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EFFECT OF SOLUTION ANNEALING ON PROPERTIES OF USED REFORMER CENTRIFUGALLY CASTED TUBES PRIOR TO REPAIR BY WELDING

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Preliminary Note – Prethodno priopćenje

The specimens of damaged tubes, ASTM A297 HK 40, are repaired by welding. Before repairing, solution annealing is used as a procedure for properties restitution. This paper explores the influence of used solution annealing procedure (1 050 °C / 2h) on mechanical and micro-structural properties. The emphasis is put on specific procedures at repair by welding.

Key words: solution annealing, repair by welding, tubes, mechanical proporties, structural properties

INTRODUCTION

Reformer catalyst tubes used by the petrochemical industry for fired heaters are commonly manufactured from high strength, creep, and corrosion resistant alloys. They are of relatively thick wall and usually produced by centrifugal casting (Figure 1). Their exploitation is limited by creep, driven by combination of internal pressure stress and through-wall thermal stresses generated by operational transients. Creep life exhaustion may happen by progressive grain boundary cavitation, depending on the microstructure of materials and exacerbated by micro-structural degradation processes, such as accompanied sigmatization.

Reformer tubes design is traditionally based on pressure stresses, conservative outside wall temperatures and factored lower bound material rupture lives, according to API-calculation formula [1-3]. The main characteristics of these alloys at temperatures up to 1000 °C are: creep and oxidation resistance, ductility at high temperature, thermal fatigue resistance and weldability after aging.

Catalytic tubes are the most important parts of reformer furnaces in ammonia chemical plants. A steam reforming process converts hydrocarbons into mixtures of hydrogen, carbon monoxide, and carbon dioxide. This reaction proceeds at a temperature range 850--900 °C and under pressure of 3,0 - 3,5 MPa.

The wall thickness is as low as possible to reduce the weight and to keep the risk of developing longitudinal creep stresses.

Irrespective of the composition of the material, the cast structure of these alloys varies according to the cooling rates. The austenitic cast materials tend to have more columnar than ferrite structure, often in the range of 90 to 100 % columnar structure when the cooling is controlled. For reformer tubes, the ratio between columnar and equiaxed grains in structure of min. 50 % / 50 % is recommended.

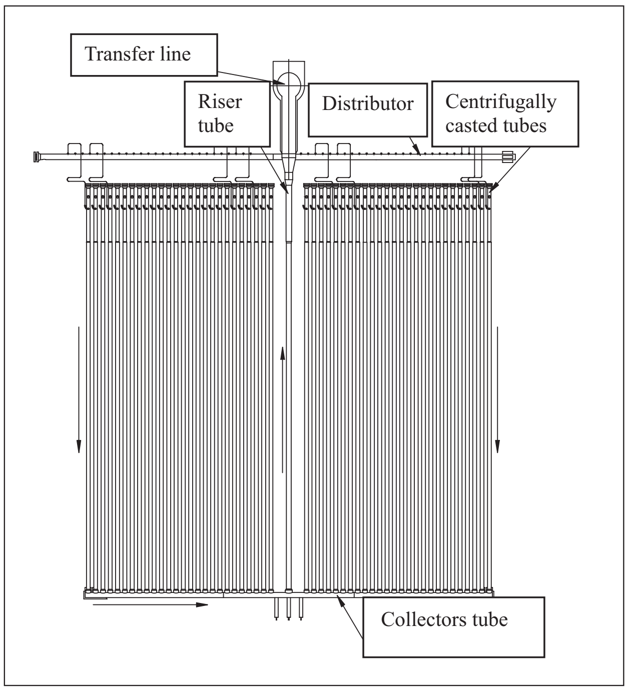

Figure 1 Reformer catalyst tubes register of 52 tubes

The foundry practices to cool the outer surface of the mould to arrest austenite structure, forms the nuclei and helps in the formation of the columnar grain by increasing the cooling rate in the direction of heat travel. A higher percentage of columnar structure is one of the important reasons for selecting a centrifugal cast material over wrought material for steam reformer tubes. The other factors that would influence the formation of

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Figure 2 WHAZ cracks propagation (magnific. 10 x)

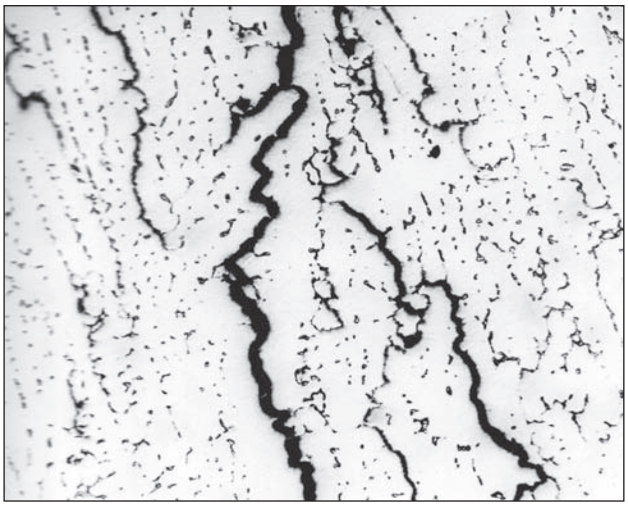

Figure 3 Middle area of fissures (magnific. 50 x)

columnar structure are the superheat temperature, mould rotation speed, and density of the fluid material [4-8].

MATERIALS AND EXPERIMENTS

After 50 000 work hours on temperature in range of 830 - 880 ºC, the tubes are inspected with eddy current method. Metallographic analysis of damaged tubes is performed on several examples with eddy current registered cracks. Evaluated damages are metallographically confirmed. Weld heat affected zone (WHAZ) crack propagation is shown on Figures 2 and 3.

The microstructure of reformer tubes (ASTM A297 HK40) is developed by “Glyceregia“ etching (HNO_3 + HCl + glycerol) [9].

Macrostructure is developed by etching in Adler’s reagent.

Properties restitution is performed in order to extend exploitation period prior to repair welding of tubes. Solution annealing procedure is conducted at a temperature of 1 050 ºC for 2 hours and cooled by compressed air.

RESULTS AND DISCUSSION

The Table 1 presents chemical analyses of samples Φ114, 58 / Φ71, 12 mm.

Table 1 **Chemical composition of tubes**

Tube material **ASTM A 297 HK 40**		Sample No. 1	Sample No. 2
Elements content, cwt / %	C	0,39	0,40
	Si	1,45	1,45
	Mn	1,30	1,32
	P	0,030	0,029
	S	0,028	0,028
	Cr	25,20	25,10
	Mo	0,43	0,43
	Ni	20,80	20,60

Mechanical properties of heat-treated and no heat-treated samples are presented in the Table 2.

Table 2 **Mechanical properties of no heat treated and heat treated tubes**

Tubes sample		Yield strength R_e / MPa	Tensile strength R_m / MPa	Elongat. δ_5/ %
1,1	No heat treatment	290	429	2,9
1,2		295	432	3,0
2,1		265	336	0,9
2,2		260	345	1,0
3,1		238	-	-
3,2		269	341	1,4
1,3	1 050 ºC / 2 hours	333	427	1,6
1,4		330	430	1,8
2,3		287	326	1,0
2,4		290	328	0,9
3,3		228	276	1,3
3,4		240	295	1,2

Table 3 **Hardness HV5 measurements on no heat treated and heat treated samples**

HV5	No heat treatment			Heat treatment 1 050 ºC / 2 h		
Sample No. Measuring	1,2	2,2	3,2	1,4	2,4	3,4
1	206	219	218	252	246	256
2	208	219	218	246	246	264
3	192	219	212	230	238	232
4	192	195	210	219	238	232
5	192	195	210	208	219	220
6	208	210	208	208	219	218
7	208	208	210	206	210	218
8	197	208	212	206	210	212
9	197	210	212	208	208	212
10	244	230	218	208	208	220
11	242	232	218	208	219	220
12	244	230	219	219	219	218
13	242	219	219	219	219	218
14	242	219	228	212	210	220
15	208	210	228	222	219	220
16	206	210	219	238	238	232
17	204	208	228	240	238	232
18	204	210	218	240	240	232
19	202	208	218	238	246	264
20	204	208	218	240	246	256

Table 3 reviews results of HV5 hardness measurements on no heat treated and heat treated samples on 20

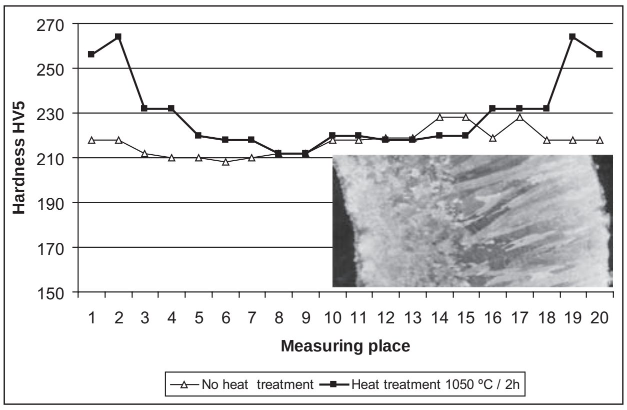

Figure 4 Diagrams of $\overline{X}$ measurements HV5

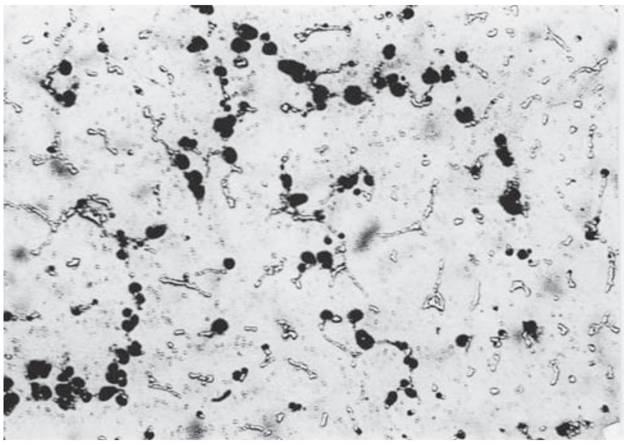

Figure 5 Microstructure in the middle of the tube thickness (magnific. 100 x)

measuring places of three samples. Figure 4 presents average HV5 values ($\overline{X}$) of performed measurements with tube macrostructure, as shown in the Table 3.

Structure is characteristic for centrifugally cast process, i.e. the 2/3 of outer side of tube thickness consists of columnar grains and the following 1/3 of thickness has equiaxed grains.

From the metallographic point of view, the state of material is classified in several stages. The presence of intermetallic phases, carbides, voids, and cracks is confirmed (Figures 5-7). The fissures propagate from inside

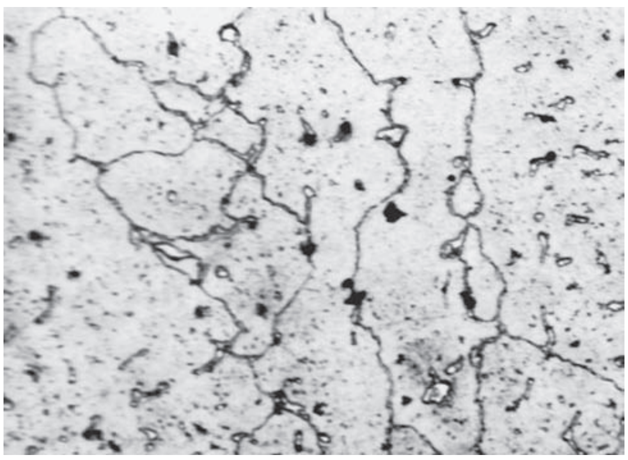

Figure 6 Microstructure of the gas heated tube outside (magnific. 100 x)

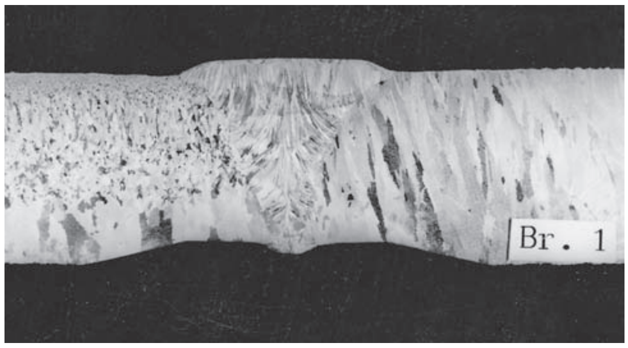

Figure 7 Macrostructure of repaired tube by welding

through equiaxed grains and end after entrance in columnar grain structure.

The analysed results of mechanical properties of solution-annealed samples are directed on unsatisfied grade of ductility**.**

Annealing temperature should be higher for min. 100 °C in order to solute carbides on grain boundaries and intermetallic phases, which will be suitable for materials ductility.

Hardness HV5 has higher values on tube thickness edges (outer because of oxidation and inside caused by carburization).

Despite of the mentioned facts, repair of solution annealed samples is successfully performed by GTA+SMA welding using (Figure 6) addition tube rotating device in flat position. ERNiCrMo-3 and ENiCrMo-3 filler metal are used. In intention to reduce hot fissures tendency of austenitic welds, heat energy input is limited on max. 1,6 kJ/mm. Root welds protection is performed with argon flow of 6 - 8 dm^3/min.

In making properly furnace tubes repair welds, the following factors have significant influence:

1. Tube wall soundness of aged reformer tubes determines the extent of stress rupture damage, oxidation and carburization:

Prior to repair welding by grinding or machining, oxidized and carburised layer must be removed at least 10 mm back from the edge of the weld. The layer is magnetic, while the unaffected matrix is nonmagnetic.

2. Effect of solution annealing in restoring ductility:

Alloys such as HK-40 and others have good as-cast ductility, but after exposure to furnace operating temperatures, there is dramatic loss in room temperature ductility.

HK-40 casting that has been in high temperature service requires solution annealing prior to repair welding, as heat affected zone cracks are expected.

3. Effect of filler metal selection on stress-rupture properties:

The difference in rupture strength between cast alloy and comparable composition welds increases along with increasing temperature.

Alternative to the usage of comparable composition is the usage of a nickel alloy welding product.

Suggested types, based on service temperatures, are shown in the Table 4.

Table 4 **Nickel alloy filler metal selection [6]**

Welding process	Tservice < 870 °C	Tservice ≥ 870 °C
SMA (AWSA5.11)	ENiCrFe-2	ENiCrMo-3
GMA and GTA (AWS A5.14)	ERNiCr- 3	ERNiCrMo-3 or ERNiCr-3

One should be cautious about usage of higher nickel alloy welds that contain over 50 % nickel, because they should not be used in sulphur containing environments over 800 °C. Before using nickel alloy products, presence of sulphur in mediums should be controlled.

4. Effect of the welding process and techniques:

In practice, it is most common to make the root pass by GTAW and to complete the joint by either SMAW or GTAW.

All repairs welding should be performed in flat position, which assures higher quality in production.

Buttering the face of bevel on a low ductility casting reduces the chance of cracking in the heat affected zone, particularly when nickel alloy filler is used. The weld metal has higher ductility and it is deposited under minimum restraint conditions. Buttered welds allow higher deposition rates and weld layer is able to absorb deformation better when butt weld solidifies. This technique may make the difference between success and failure when solution annealing is impossible.

Preheat is usually not used. If the section size is over 20 mm thick, the alloy may be preheated to 100…200 °C. Usually, no post weld heat treatment is required. Suggested interpass temperature is 120 °C on resolution- annealed castings, and 60 °C is suggested on used no-solution annealed castings.

The alloys are susceptible to crater cracking, so weld crater shall be carefully filled before extinguishing the arc.

Residual slag is very corrosive to the alloy at high temperatures.

All slags between passes and from the finished weld have to be removed with hammer and/or stainless steel wire brushes.

Penning of welds is controversial when the fill passes should be penned.

CONCLUSIONS

Metallographic analysis of damaged tubes was performed on one example with eddy current registered cracks. The registered cracks were evaluated and presence of irregularities (intermetallic phases, carbides, voids, and cracks) was metallographically confirmed. The fissures propagate from inside through equiaxed grains and end after entrance in columnar grain structure.

Before repairing, properties of used tubes were restored by solution annealing. Results of testing pointed our necessity for solution annealing at higher temperatures in order to restore ductility of used tubes.

If solution annealing is impossible, buttering the bevels faces on a low ductility casting with nickel alloy filler reduced the possibility of cracking in the weld heat affected zone (WHAZ).

There are many factors that influence welds in properly performed furnace tubes repair. If correct procedures are followed, repair welding of high temperature reformer tubes will prolong their service life.

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