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Effect of QPQ Technology on Mechanical Properties and Corrosion Resistance of Petroleum Tubes

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Quench polish quench (QPQ) is a specialized type of nitrocarburizing case hardening that increases corrosion resistance. In recent years, QPQ technology has attracted the attention of other industries, such as piston rod, oil and other industries. The workpiece treated with QPQ has good abrasion resistance and high corrosion resistance. The surface of the oil pipe is prone to rust, which inevitably affects its performance in the well. Aiming at the problems in practical application, the test method was used to evaluate the corrosion resistance of the treated samples in the atmosphere. By using API standard tensile test and electrochemical corrosion test, the mechanical properties and corrosion resistance of N80 treated with QPQ were studied.

1. Introduction

The loss caused by equipment corrosion is very serious in China's oil industry every year, and the economic loss is about 2 Billion RMB (Yao, et al., 2017). In recent years, some oil fields began to use nitriding technology to deal with oil pipe, and the corrosion resistance of the oil pipe is improved (Zhang et al., 2017; Amyotte and Khan, 2016; Zhao et al., 2016). However, the corrosion resistance of nitriding tube is still not ideal. The mechanical properties cannot meet the standard requirements, and some oil pipe is fractured (Cajner et al., 2015; Vairo et al., 2017; Hansen and Kjellander, 2016). The tube fracture mainly happens on its thread and the location is only on the tail. Quench polish quench (QPQ) is a specialized type of nitrocarburizing case hardening that increases corrosion resistance. It is sometimes known by the brand name of Tufftride, Tenifer or Melonite (Fu et al., 2016). Three steps are involved: nitrocarburize, polish, and post-oxidize. The process starts with a standard salt bath nitrocarburizing cycle, which produces a layer of iron nitride (Lu et al., 2015). Next, the workpiece is mechanically polished; typical polishing processes include vibratory finishing, lapping, and centerless grinding. Finally, the workpiece is re-immersed into the salt quench bath for 20 to 30 minutes, rinsed, and oil dipped. This last step optimizes the corrosion resistance by creating a layer of iron oxide about 3 to 4 micrometers thick (Yang et al., 2016). It also gives the workpiece a black finish (Wang et al., 2014). Moreover, the QPQ technology has the advantages of no deformation, no pollution and energy saving. Therefore, it is called a revolutionary new technology in the field of metal technology. In this paper, the samples were treated with different processes, and the changes of mechanical properties such as yield strength, tensile strength and elongation and corrosion resistance was studied.
QPQ technology is actually a kind of salt bath composite treatment technology. Its main technology is salt bath nitriding or salt bath nitrocarburizing, which is evolved from salt bath nitriding technology. By titration, the active ingredient of cyanide and cyanate in salt bath sample can also be determined by quantitative chemical test. Consumption can be added according to the manufacturer's instructions. Because of its good wear resistance, high corrosion resistance, small deformation and high production efficiency, people are naturally concerned about the increasing equipment (Hebda et al., 2015). But in the deeper disaster, the salt bath nitriding in the lower part of the citrus disaster is poor. It is well known that oxygen in the air not only causes cyanide to form cyanate, but also plays a favorable role in the formation of nitrided layer. Therefore, the

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amount of air is adjusted according to the size of the pan. The lower part is sent to the salt bath in a precise way, which improves the nitriding effect (El-Sayed et al., 2015).

2. QPQ technology and preparation of experimental materials

Quench polish quench (QPQ) is a specialized type of nitrocarburizing case hardening that increases corrosion resistance. It is sometimes known by the brand name of Tufftride, Tenifer or Melonite. Three steps are involved: nitrocarburize, polish, and post-oxidize. After nitriding and oxidizing, a uniform and dense infiltration layer is formed on the surface of material, which can significantly improve corrosion resistance and wear resistance (Łabanowski, et al., 2015; Ong and Karim, 2017; Sanabria et al., 2017; Amyotte and Khan, 2016; Liu et al., 2016). At the same time, the technology uses pollution-free salt bath formula. It has the advantages of no pollution, small deformation and low energy consumption. In this paper, the most widely used N80 steel is considered as the research object.

2.1 Experimental materials and equipment

The preparation steps of electrochemical corrosion experiments are as follows: N80 seamless tubing produced by Angang is used as test material. The specifications are 15mm×3mm×20mm. The number is 6 / group × 6 group, a total of 36.

Method for preparing API standard tensile test sample: the wire cutting method is used to intercept QPQ treated and untreated N80 tubing. The number of each is 6, a total of 12 pieces.

Laboratory equipment includes: preheating furnace, external heating crucible furnace, the power is 25kW, and the temperature is 300-550 °C. Nitriding furnace, external heating crucible furnace, the power is 25kW, and the temperature is 450-650 °C. Oxidation furnace, external heat crucible furnace, the power is 25kW, and the temperature is 300-450 °C. Cleaning sinks and sumps, temperature control systems and wires.

The main instruments are: metallographic microscope: universal 4XC metallographic microscope. Microhardness tester: HX-100TM type microhardness tester. The load is 0-1000g. Electronic balance: the accuracy is 1/10000. Scanning electron microscope: JSM-6390LV scanning electron microscope. Universal tensile testing machine. Electrochemical workstation.

2.2 Experimental method

Parameter setting of API standard tensile test: tensile tests were performed on a universal tensile testing machine. Size B=19.1 mm, and thickness d=5.51 mm. The force loading speed is 5MPa/s, and the gauge distance is 50.8mm. The mechanical properties were calculated from tensile tensile data including yield strength, tensile strength and elongation.

Parameter setting of electrochemical corrosion experiment: electrochemical corrosion experiments were performed on PARSTART 4000 electrochemical workstation. When measuring the curve, the main parameters of the instrument are set as follows: initial potential (V): -0.3, final potential (V): 1.6, scan rate(mV/s):0.167.

The reference electrode used in the experiment is saturated KCl solution, that is, dry mercury electrode. The relative voltage is 0.2042V.

3. QPQ experimental results and discussion

3.1 The mechanical properties after QPQ treatment

The flow chart of the QPQ process is shown in Figure 1. The specific parameters of the QPQ process are: Wash with 80°C for 15 min, 380°C preheat 40min, 650 °C salt bath for 90 min, 380°C salt bath oxidation 40min, air cooled to 180 °C, then water-cooled and polished, 380 °C secondary oxidation 15min, water cooling. As shown in Figure 2, the untreated sample is yielded at point A. AB is the deformation hardening stage, BC is the necking stage. QPQ treatment sample is yield in DE section. EF segment is deformed hardening stage, and FG is necking stage. As can be seen from the curve of force and displacement, the displacement of the QPQ treated sample was about 1 mm, while the displacement in the untreated specimen was about 5 mm. The sample did not neck process, or necking is not obvious, and the fracture does not contain diffusion area. In addition, the crack propagation results in the surface rupture, and the loading force suddenly drops during the displacement process, such as point K in Figure 2. The effect of Ni, Cr-C and Cr-Ni on the surface is similar to that of the surface. The direct cause of the decrease in the surface elongation of the QPQ sample is also due to the presence of microcracks. The difference is that the microcracks on the surface of the QPQ specimen are sprouted by the loose layer during the stretching process (Dalibon, et al., 2016). Microcracks in the coating are caused by defects such as surface impurities and bubbles (Bellas, et al., 2016).

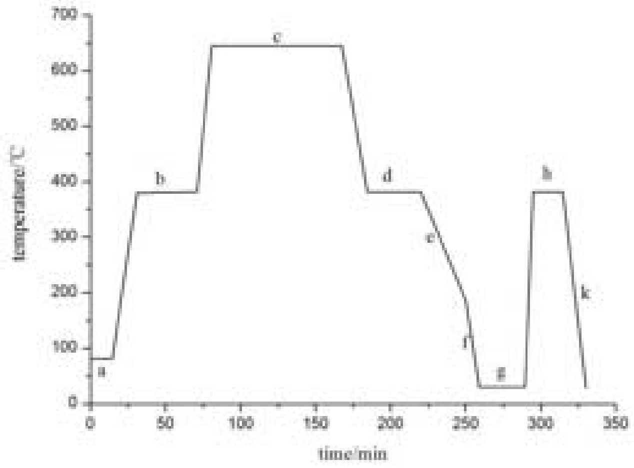


Figure 1: The flow chart of the QPQ process

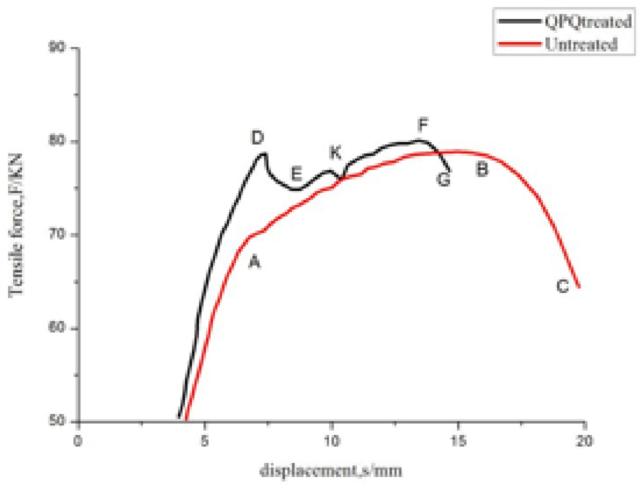
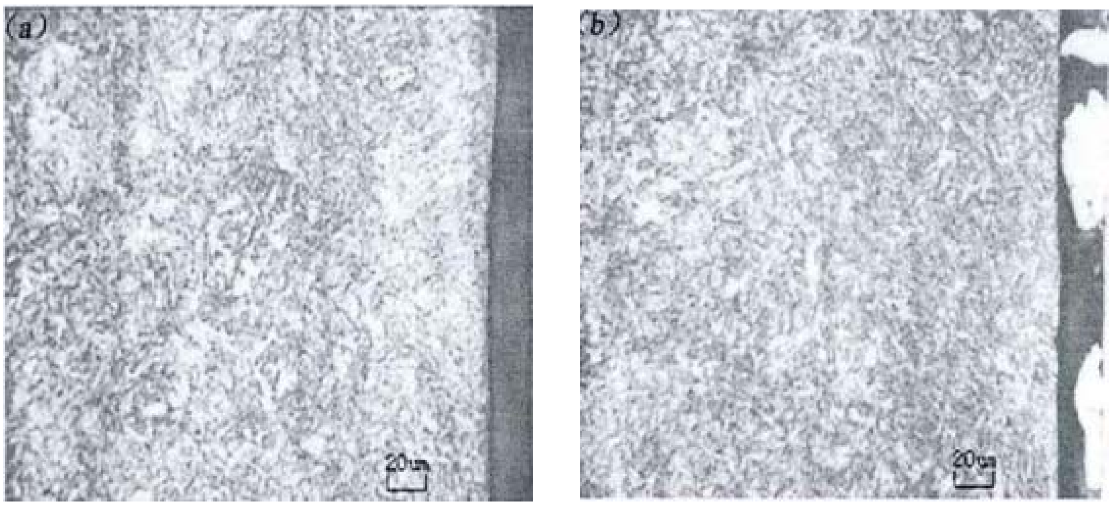


Figure 2: The force and displacement curve of N80 steel treated by QPQ

The average yield strength of QPQ treated samples is 708.5MPa, and the average tensile strength is 760.2MPa. The average yield strength of the untreated specimen is 699.5MPa, and the average tensile strength is 781.8MPa. The yield strength difference and the tensile strength difference of the two groups are not more than 35MPa. This indicates that the mechanical strength of the two sets of samples is comparable. The carbon and manganese contents of the materials are high, and the yield strength of the two sets of samples is close to the upper limit of the API standard. After QPQ treatment, N80 steel plastic deformation is significantly reduced, and the average elongation is decreased by 5%. The mechanical properties of the 6 sets of samples have changed (the strength is slightly improved and the plasticity is reduced), which still meets the mechanical performance requirements of the API.

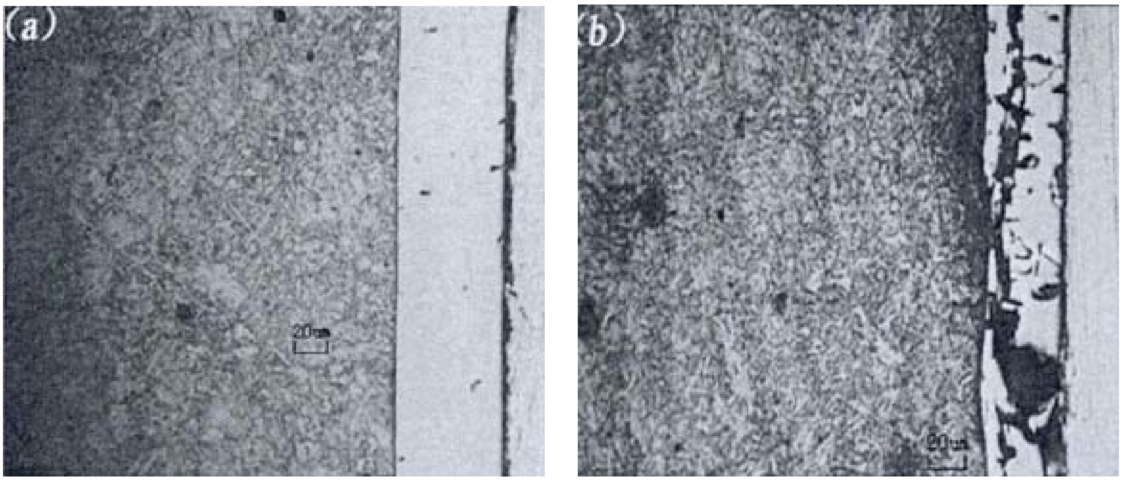
Table 1: Results of the tensile experiment

	API	Untreate						QPQtreaed					
Rt0.5/Mp	552~758	710	688	695	708	703	693	722	709	715	699	705	701
Rm/Mp	≥689	796	781	752	791	789	787	763	757	766	753	766	756
A50.8mm/%	≥14	19.5	21	19.5	21	20.5	22	17	14.5	17.5	15	15	14.5



(a) before electrochemical corrosion (b) after electrochemical corrosion

Figure 3: N80 steel galvanized film



(a) before electrochemical corrosion (b) after electrochemical corrosion

Figure 4: N80 steel chrome layer

3.2 The corrosion resistance after QPQ treatment

Due to its special service environment, oil piping is more demanding for corrosion resistance. In this paper, N80 steel was treated with chrome plating, galvanizing, gas nitriding, QPQ and salt bath, and the corrosion resistance of each process was evaluated comprehensively. The corrosion potential of N80 steel is high, which indicates that the corrosion rate of QPQ treatment is the fastest. The corrosion potential of N80 steel treated by QPQ is slightly higher than that of N80 steel treated by salt bath, and the corrosion rate is relatively small. This is because: (1) by polishing, the loose structure of the surface hole is removed. The ability of the surface to adsorb the charge ions in the electrolyte is weakened; (2) polish makes the surface smooth, and the corrosion area is small; (3) By secondary oxidation, the surface of the oxide film is denser. Electrolyte solution of the charge ions is more difficult to pass through the oxide film, and it is difficult to form corrosion circuit.

The sample was formed on the surface with uniform and dense $Fe_{(2-3)}N$ at a temperature of 530 °C. The electrochemical corrosion test data is good at the initial stage, and it shows a completely passive trend. However, after a brief passivation, corrosion increases abruptly as the voltage increases. This may be due to the infiltration layer is very thin, and it is only about 7μm. In the long-term corrosion or the high corrosive medium conditions, the infiltration layer is corroded, thus losing the protective effect. The electrochemical corrosion resistance of galvanized steel N80 is the worst. Surface galvanization cannot form a stable corrosion products, and the corrosion continues. Since zinc is more active than N80 steel substrate, corrosion rate is

faster than matrix corrosion. Chromium oxide is more stable and denser, so the chrome-plated electrochemical corrosion process is slower than galvanizing. As shown in Figure 3, galvanized N80 steel is based on the principle of anode protection. The galvanized layer with high surface potential does not form a stable passivation film, and the opposite part is dissolved, causing the N80 steel substrate to be exposed to the electrolyte, and the corrosion is accelerated.
As shown in Figure 4, the chrome-plated layer is similar to the galvanized layer, and there is also the phenomenon of electrochemical corrosion dissolution. However, under the same conditions, the chromium corrosion products are more stable than the corrosion products of the galvanized layer. Therefore, the corrosion potential is higher, and the polarization current in the polarization curve is also smaller.

4. Conclusions

By performing the API standard tensile test and electrochemical corrosion comparison experiment, the comprehensive performance of N80 steel treated by QPQ was studied. The main conclusions are as follows:
(1) The QPQ treatment of N80 steel still maintained the original mechanical strength. Although the elongation was decreased by 5%, and the plasticity was decreased significantly, the QPQ treatment technology of the mechanical performance indicators still meets the API requirements. The outermost layer of N80 tubing surface treated by QPQ is loose. When squeezed and stretched, it is prone to cracks, thereby reducing the strength and plasticity of the material. At the same time, the corrosion resistance of materials is reduced because of the layer is damaged. For parts that are subject to both load and corrosion conditions, QPQ process or appropriate polishing method was used to reduce the outer loose.
(2) Compared with untreated, gas nitriding, salt bath compound treatment, chrome and galvanized, the corrosion current density of N80 steel treated by QPQ technology is the smallest, and the impedance value is the largest. The chrome and galvanized N80 steel was dissolved. The corrosion products of the coating are more unstable, so the corrosion rate of the galvanized N80 steel is very fast. The compound layer is too thin, and about 3/4 is a loose layer, so it shows the passivation tendency in the low electrochemical corrosion environment. Once the corrosion voltage increases or the corrosion time is prolonged, the passivation tendency disappears and the protection is lost.
(3) After electrochemical corrosion test, the N80 steel treated by QPQ has been completely passivated. It has a high corrosion resistance. According to this process, we can deal with similar material and oil equipment, and performed field experiments in oilfield environment to verify its applicability.

Reference

Amyotte P., Khan F., 2016, What do gas blows, iron dust accumulations and sulfidation corrosion have in common?, Chemical Engineering Transactions, 48, 739-744, DOI: 10.3303/CET1648124

Bellas, L., Castro, G., Mera, L., Mier, J.L., García, A., Varela, A., 2016, Effect of Carbonitriding in a Salt Bath by a QPQ Scheme on Stainless Steel 321 Microstructure and Service Properties. Metal Science and Heat Treatment, 58(5-6), 369-375.

Cajner, F., Kovačić, S., Rafael, H., Vugrinčić, A., Šimunović, V, Gržeta, B., 2015, Influence of nitriding on corrosion resistance of martensitic x17crni16□2 stainless steel. Materialwissenschaft Und Werkstofftechnik, 9999(9999), 69-77.

Dalibon, E.L., Brühl, S.P., Trava-Airoldi, V.J., Escalada, L., Simison, S.N., 2016, Hard dlc coating deposited over nitrided martensitic stainless steel: analysis of adhesion and corrosion resistance. Journal of Materials Research, 31(22), 3549-3556.

El-Sayed, A.R., Ibrahim, E.M.M., Mohran, H.S., Ismael, M., Shilkamy, A.S., 2015, Effect of indium alloying with lead on the mechanical properties and corrosion resistance of lead-indium alloys in sulfuric acid solution. Metallurgical and Materials Transactions A, 46, 5, 1995-2006.

Fu H., Zhang J., Huang J., Lian Y., Zhang C., 2016, Effect of Temperature on Microstructure, Corrosion Resistance, and Toughness of Salt Bath Nitrided Tool Steel. Journal of Materials Engineering and Performance, 25(1), 3-8.

Hansen O., Kjellander M., 2016, Potential for major explosions from crude oil pipeline releases in varied terrain, Chemical Engineering Transactions, 48, 439-444, DOI: 10.3303/CET1648074

Hebda, M., Debecka, H., & Kazior, J., 2015, Influence of silicon addition on the mechanical properties and corrosion resistance of low-alloy steel. Bulletin of Materials Science, 38, 7, 1-6.

Łabanowski, Jerzy, Świerczyńska, Aleksandra, Topolska, S., 2015, Effect of microstructure on mechanical properties and corrosion resistance of 2205 duplex stainless steel. Polish Maritime Research, 21, 4, 108-112.

Liu Y.X., Wang R.T., Chao M.W., Zhang L.J., 2016, Numerical simulation study on erosive wear of esp, Chemical Engineering Transactions, 55, 127-132, DOI: 10.3303/CET1655022

Lu J.W., Wang Q.Y., Zheng B., 2015, Influence of qpq salt bath composite processing on microstructure and property of a certain type aviation piston engine ring. Applied Mechanics & Materials, 751, 26-29.

Ong C.C., Karim K.A., 2017, Inhibitory effect of red onion skin extract on the corrosion of mild steel in acidic medium, Chemical Engineering Transactions, 56, 913-918, DOI: 10.3303/CET1756153

Sanabria CJ., Laverde Catano D., Pena D.Y., Merchan-Arenas D., 2017, Influence of temperature and time on the corrosion by sulfidation of aisi-316 steel exposed under transfer line, Chemical Engineering Transactions, 57, 715-720, DOI: 10.3303/CET1757120

Vairo T., Magrì S., Qualgliati M., Reverberi A.P., Fabiano B., 2017, An oil pipeline catastrophic failure: accident scenario modelling and emergency response development, Chemical Engineering Transactions, 57, 373-378, DOI: 10.3303/CET1757063

Wang X., Wu C.Y., Sun M.L., Xie C.S., 2014, Effect of nitrocarburizing temperature during QPQ treatment on microstructure and properties of 45 steel. Heat Treatment of Metals, 8, 031.

Yang, W.J., Zhang, M., Zhao, Y.H., Shen, M.L., Lei, H., Xu, L., 2016, Enhancement of mechanical property and corrosion resistance of 316 l stainless steels by low temperature arc plasma nitriding. Surface & Coatings Technology, 298, 64-72.

Yao Q.T., Tong W.P., Li M.Y., Zhang G.L., 2017, Neutral Molten Salt-Bath Carburizing of Ti6Al4V Alloy with Nanocrystalline Surface Layer at Low Temperature Assisted by Surface Mechanical Attrition Treatment. Key Engineering Materials, 727.

Zhang S., Li H.J., Wang L., Liu D.Z., Ping E.S., Zou P., Ma T.L., Li N., 2016, New pyrazine derivatives as efficient inhibitors on mild steel corrosion in hydrochloric medium, Chemical Engineering Transactions, 55, 289-294, DOI: 10.3303/CET1655049

Zhang L., Ren C., Yu Q., Zhang,J., Sun S., Ren Q., Gao W., 2017, Microstructure and properties of 1Cr12Ni2WMoVNb (GX-8) steel bored barrels with and without QPQ treatment. Surface and Coatings Technology, 315, 95-104.

Zhao X.G., Zhou Y., Zhao J.Y., Zhan G., Yang P., 2016, Safety prediction of soleplate corrosion state in petroleum storage tank based on grey theory model, Chemical Engineering Transactions, 51, 271-276, DOI: 10.3303/CET1651046.