Research on cold work hardening and heat treatment problems of waveform expansion joint for austenitic stainless steel

ERGENG ZHANG*, ZEMING FU, ZHIWEN WANG[a]
School of Mechanical Engineering, Shanghai Institute of Technology, Shanghai, P.R. China
[a]*School of Mechanical and Automation Engineering, East China University of Science and Technology, Shanghai of China*

Based on an explosion case of stainless steel waveform expansion joint happened from wet H2S stress corrosion cracking, this article carries out analysis that the accident caused by the brittle fracture of low stress is closely related to cold-work hardening of austenitic stainless steel and massive deformation martensite. And it also suggests that the solid solution treatment to austenitic stainless steel will be favorable to mitigation of stress corrosion cracking occurrence and reduction in stress corrosion crack growth rate, then the modification suggestion to related regulations was given.

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Austenitic stainless steel because of its excellent corrosion resistance and cold performance is widely used in pressure vessels and pipes, in many cases it is to become the first choice of wave expansion joint material. But its strong cold hardening behavior is often ignored, this tendency of the stress corrosion cases will lead to appear faster stress corrosion cracking [1-6], or even serious consequences. So when austenitic stainless steel faces stress corrosion environment, how to consider the influence of processing sclerosis is a very important research topic.

1. Analysis on the accident of stress corrosion cracking of waveform expansion joint for austenitic stainless steel

A set of ammonia synthesis device with Ø 600 pipeline, by 16 MnR rolling and one of the six waveform expansion joint chooses 304 stainless steel. This expansion joint is completely manufactured according to the standard of GBl6749-1997 “pressure vessel waveform expansion joint”.

The maximum working pressure for 2.17 MPa, the operation temperature of 240 ^{o}C and the nominal thickness of 10 mm is for the wave expansion joint. Shift gas contains 100 mg/m^3 of H_2S and saturated vapour. After six months of installation and operation, the explosion occurred unexpectedly without any overpressure cases. The explosion was happened in a wave of ring to section, and no signs of overall plastic deformation is found at the explosion of the expansion joint.

The explosion of wave section has 7 cracks varying in size, all of which began in the wall of the surface crack. And the longest crack of 150 mm, depth of wall thickness of 0.94, and the remaining wall thickness of 0.4 mm are found inside. Such explosion formed the shear lip. The accident is caused by the largest crack, and the fracture of the radiation and person word lines are showed this point. As a result, it's a typical low stress brittle fracture explosion accidents.

Because the wave expansion joint worked in environment of higher concentrations of H_2S, total of 14 times operation and shutdown are happened in the half year's trial operation. Every shutdown time, the saturation steam in the gas phase will form the condensate, H_2S dissolved in water film becomes a wet H_2S environment. Sulfur content as corrosion products on the fracture reaches 9.13%, such austenitic stainless steel of 18-8 type as 304 etc. of will form the stress corrosion cracking in the wet H_2S environment.

Other waves are also found similar crack (but no explosion occurring). Sampling of the crack tip for metallographic analysis shows that the crack turns more twists and turns, basically belonging to wear crystal craze, with some branches in crack, see Fig. 1.

The crack surface (namely the fracture) is analyzed by scanning electron microscopy (SEM), it is seen there is a crystal cleavage fracture on the surface of crack, and not only the obvious tored ridge is on the fracture, but the obvious chicken claw grain is at the end of ridge (see Fig. 2). This is typical of hydrogen brittleness fracture, proving that wet H_2S stress corrosion cracking mechanism belongs to hydrogen induced cracking. Documents [7,8] have illuminated that after a strong cold work, austenitic stainless steel in H_2S environment is also likely to hydrogen brittleness.

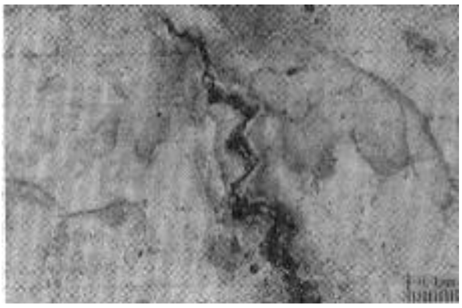


Fig. 1. Crack tip metallography (100×).

Fig. 2. Palmatum pattern of the fracture (200×).

The above is the typical case of the stress corrosion cracking happened at the wave expansion joint for austenitic stainless steel in the wet H_2S environment. Many stainless steel expansion joint leakage of failure happened in Oil refining and petrochemical enterprise in China actually, but their analysis are not enough, using the new for the old or the high alloy generation austenitic stainless steel material with nickel content of more than 22% upgrade to try to solve the above problem. In fact serious cold hardening has a close relationship with stress corrosion resistance ability declined obviously for the austenitic stainless steel.

2. Analysis on austenitic stainless steel manufacture sclerosis and deformation martensite

In the above example, expansion joint work-hardening is very obvious. Usually the hardness of solid solution state austenitic stainless steel is HB130-180, whereas the hardness of the expansion joint in the wave (minimum deformation in cold work) is HB228, and the hardness in the wave (the large deformation in cold forming) is up to HB453, the hardness of longitudinal seam in the wave has also reached HB377, so apparently manufacture deformation has greatly increased the material of hardness. All of the stress corrosion crack was focused on the expansion joint of the wave place, which is dangerous. Strong cold hardening for austenitic stainless steel is relevant to the grid slipping and dislocation, but it has a close relationship with forming a large number of deformation martensite organization [9]. Fig. 3 is the wave photos of the mother material metallographic. Photos of the material have explained there is not an austenitic single-phase organization, 40% of flake and acicular martensites organization is found in or outside the wall. Because of this, the hardness of material can rise to HB453. At this time of magnetic material has become very obvious. Many literature briefly elaborated the stress corrosion after deformation and hardening for austenitic stainless steel becomes more sensitive [1].

(a) Peak metallography of the outer walls (100×)

(b) Peak inside wall at the metallographic (100×)

Fig. 3. A large number of deformation martensite appeared in the crest of the expansion joint material.

Wet H_2S stress corrosion cracking appeared not only in the process of cold hardening of expansion joint, but also in the process of 304 steel cold spin forming of the bottom sealing head in liquid phase mother material reported by the literature [10], containing more than 3% of H_2S, and the hardness of sealing head containing massive NH_3 and H_2O after molding manufacture is HB285 ~ 307. This is also the case of stress corrosion cracking occurred in 304 stainless steel processing sclerosis in wet H_2S environment. Another case is: the head top of a large oxygen chlorinated reactor spinning with 304 stainless steel cold forming in a chloralkali plant is used for many years, the outside wall in the corner of the head (cold spinning the max. deformation), because of the contact with chlorine, produces many of the bifurcation stress corrosion cracking.

3. Solid melting heat treatment experiments

18-8 type of austenitic stainless steel usually delivery as solid solution state. Solid solution treatment is over 1000 ^{o}C, which can make the alloy element, carbide and other separation phase to dissolve the austenitic organization. Through the chilling, we can keep the single austenitic organization at the normal temperature. So the austenitic organization is the semi-stable state. In the cold deformation process, martensite transformation produces, namely which appears to deformation write austenite, and emerge of a strong magnetic.

If hardened processing of the expansion joint sampling is repeated with the solid solution treatment, namely heated to 1050 ^{o}C, heat preservation for 2 hours, then cooled in water or air. The metallographic after solid solution treatment will resume single-phase austenitic organization (see Fig. 4), then the martensite organizations disappear completely, and the hardness is greatly reduced (see Table 1).

The difference of the impact toughness for another austenitic stainless steel before and after solid solution treatment is very big too, as shown in Table 2. From Table 2, the impact toughness data shows that deformation sclerosis have made austenitic stainless steel toughness reduced greatly and the corresponding brittle increased greatly, if such big brittle materials is used in the environment of H_2S corrosion, stress corrosion will increase greatly.

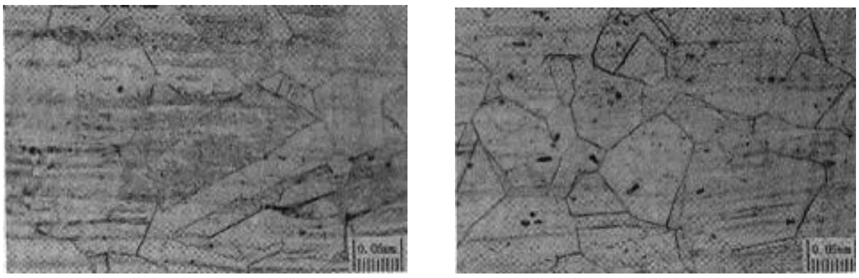
From the measurement data of Table l and Table 2, it can be seen that cold hardening cause the hardness of austenitic stainless steel increasing, impact toughness dropping, through the solid solution treatment, the hardness of the above material can be reduced, and toughness can be restored too. So to prevent or slow the stress corrosion cracking, any the austenitic stainless steel components after cold hardening, the solid solution treatment is needed, otherwise serious problems will occur easily.

Table 1. Comparison of hardness before and after the solution treatment.

Sample No.	Solution treatment			Hardness (HB)	
	Temperature (℃)	Holding time (h)	Cooling medium	Before the solution treatment	After solution treatment
1#	1050	2	Water-cooled	420~485	205~195
2#	1050	2	Air-cooled	295~390	125~130

Table 2. Impact toughness values before and after the solution treatment.

Sample No.	Impact energy Akv (J)	
	Before the solution treatment	After solution treatment
1#	89	263
2#	87	280
3#	84	257



(a) Water-cooled (200 ×) (b)Air-cooled (200 ×)

Fig. 4. Solid solution treatment to eliminate the deformation martensite after metallographic.

4. Recommendations on the specification of expansion joint

Such regulation in the 7.3.2 item of “pressure vessel expansion joint” (GBl6749-1997) [11] regarding: “the corrugated pipe for austenitic stainless steel after cold work forming does not need the heat treatment. The corrugated pipe for austenitic stainless steel after heat work forming should be solid solution treatment”. Obviously, this item considers of preventing intergranular corrosion from the above material. There is no regulation and explanation in the provisions for the stress corrosion happening apparently, many cold forming austenitic stainless steel components, wave expansion joint is one of the biggest cold deformation component. After forming, the hardness of this component is quite high, and toughness is quite low, and deformation martensite organization is massive, and it is quite dangerous in stress corrosion environment. Therefore the suggestion is that above standard be increased a paragraph of text: **“**When the presence of stress corrosion cracking possibility, austenitic stainless steel should be in solid solution treatment after cold forming”.

Not that solid solution treatment after cold forming can completely eliminate the possibility of stress corrosion, but can significantly retard stress corrosion cracking occurrence and reduce the stress corrosion crack growth rate, at the same time can avoid eventually occurs due to stress corrosion cracking in low stress brittle fracture. When the hardness of the material is reduced and toughness after recovery, will fundamentally change and only appear leak after penetrating the crack (leak before burst), without the occurrence of low stress brittle fracture of the explosion. Solid solution treatment of the fundamental purpose is to.

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*Corresponding author: ergengzhang@163.com