A Case Study of Welding Related Failures and Repair of the Reactor of Warm Argon Unit in Air Separation Plant -VSP

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INTRODUCTION

Tonnage oxygen plants basically produce oxygen by the cryogenic liquefaction process. Besides oxygen, nitrogen and argon are also separated from the air in this method of oxygen making The basic process involves liquefying the air at cryogenic temperatures and separating it into its constituent components by fractional distillation One of the by products of these oxygen plants is argon .

Crude argon containing 89% to 94% oxygen is extracted from the main column. Oxygen is further distilled off in the crude argon column to get 2-3 % oxygen content. Then this is fed to the warm argon unit In this unit the oxygen is treated with hydrogen and water results. The ensuing product is then fed to pure argon column to remove the nitrogen and secure the pure argon containing oxygen content less than 10 ppm(parts per million).

The vessel where the oxygen is treated with hydrogen is known as the R10 reactor This contains a catalyst known as palladium were the exothermic reaction takes place. The temperature of the reactor during the operation of the warm argon unit is about 540 deg centigrade.

The vessel is made of austenitic stainless steel, stabilized with the addition of 0.5 % titanium. cracks were found in the dished end in the vicinity of the heat affected zone of the circumferential weld

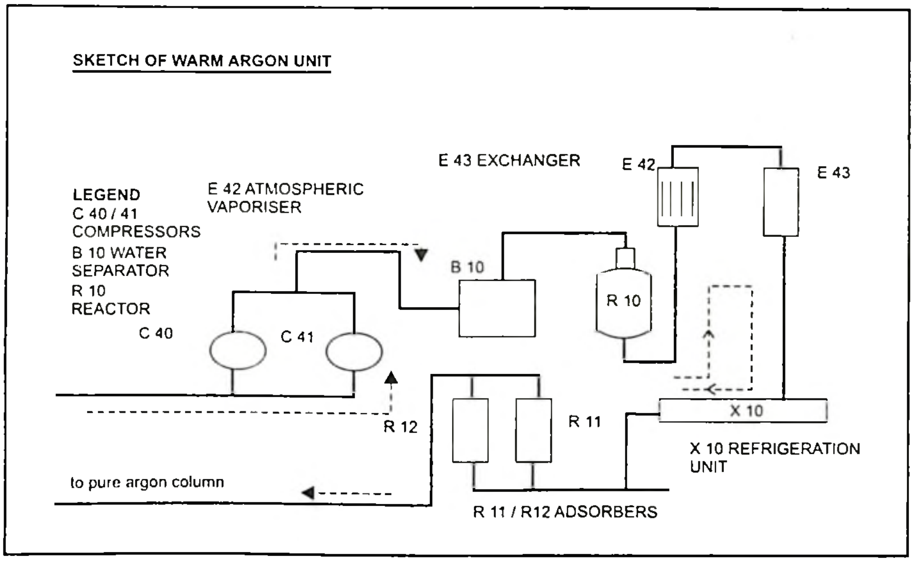

Figure 1

PROCESS DESCRIPTION

The warm argon unit where the reactor of our study (R10) is present, is as shown in the figure.1. Crude argon comes from the crude argon column to crude argon compressors C40/C41 where it is compressed along with hydrogen which had already been injected before entering into the crude argon compressor The compressors are of water ring type where the mixture is compressed in the presence of water. The pressure which is 0.25 kscg at the suction is raised to 4.0 kscg at the discharge It then goes to the water separator B10 From the water separator B10 the mixture heads towards R10 where the catalyst palladium is present It is here the exothermic reaction of hydrogen and oxygen takes place and the temperature goes to 540 o C.

The mixture thus rendered devoid of oxygen is cooled in the atmospheric vaporizer E42 to nearly 45°C and then in the water cooled shell tube exchanger E 42 to 25°C and further to 10°C at the outlet of refrigeration unit X 10. Later the mixture is sent to another water separator B 11 (not shown in fig) ,then to adsorbers R11/ R12 and finally to pure argon column.

R10 REACTOR

The reactor R10 is as shown in the figure(figure-2) below. The material specification of reactor is as follows :

The top and bottom dished ends are of

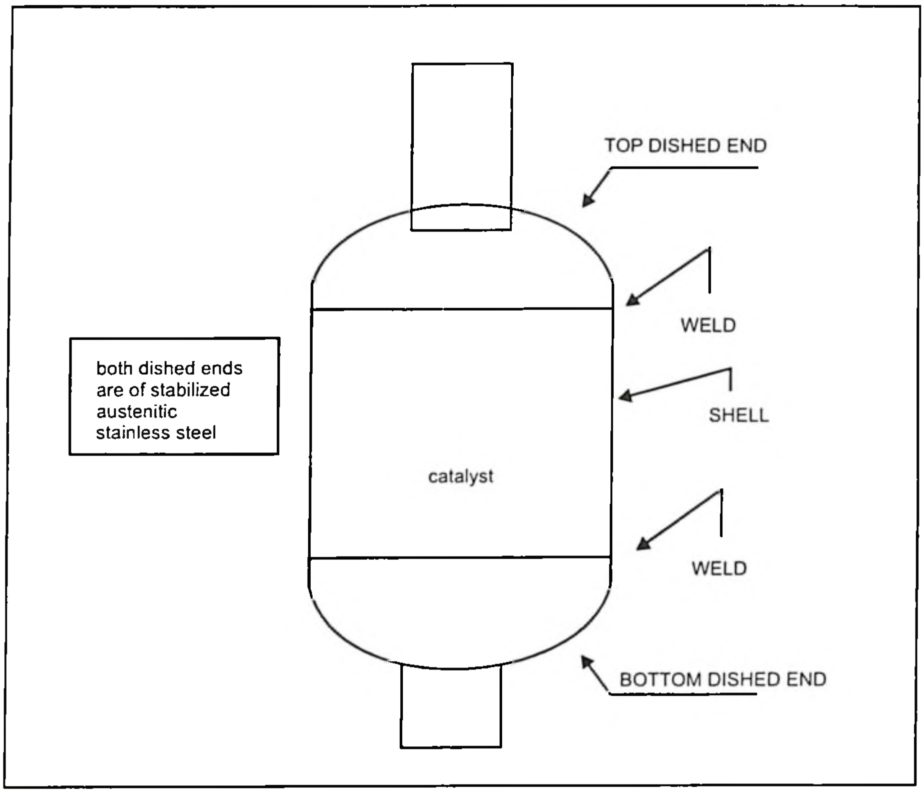

Figure 1

ASTM A 403/ WP 321.

The chemical composition of the material is as follows :

Carbon - 0.08 %
Chromium - 18.5%
Nickel - 11%
Titanium - 0.5%

Thus the steel used for dished ends are stabilized austenitic stainless steels as will be clear from the figure-2 shown below. The reactor as such will be subjected to a temperature profile of 540°C and since at this temperature there is a tendency for intercrystalline carbide precipitation known also as sensitization, stabilized stainless steels are needed.

In these stabilized stainless steels some special elements such as titanium- in this case- are ,:. added which have a high affinity for carbon. So titanium carbides are easily formed compared to chromium carbide.

FAILURE ANALYSIS

Cracks in the R 10 Reactor - on observation - were found to be as follows:

These were in the vicinity of the heat affected zone (HAZ) of the circumferential weld on the top dished end.

The cracks were of the nature of minute striations, .criss-crossing each other and were transgranular and branching.

The possible reasons for the failure of this sort were studied. These sort of failures normally occur due to

1. Knife-Iine attack
2. Hydrogen attack
2. Stress corrosion cracking.

Knife-Iine attack: Stabilized austenitic stainless steels are not susceptible to weld decay, but they can be susceptible to a different type of intergranular corrosion attack, called the knife- line attack. Knife-Iine attack is due to the precipitation of chromium carbide and it occurs in stabilized steels.

Titanium carbide has a precipitation range between 800°C to 1000°C and beyond this temperature it gets dissolved. If the cooling rate is rapid through the precipitation range then titanium carbide might not re-precipitate during cooling thus leaving enough free carbon atoms. When the weld is reheated, during the high temperature service, titanium carbide does not form again since the temperature is not high enough. (figure 3)

Hvdrogen attack : Hydrogen attack or precisely high temperature hydrogen attack called HTHA is a form of internal decarburization that occurs in steels exposed to high temperatures and pressures.

Internal decarburization and fissuring is caused by hydrogen permeating the steel structure and reacting to form other gases, such as methane CH 4. The methane cannot diffuse out of the steel and typically accumulates at grain boundary voids. This results in highly localized stresses ,leading to fissures ,cracks or blisters in the steel causing substantial reduction in mechanical properties. Surface decarburization also occurs and is caused by the exposure of steel to certain gases such as air , oxygen or CO2 .The usual effects of surface decarburization are a slight, localized reduction in strength and hardness but these are small.

HTHA occurs inside the steel along the grain boundaries and it occurs as follows:

$Fe_3C \longrightarrow Fe_3 + C$ (in solution)

Diffusion of carbon to reaction site

$C + 2H_2 \longrightarrow CH_4$

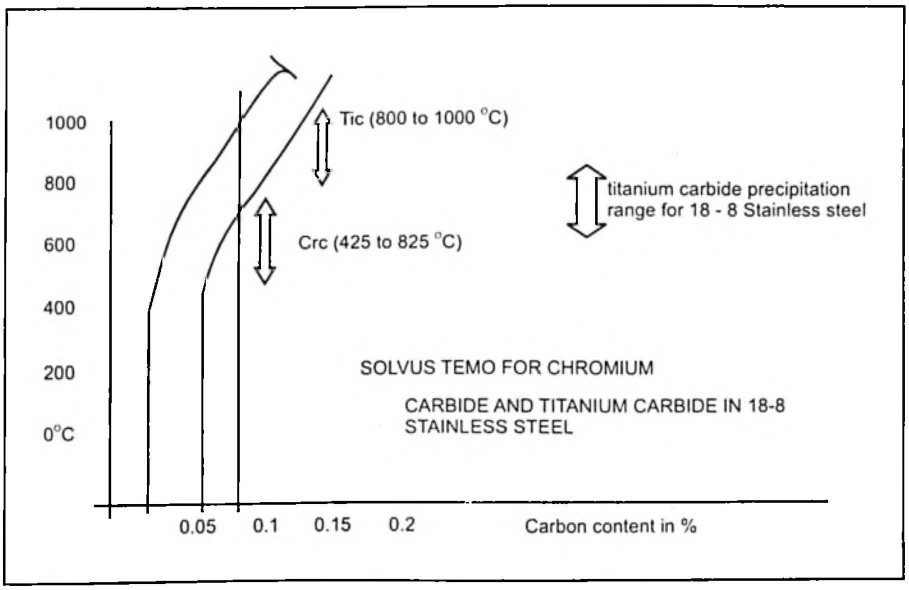

Figure 3

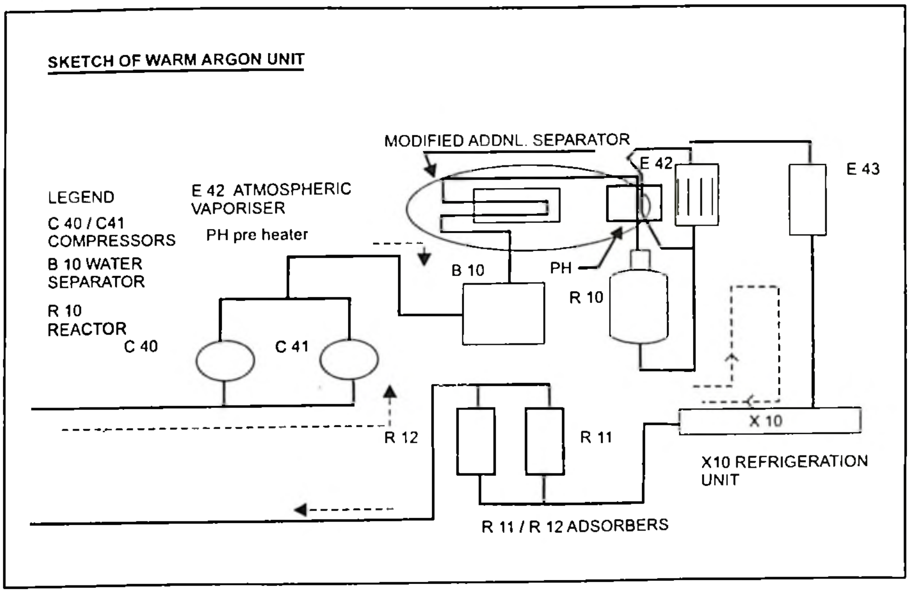

Figure 4

Thus Carbon in solution reacts to form methane.

In hydrogen attack, the reaction occurs at grain boundaliies, where CH_4 (methane) exerts internal pressure and forms fissures in enlarged pores and subsequent cracks In welds.

Austenitic stainless steels are fairly impervious to hydrogen attack. The solubility of hydrogen in austenitic stainless steels is about an order of magnitude greater than ferritic stainless steels. The diffusion coefficient of hydrogen through austenitic stainless steel is roughly two orders of magnitude lower than ferritic stainless steels. Thus a sound austenitic stainless steel can reduce the partial pressure of hydrogen acting on it.

Addition of carbide stabilizers to steel reduces the tendency towards fissuring. Elements such as titanium, molybdenum, tantalum reduce the number of nucleation sites by forming more stable alloy carbides that resist breakdown by hydrogen and decrease the propensity to form methane.

Stress corrosion crackin : Stress corrosion cracking of austenitic stainless steels can be due to the simultaneous application of tensile stresses and specific corrosive media. The cracking can be intergranular or transgranular but is mostly transgranular .Austenitic stainless steels are subjected to Stress Corrosion Cracking and can occur in oxygenated boiling water environments and in pressurized water reactors.

Methods of controlling SCC include :

- A stress relieving or annealing heat treatment to reduce the stress to a safe level.
- Removal of oxygen or water or any other corrosive media from the environment.
- Minimizing the possibility of hydrogen attack.

PROBLEM IDENTIFICATION

- The probability of failure due to carbide precipitation is ruled out as the material is a stabilized stainless steel.
- The possibility of failure due to knife-Iine attack is also negligible as this is possible only with the dissolution of titanium carbide. But dissolution of titanium carbide is possible only if the temperature goes beyond 1000°C . As the Reactor in our case is not subjected to temperatures beyond 540°C, the possibility of knife-Iine attack cannot occur during service.
- The possibility of hydrogen attack is also negligible as the material of the reactor is made of stabilized

austenitic stainless steel. Stabilized ASS has excellent resistance to hydrogen attack as explained previously. .

- The possibility of failure due to stress corrosion cracking is quite probable and plausible. This is further corroborated by the following facts.
  - The cracking was mainly transgranular and branching
  - The top dished end bore the brunt. At the top dished end the presence of free oxygen, boiling water and the presence of stress must have generated and accelerated the failure.

REMEDIAL MEASURES

To kill the possibility of stress corrosion cracking the presence of oxygen and free water should be curtailed or minimized. Presence of oxygen cannot be curtailed at the entry point of the reactor but the presence of free water can be minimized.

This is achieved by providing another additional water separator. at a higher datum and a pre heater (as shown in the figure-4).

The purpose of the additional separator is to drain out the excess water ,while that of the preheater is to raise the temperature of the mixture to the range of 80 a C before entry into the reactor dished end -by utilizing the exiting high temperature gas at the outlet of R10 reactor. This drives away whatever free water is present thus minimizing the chances of stress corrosion cracking.

REPAIR

During the welding of the new dished end, the temperatures in and around the vicinity of weld zone were monitored carefully using a non contact temperature instrument. The temp drop was ensured to happen gradually. As titanium carbide forms in the temperature of 850°C, provided adequate duration was given, the weld area was sustained at this temperature for nearly 1.5 hours after the completion of welding to promote the formation of titanium carbide.

CONCLUSIONS

- In stabilized austenitic stainless steels failures due to stress, corrosive media etc. should also be looked into and measures to avoid, minimize the deleterious effects should be studied and implemented.
- The precautions during the cooling down of the weld, should be observed carefully so that sufficient carbon is tied with titanium leaving no scope for the formation of chromium carbides.
- The possibility of ferrite phase formations in the weld were also looked into. Based on the base metal composition and from Schaeffler diagrams the amount of ferrite present was determi.ned to be in the range of 4 to 8 percent only which is much below the danger values of 10% and above. The possibility of sigma phase formation is also ruled out as the base metal contains only 18.5% chromium, which is less than the stipulated 20% for sigma phase formation.

The Reactor is working satisfactorily without any failure till date.

REFERENCES

1. P. F. Timmins : Solutions to hydrogen attack in steels, ASM INTERNATIONAL, The materials information society.
2. ASME SEC IX RULES of Construction of Pressure Vessels.
3. R. S. Parmar; Welding Engineering and Technology.