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"Research Note"

FAILURE ANALYSIS OF HP40-Nb MODIFIED PRIMARY REFORMER TUBE OF AMMONIA PLANT*

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Abstract – Micro-structural failure analysis of the heat resisting HP40 Nb modified alloy was studied by light and electron methods. Samples from the failed reformer furnace tube were cut and prepared for metallographic examination. Examination with electron microscope was carried out with secondary and backscattered electron detectors; x-ray analysis was conducted at the grain boundary areas. In tubes, which are filled with a supported nickel catalyst, methane reacts with steam, carbondioxide and oxygen into synthesis gas. The overall heat of reactions may be positive, zero, or negative, depending on the process conditions. The catalyst plays a key role in developing overheating in the tubes. The catalyst deactivation caused by feeding is heavier than that designed hydrocarbon. Using an unsuitably designed hydrocarbon causes a thin layer of carbon coating on the catalyst surface. Overheating due to catalyst poisoning caused creep failure. The presence of inter-granular voids in the microstructure of the failed tube seems to be the result of creep phenomenon.

Keywords – Ammonia plant, HP40 Nb modified steel tube, catalyst failure, creep

1. INTRODUCTION

Natural gas is the most important raw material for production of ammonia, methanol, hydrogen, carbon monoxide, and many other important products. In almost all cases it is converted catalytically by reaction with steam and/or oxygen-containing gas. The related technologies, such as the various versions and combinations of steam reforming and auto-thermal or secondary reforming are, thus, the key technologies in petrochemical and fertilizer industries today[1].

The heart of the hydrocarbon steam reforming process in the production of ammonia is the tubular primary reformer, where the hydrocarbon feed reacts with the steam to produce synthesis gas in catalyst-packed tubes. The main reactions in the primary reformer are:

The steam reforming of higher hydrocarbons $C_nH_{2n+2}+nH_2O \rightarrow nCO+(2n+1)H_2, \quad \Delta H\rangle 0$

The steam reforming of methane $CH_4+H_2O \rightarrow CO+3H_2, \qquad \Delta H\rangle 0$

The water gas shift reaction $CO+H_2O \rightarrow CO_2+H_2, \qquad \Delta H\langle 0$

The process is highly endothermic [2].

The reformer tubes are usually subjected to carbonization, oxidation, overheating, and stress corrosion cracking (SCC), sulfidation and thermal cycling during their application. Previously stainless steel 304, 310, 347 were used as tube materials, however, these materials developed cracks that very frequently led to premature tube failure. In the mid-60s, the HK40 (25Cr/20Ni) alloy was developed and proved to be a good material for vertical reformer tubes [3].

In the 80s, HP(25Cr/35Ni) modified alloys were developed by using certain metals such as molybdenum, niobium, tungsten, titanium.

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2. MATERIALS AND EXPERIMENTS

A failure occurred in a primary reformer tube of Razi petrochemical complex after 12350 hours of its operation. The tube and all of the catalyst were replaced. From the failed part of the tube, many test samples were made for tensile, impact and compositional analysis. The tensile and impact test preformed according to the ASTM-E8 and ASTM-E23-28, respectively. The results are shown in Table 1.

Table 1. Properties of in service and as cast material

Material	UTS (MPa)	0.2%Proof stress (MPa)	El%	Charpy impact energy(kgf cm)	Hardness HV(30)
In service	392	208	4.58	4.45	153
As cast*	450	250	8.00	-	-

* Heat resistant alloy for hydrocarbon processing, technical papers, MANIOR Industries

3. MICROSTRUCTURE

The microstructure was examined using optical and scanning electron microscopes. The phases observed were analyzed using an energy dispersive x-ray analyzer system (EDX) in conjunction with a SEM. The structure consisted of massive primary carbides in an austenitic matrix; in addition, fine secondary carbides were precipitated within the austenite grain upon exposure to elevated temperatures. In serviced material which was removed from the damaged part of the tube, the temperature was high, the number of secondary carbides were reduced, and the interdendritic carbides had undergone significant agglomeration and coarsening [4].

Figure 1 shows the SEM microstructure of the damaged material. The figure shows niobium and chromium rich carbides in the grain boundary in the damaged part of the tube. Grain boundary voids are shown in the optical microstructure. Appearance of the void indicates the occurrence of creep and grain boundary deformation phenomenon in the tube [5]. The various phases were analyzed (Fig. 1).

4. CATALYST AND CAUSES OF FAILURE

It seems that catalyst plays key role for developing several forms of overheating in the tubes. Several typical forms of overheated tubes are shown in Fig. 2 [6].

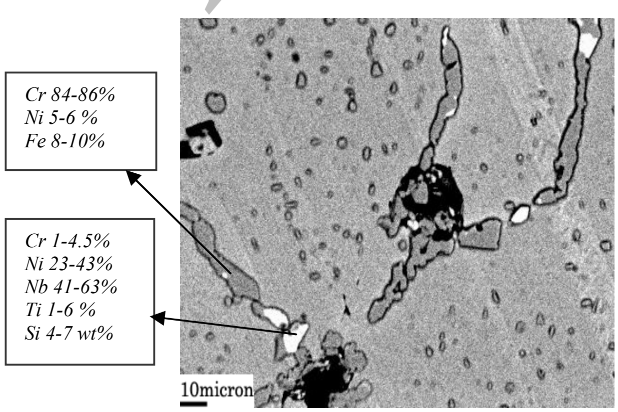

Fig. 1. Back scatter SEM photo of dominant phases in grain boundary. Dark phase is chromium rich carbides, light phase is niobium rich carbides

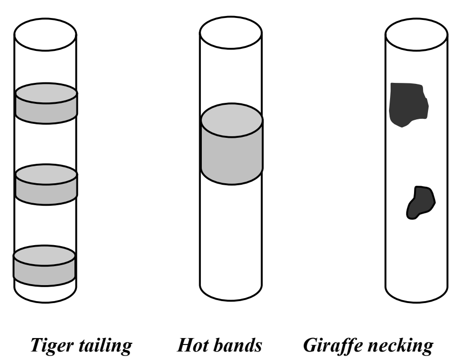

Fig. 2. Forms of overheated tubes [6]

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5. DISCUSSION AND CONCLUSIONS

The periodic reports of the company with the data in Table 2 is shown.

Table 2. Periodic reports of the company data

conditions	Pressure drop(psi)	Ave. temp. ^{o}C	CH4 slip%*	Max. tube temp. ^{o}C
Seven months before the failure	51.6	895	9.8	925
Eight months after replacement of tube and catalyst	36.7	850	11.2	885

* Methane slip is equilibrium concentration of methane at the reformer outlet

The number of shutdowns in one year was 25, and on several occasions, the hydrogen compressor had failed and very bad quality gas was fed into the reformer. Before the failure, "Giraffe Necking" signs were seen; after the failure, carbonated and crushed pellets were observed. By comparison of the two pressure drop (before failure and after replacement of tube and catalyst) and with respect to the tube appearance and presented microstructures, it is concluded that:

1. As the content of the reports before the failure show, heavier than designed hydrocarbon was fed to the reformer. This heavier hydrocarbon was not compatible with the catalyst, and carbon formation occurred.
2. In extra shutdowns, during warming up of the reformer, the tubes expanded and the catalyst, which expands less than the tube wall, settled down in the tube. During subsequent partial or full reformer cooling, the tubes contraction resulted in crushing of these catalyst pellets.
3. Catalyst break up, which was induced by extra shut downs and improper catalyst charging, resulted in an increase in pressure drop.
4. Due to carbon formation and chocking, there was no consumption of heat flux and therefore, local overheating occurs which finally caused creep and failure of the tubes.

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