Incident at ExxonMobil Chemical Plant in Singapore

Summary of Events

On November 14, 2002, 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 spinnng. 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.

Background

The two 304 stainless steel vessels are a drum and a heat exchanger that operate at temperatures of approximately minus100^{o}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^{o}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^{o}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^{o}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^{o}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^{o}C to minus 100^{o}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^{o}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.