T2000

STAINLESS STEEL DRUM FAILURE AT OLEFIN PLANT

Brian J. Fitzgerald, Jeffrey P. Jones, Gregory E. Yeo, ExxonMobil Chemical Company
Ngok-Jin Chow, ExxonMobil Asia Pacific PTE LTD
Matt Findlay, ExxonMobil Chemical Ltd.

Plant Safety
April 24, 2006

Prepared for the AIChE 2006 Spring National Meeting, EPC Conference
Orlando, FL
April 24-27, 2006
Abstract

Two 304 stainless steel vessels in the demethanizer circuit of an olefins unit developed through wall cracks and leaks. Both cracks occurred in 304 stainless steel 2:1 elliptical heads manufactured by cold spinning. The heads were in the "as spun" condition. The unit was immediately shut down under controlled conditions and no personnel injuries occurred. No other equipment in the unit was damaged.

Introduction

Modern ethylene plants make extensive use of low temperature stainless steel alloys, specifically in the low-temperature / high pressure demethanizer and feed chilling areas. Stainless steel is preferred in this application because of its high material toughness at low temperature, which is commonly minus 100°C and below.

The ExxonMobil Singapore Olefins Plant started up in 2001 and utilizes 304 stainless steel in the services typical of a modern plant, including the chill train flash drums, chill train heat exchangers, and the demethanizer area. These heat exchangers are chilled by ethylene refrigerant, with refrigerant temperatures as low as minus 100°C.

Background

The two subject 304 stainless steel vessels are the demethanizer reflux drum and a chill train heat exchanger, both of which operate at temperatures of approximately minus 100°C. The drum diameter is 2000 mm with a head thickness of 40 mm and the heat exchanger head diameter is 590mm with a head thickness of 14mm. The heads were manufactured by cold spinning and were not heat treated after spinning or before use.

On November 14, the olefins unit was in its second start up when a gasket leak in another vessel caused the start up to go into a "hold" mode while the gasket was repaired.
During this hold period the temperatures of the two 304 stainless steel vessels that developed leaks increased to warmer than minus 50°C with internal hydrogen partial pressures of 210 and 2100 KPa.

After the gasket was repaired, the start up sequence resumed and was completed normally with both vessels reaching their operating temperature of approximately minus 100°C. Shortly after normal operating conditions were established, a leak was noted in one vessel and approximately 1 hour later the leak in the second vessel was found.

**Data/Observation**

- The through wall leaks in both heads were oriented in the meridional direction and located in the flange region of the heads. No cracks were present in vessel shell sections, welds or heat affected zones.
- Both heads were manufactured by cold spinning and were not heat treated after spinning or before use.
- The flange region of both heads had hardness numbers greater than 265 Vickers.
- The flange region of both heads had magnetic readings greater than 7.5 ferrite number as measured with a Severn Gage.
- Metallographic examination of a head cross section showed the crack path followed a continuous network of martensite and the failure mode was quasi-cleavage.
- Literature data and consultation with industry experts indicates that 304 stainless steel with strain-induced martensite has an expected toughness at minus 100°C of 150 to 200 MPa m\(^{1/2}\) or greater with a ductile rupture failure mode. However, if the martensitic phase is saturated with hydrogen the toughness decreases and the failure mode changes to quasi-cleavage.
- Calculation and consultation with industry experts indicates significant hydrogen diffusion can occur at approximately minus 50°C and warmer.
- Stress analysis showed that residual forming stress is proportional to D/t and is the dominant load for the two heads.
- Resumption of the cool down sequence after the gasket repair reduced vessel temperatures from approximately minus 30°C to minus 100°C in 25 minutes. The temperature change reduced the solubility of hydrogen in the austenite/martensite structure.
Conclusions

- 304 stainless steel 2:1 elliptical heads can form strain-induced martensite during cold spinning.
- The most likely failure mode of the heads is hydrogen induced cracking. Hydrogen charging may have occurred from process hydrogen when vessel temperatures were minus 50°C and warmer or possibly from wet lay up after hydro.
- Hydrogen saturation of the martensitic phase in the heads most likely occurred when the vessel temperatures were lowered to the normal operating temperature after repair of a leaking gasket.
- Low D/t ratio of the heads results in high level of sustained residual forming stress normal to the crack direction.
- Thermal stresses were not significant but produced a low magnitude strain rate when superimposed on the high residual forming stresses plus the low toughness due to hydrogen saturation of the martensitic phase likely led to crack propagation.
- Solution annealing of 304 stainless steel heads after cold spinning will remove strain-induced martensite and susceptibility to hydrogen induced cracking.
Summary

- Introduction to cold failure mechanisms
- Brief overview of the facility
- Description of the failure
- The investigation and learnings
Cracking Schematic

- Crack propagation occurs if the applied stress intensity \( K_i \) > the material toughness \( K_{ic} \).

- Materials toughness, \( K_{ic} \), reduces to low values as hydrogen saturation occurs in cold worked 304 stainless steel.

**“A” (Defects):** Cold Work defects, i.e. laps, tears, etc.

**“Kic” (Toughness):** Cold Work i.e. residual stress & microstructure, Hydrogen Saturation

**“σ” (Stress):** Dynamic or Static i.e. pressure, thermal, residual
Overview of the Facility

- New olefins plant in Singapore: Initial startup 2001
- Modern, efficient design with low temperature demethanizer and chilling train with -100°C ethylene refrigerant
- All equipment shown 304 SS with design temperature ≤ -100°C
Events Leading Up to the Failure

- Plant was new and recently started up for the first time
- Gasket leak in another plant area required short trip of unit, ~18 hours. Reflux drum warmed to >-50° C for ~12 hours
- During restart:
  - Reflux drum pressure increased from 7 to 34 Bar over 2 hours. Gave rise to period of positive slow strain rate.
  - Thermal gradient in reflux drum occurred when level increased and vessel at -30°C cooled to -95°C in 25 minutes
  - Thermal gradient in feed chiller occurred when ethylene refrigerant flow was started
- Leaks discovered in the vessel heads within hours of the restart. Unit was shutdown safely.
Analysis of the Cracks:

- Two 304 SS Cold Spun Heads developed through wall cracks during 2nd start-up of a new olefins plant. The heads were fitted to horizontal vessels.
  - Reflux Drum: @ 9 o’clock position in head flange; 20 mm long; vessel diameter 2000 mm; head thickness 40 mm; D/t is 50.
  - Feed Chiller: @ 6 o’clock position in head flange; 12 mm long; vessel diameter 590 mm; head thickness 16 mm; D/t is 37.

- Heads were cold spun by same manufacturer.
- Heads were not heat treated after cold spinning; Cold spinning is not required by ASME code.
- Heads had magnetism in the flange and knuckle areas indicating formation of strain-induced martensite and cold work (residual stress) from cold spinning.
Feed Chiller Leak

- Crack in base metal; stops at edge of heat affected zone
- ID view shows single, discontinuous crack
- Cross section shows non-branching, “step-wise” cracking
- Cross section hardness between $R_C$ 29 to 40 ($R_B$ 85 typical for solution annealed 304)
Root Cause - Chronological Order

- Root Cause: Head was not solution annealed after cold spinning
- Crack Mode: Hydrogen Induced Cracking (HIC)

Cold Spinning of Head

Low D/t ratio:
  - High Stiffness
  - Martensite Transformation
  - Pre-existing Defect Formation

Solution Anneal at this point would stop HIC mechanism

H$_2$ diffusion into head
  - Process pick-up
  - Wet Lay-up Corrosion

Residual forming stress is major (static) load
  - Pressure and/or thermal stress is dynamic load

Crack Propagates
Root Cause - Contributing Factors

- **Root cause**: Cold spun heads were not solution annealed
  - Crack mode: Hydrogen Induced Cracking (HIC)

- **Fabrication factors in root cause**:
  - Low D/t ratio - “stiff” head with high residual stress.

- **Process factors in root cause**:
  - Pressure/Temperature during brief shutdown $H_2$ charging during plant upset period and/or during “wet” lay up from hydro.
  - Cool down rate after exposure to hydrogen at temperatures warmer than (minus) $-50^\circ C$.
  - Re-pressurization rate at startup - slow positive strain rate. superimposed on high residual forming stresses.
  - Thermal shock
What Has Changed?

Cold spun heads have been manufactured for over 20 years. Why did we see failures? Two reasons became clear during our root cause analysis:

1. Shop internal procedures do not always require solution annealing of cold spun 304 heads. In the past, head shops required solution annealing of cold spun 304 heads but some heads are now produced to “code requirements only”.

2. 304 stainless steel (and other SS’s) produced at the lower limit of its chemical composition range can result in austenite that readily transforms to martensite when cold worked.
Conclusions

- Cold spun 304 heads form martensite; martensite is susceptible to Hydrogen Induced Cracking (HIC).
- Hydrogen charging can result from diffusion of process hydrogen when temperatures are warmer than (minus) -50°C (or possibly wet lay up from hydro.)
- Hydrogen saturation occurs when temperatures are lowered during start up.
- Heat Treatment of cold spun 304 can remove the martensite and possibility of HIC.
- Strain rate due to pressure and temperature changes is sufficiently slow to enable HIC of crack tip and sustained crack growth.
- Thermal shock will superimpose on residual and pressure stresses. Could trigger leak-before-break fracture due to high residual stress and low toughness.