CORROSION OF COPPER PIPES JOINTS IN SIMULATED OPERATING CONDITIONS

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Resume

Joining of copper pipes used for liquid media transport are made as demountable and fixation joints. This work deals with corrosion behavior of the joints made by soft soldering, hard soldering and fitting. Corrosion properties of the joints were studied after 11 month exposition in conditions simulated the operating environment. The experiment was made in the 3% NaCl solution, at temperature 20° C for 16 hours and at 80° C for 8 hours per day, the solution was flowing 8 hours by the average rate 0,27 m.s⁻¹. Evaluation of the joints corrosion attacks was made visually, by light and electron microscopy with chemical analyses of corrosion products..

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1. Introduction

Copper pipes are used for gas and liquid various media distribution in industrial branches. They are used for the reason of very good corrosion resistance and high durability of copper [1-3]. The corrosion products in aqueous environments at ambient temperature (predominantly Cu_2O) are responsible for corrosion protection. This film is adherent and follows parabolic growth kinetic [4]. For the corrosion reaction the copper ions and electrons must migrate throug the Cu₂O film. According to authors [5,6] the corrosion products in aqueous environment with chlorides are created by copper oxides and traces of the $Cu_2(OH)_3Cl$. The chemical composition of corrosion products are changed in the scale of the pH from 5 to 14 (Cu/Cu₂O/CuCl₂/CuO/Cu₂(OH)₃Cl). In the acid

region is stable the $Cu_2(OH)_3Cl$ and in the alkaline the CuO [7-9].

Because of differences in device geometry of distribution lines, copper pipes must be bent in certain locations or connected to another circuit. It can brings changes in corrosion behaviour of tube systems. At present time mainly three types of joints are applied to copper pipes. They are the permanent joints made by soft or hard soldering and the joints formed by pressing with plastic ring which creates a jointing between the copper pipes (the fitting). The joints in copper pipes comprise inhomogeneity, which influence e.g. media flow, sedimentation of corrosion products and thus the corrosion process. The goal of the work was to study a synergetic effect of mechanical and chemical loading on metal pipes joints to their corrosion behavior. The corrosion damage was evaluated visually and by light and electron microscopy.

2. Experiment

Corrosion behavior of the copper pipes joints was verified by a long-term experiment. The experimental conditions simulated real conditions in an operation service. During a day marginally conditions (temperature 80 °C, flowing) were set because even their short-term activity can influence corrosion processes.

2.1. Experimental equipment

For the experiment it was made the equipment of technical copper $(99.5\% \pm 0.5\%)$ Cu) in which three types of permanent joints [1, 10, 11] (soft and hard soldering and one type of the molded joint) were made (Fig. 1). Joints were formed under the conditions:



Fig. 1. The experimental cell with the marked joints and direction of corrosion medium flow

- Soft soldering (Fig. 1, area 2, 5, 11) was performed according to DIN 1707 solder L-SnCu3 (DIN EN 29453, S-Sn97Cu3) at 230°C.
- Hard soldering (Fig. 1, area 4, 6) was performed according to DIN 8513 (EN 1044) using flux and solder CP 203 a L – CuP6 at 730°C.
- 3. The fitting was created by pressing of Cu pipes with the polymers (Fig. 1, area 3, 9).

2.2 Experimental conditions

Experimental conditions were chosen to simulate operating conditions in practice. The experimetnal equipment was filled by the 3% sodium chlorid solution, 16 hours exposed at 20 \pm 2 °C without flow of the solution, 8 hours at 80 °C with flow of the solution by the rate of 0.27 m.s⁻¹, caused by electric pump and observed by flowmeter.

3. Results

The joints moulded by hard soldering were uniform and compared with the copper they did not shown any special corrosion behavior due to the influence of the corrosion environment. The better adhesion of corrosion products was observed in the crevice created by the joint against to the smooth areas of the copper pipes. The character of the corrosion products and the character of corrosion of the copper pipes apart from the joints are shown in the Fig. 2 and 3.

In the Fig 4, where the surface of the copper pipes after the experiment is shown, it is possible to see clearly also with naked eye (Fig. 4a). There is shown on the joint metallography (Fig 4b), that the joint was not affected. On the boundary copper – joint there are visible nuclei of the intergranual corrosion, which can be created due to the stresses on the phases boundaries (Fig 4c).

The joints prepared by the soft soldering differ from the copper pipes by the corrosion potential, because the solder consists of 97% of Sn with markedly different electrochemical properties (standard potential of Sn is -0,16 V and Cu is +0.35 V). The studied soft joint (metallographic evaluation is shown in the Fig 5c) was non-uniform in circuit and on some places it was missing. Although, tin has good corrosion properties and creates the stabile oxides SnO, SnO₂, in the pH range of 3.5 - 9, on the surface, [3,4]. In spite of the fact tin was

attacked by the pitting corrosion in the experimental conditions. The corrosion was caused by the presence of the chlorides, flowing and elevated temperature. The oxide layers were eroded by the flowing medium with solid particles of the corrosion products and presence of the chlorides. The elevated temperature created suitable conditions for the local attack. In the Fig 5 (a) it is shown the microstructure of the solder, the surface of the joint pitting is in Fig 5 (b) and the corrosion pits visible on the edge of the cut are in Fig 5 (c).



Fig. 2. Corrosion products on the surface of the copper pipes after the exposition in flowing solution



Fig. 3. Corrosion of the copper pipes after exposition in flowing solution



Fig 4. Character of the corrosion products on the hard soldering area (4a), character of the hard soldering joint (4b) and detail of the joint with marked locality of intergranular corrosion nucleus (area 6 from Fig 1)



Fig. 5. Microstructure of the solder (a), detail of the soft solder pitting (b), pits close to the cross cut (c)



Fig. 6. Corrosion products (a)and soft solder surface morphology after exposition (b)

The presence of the tin in the corrosion products shown in Fig. 6 a was confirmed by the EDAX analysis [12]. The presence of tin was not confirmed on the areas, where the corrosion products fallen of the copper pipe surface. The solder morphology after the corrosion attack was 3D documented, see Fig. 6b. Also the corrosion products on the copper pipes analysis of the joints, obtained during its evaluation by SEM, are the proof of the tin solder dissolving. Fitting joints were molded by the way shown on the Fig. 7a. This joint made a perfect wafer without any interlayer between the pipelines. It was visible on the corrosion behavior of the joint. After the cutting of the specimen exposed in described corrosion conditions, the corrosion products were uniform in whole surface and after the moving of the joint, the hidden area of Cu pipeline was unexploited, as it is shown on the arrowed place in the Fig. 7b.



Fig. 7. Design of the fitting (a) and the state after the exposition (b)

4. Conclusions

Joints molded by hard soldering were not attacked more intensively than basic material - technical copper. The crevices origin in the places of molding of these joints, where copper pipes join in rectangle.

Stagnation of operating medium in these crevices creates conditions for corrosion. Geometry of crevices can also cause changes in flowing of operating solution and so it can increase its mechanical effect.

Tin joint is attacked by pitting corrosion in medium containing chlorides. By actual dimensions of joint their stability was not endangered by decreases in mass. Empty places originated by soldering, that can create a crevice with different corrosion conditions in comparison with pipeline system, can become an exception.

Fitting joints formed by pressing plastic rings tighten excellently even in aggressive 3 % NaCl solution. They resist high temperature too and they present only a mechanical barrier. The hidden areas next to place of covering were evaluated after demounting of joint. Studied areas were in untouched state without any sign of corrosion or in-leak between joined pipes.

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