for carbon, no evidence of carburization in the microstructure was found. Also, the sample was taken easily with a hacksaw; carburized metal is usually quite hard and resists most metal-cutting methods except grinding. Microprobe analyses showed sulfur randomly distributed throughout the microstructure. Sulfidation from contaminated fuel gas or insulation could be a contributing factor.

Another inspection is planned late this year to determine adequacy of repairs and conduct further studies.

Summary

Recent inspection of a primary reformer showed cracks in Incoloy 800 alloy manifold tubing-to-tee butt welds in four of eight catalyst tube rows. Surfaces around the cracks showed varying degrees of oxidation and magnetism, to a maximum depth of ¼ in. All cracks were confined to the oxidized metal layer.

Successful repairs were made by grinding the cracks and surrounding brittle oxidized metal layers to sound metal, and welding with metal-arc and "Inco-Weld A" electrodes.

Limited metallographic examination and X-ray fluorescence microprobe analyses of a manifold tubing sample showed evidence of internal oxidation. Chromium was oxidized preferentially, and was segregated along with oxygen, silicon and titanium at heterogeneous zones and in grain boundaries.

The exact cause of internal oxidation is unknown at this time. A possible cause is local oxygen depletion; sulfidation may be a contributing factor. Further inspections and studies are planned. #

Literature Cited

1. Copson, H. R., and F. S. Lang, "Some Experiments on Internal Oxidation of Nickel-Chromium Alloys," *Corrosion, 15* (April, 1959).

G. Korbin is a consultant, DuPont Co., Engineering Department, Engineering Service Division, Materials Engineering Group. He is presently assigned to Gulf Regional Office located at the Beaumont, Tex. Works site. He is a graduate of the University of Conn. with a degree in chemistry. Korkin has been certified by NACE as qualified in one or more phases of the field of corrosion control.

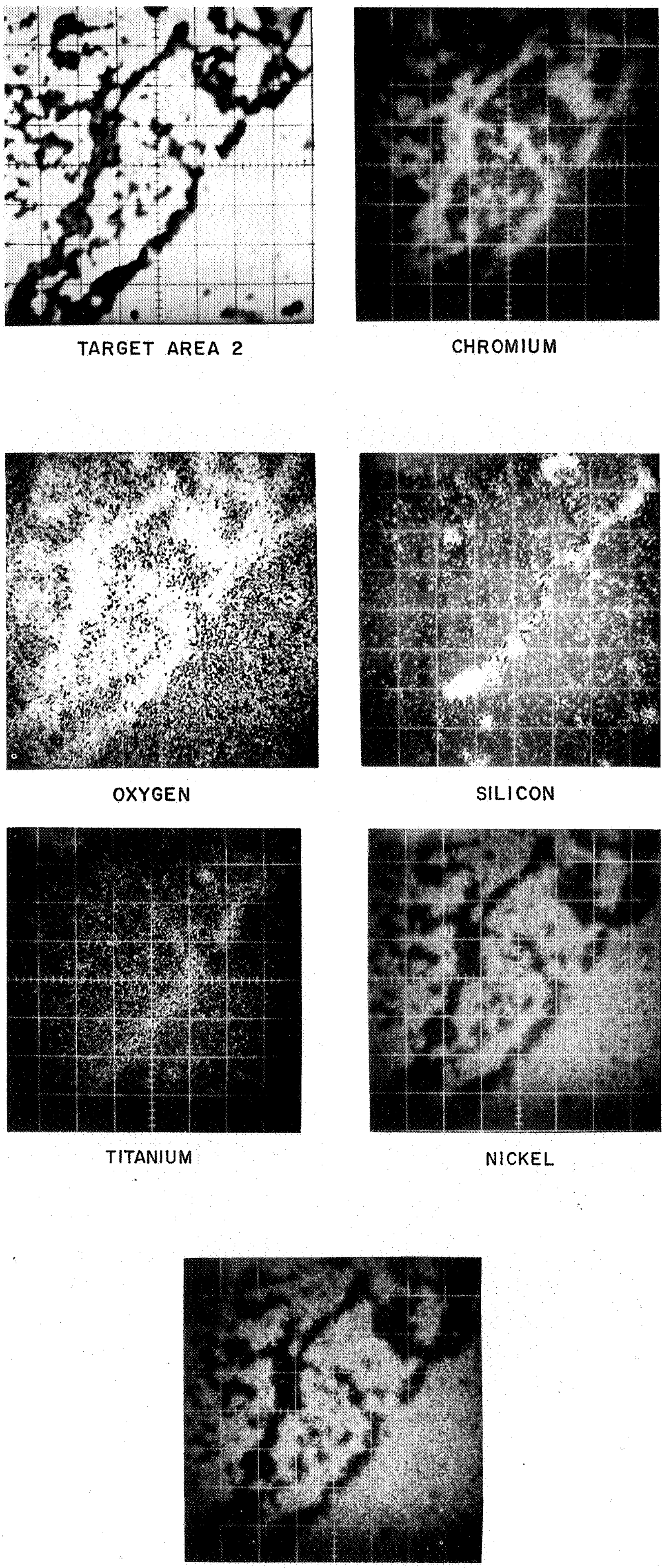

Figure 9. X-ray fluorescence microprobe micrographs of Target Area 2.

Discussion

Q. On these cracks that you found, do I understand that you made a routine dye penetrant inspection?
KOBRIN: Yes.
Q. Why did you look?
KOBRIN: Any time we have a turnaround, we inspect welds throughout the reformer system. We feel it is good practice to make periodic inspections of our reformer.
Q. Were any of the cracks that you found left unrepaired?
KOBRIN: No.
Q. If, after all the testing that you've done, an examination should show similar cracks again, would you leave them unrepaired?
KOBRIN: I doubt it. We don't like to leave cracks unrepaired, because of possible propagation in service. Temperature and pressure tends to open up rather than heal cracks.
Q. Were any of these cracks leaking in service?
KOBRIN: To my knowledge, none were leaking.
Q. **Materials Protection**, September 1968, has a report by Messrs. Fitzharris and Byrd concerning what may be a similar type of occurrence. Have you seen that report?
KOBRIN: No.
Q. They indicate a segregation of titanium and sulfur, magentization and several aspects that were similar to what you reported.
KOBRIN: Was the material Incoloy also?
Q. They reported this attack on both Incoloy and HK40, and it occurred inside the tubes, incidentally. They lay it to boiler water treating chemicals. You may see some similarity there.
Q. You referred to polishing an area and making a weld which would be a weldability test on material. Was this on new material?
KOBRIN: No. This was on the same manifold but well away from the tees and any area showing oxidation or magnetism.
Q. Would you expect Type 316 stainless, a common header material before Incoloy 800, to possibly exhibit the same failures under similar circumstances?
KOBRIN: I've never seen internal oxidation in an austenitic stainless steel. I would expect sigma phase, perhaps, but I'm not aware of any cases of internal oxidation in austenitics.
Q. Do you have a history of the header? How many times did you shut down? Did you go through the 900°F. zone which could age the metal?
KOBRIN: I'm sure this data is available, but I don't have it with me. I expect this would affect the HK, from an aging standpoint, a lot more than the Incoloy. At least this is what we're led to believe.
Q. So you don't think that the cracks were due to aging in this case?
KOBRIN: No. In my opinion, they formed in the brittle oxidized material possibly during a start-up or shutdown. Once we got rid of this brittle material we seemed to be in sound metal, although we did no mechanical testing. Also, the underlying metal accepted a weld very nicely.
Q. So, in conclusion, you can say that the cracks had nothing to do with the number of shutdowns and start-ups of your reformer?
KOBRIN: As far as I know, they did not.
Q. I was interested in the ascicular precipitate which you described in one of the micrographs. Did this precipitate extend throughout the tube or was this a surface effect also?
KOBRIN: It was within the unsound metal layer. Once we got back into sound metal, we did not see this precipitate.
Q. Was this structure particularly hard? Did you do any testing on it?
KOBRIN: We made Vickers microhardness tests on the heterogeneous phase, but not on the needle-like phase.
Q. It looked to me like nitrides which I have seen on HK alloy heated in flue gas.
KOBRIN: This is quite possible.
Q. How long was your plant in operation? Is this the first time you noticed these cracks?
KOBRIN: The plant operated about a year prior to June of this year. This is the first time the cracks were noticed.
Q. These tubes that you have mentioned, are these the same five tubes we heard about this morning that failed?
KOBRIN: No. I think sometone reported on failures of HK40 catalyst tubes this morning. My paper described failure of an Incoloy manifold.
Q. How do you explain the corrosion occurring only at the tee going into the riser on the header and not throughout the entire header?
KOBRIN: I don't know. This tee is at the hottest part of the manifold. Perhaps there is a critical temperature that is involved with this type of attack.
Q. Were your headers insulated pretty much the same from end to end?
KOBRIN: Yes.
Q. You said that each time you made a weld you cooled down and tested. Just as a matter of interest, would you say from where you cooled down and how you cooled down?
KOBRIN: We let the weld cool naturally until it could be tested with liquid dye penetrant. For example, we used narrow, fairly short stringer beads, laying in one bead at a time. After cooling, each bead was cleaned and dye penetrant tested, before depositing another bead. We felt that we had to limit the amount of heat input in order to get a sound repair.