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FAILURES OF BRASS CONDENSER TUBES

LOMOVI KONDENZATORSKIH CEVI OD MESINGA

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Keywords
- condenser tubes
- brass
- stress corrosion cracking
- dezincification

Ključne reči
- kondenzatorske cevi
- mesing
- naponska korozija
- decinkacija

Abstract

Causes of failure of brass condenser tubes (CuZn28Sn1) in a thermal power plant in Serbia are analysed. Results of testing by Fourier transformed infrared spectroscopy (FTIR) have indicated the presence of ammonia and nitrogen compounds on fracture surfaces and on the inner surface of the tubes. These compounds are specific agents that cause stress corrosion cracking (SCC) in brass. Analysis of fracture surfaces using scanning electron microscopy (SEM) has shown the brittle transgranular fracture due to the occurrence of SCC. The resistance of brass condenser tubes to other types of corrosion, such as erosion, general and selective corrosion (dezincification) is also considered. Some procedures are proposed to reduce the risk of SCC in the brass condenser tubes.

Izvod

Analizirani su uzroci pojave loma kondenzatorskih cevi od mesinga CuZn28Sn1 u jednoj termoelektrani u Srbiji. Rezultati ispitivanja metodom Furijeove transformisane infracrvene spektroskopije (FTIR) ukazuju na prisustvo amonijačnih i azotnih jedinjenja na površini loma i na unutrašnjoj površini cevi. Ta jedinjenja su specifični agensi za pojavu naponske korozije mesinga. Analiza površine loma primenom skening elektronske mikroskopije (SEM) pokazala je prisustvo krtog transkistalnog loma nastalog usled pojave naponske korozije. Razmatrana je otpornost cevi od mesinga CuZn28Sn1 prema drugim vidovima korozije, kao što su eroziona, opšta i selektivna korozija (decinkacija). Predloženi su postupci za smanjenje rizika od pojave naponske korozije u kondenzatorskim cevima.

INTRODUCTION

After a general overhaul of a thermal power plant in Serbia in November 2014, failure of hundreds of brass condenser tubes occurred during the hydrostatic test. Also, it was noted that some backing plates had fallen off from the tubes before this test. Due to the flood in May 2014, the feed river water contained more organic and inorganic substances than usually. Before the overhaul, the thermal power plant block with brass condenser tubes was about six months out of exploitation. The failure of brass condenser tubes was also observed in previous years during overhauls, but in lesser quantity. The power plant has most condenser tubes made of brass CuZn28Sn1. Other tubes are made of a copper nickel alloy (CuNi90-10). Fracture is observed only in condenser tubes of brass CuZn28Sn1 (admiralty brass). Condenser tubes of brass CuNi90-10 were undamaged.

The aim of this study is to reveal the cause of failure of brass condenser tubes and propose appropriate procedures to prevent fracture of condenser tubes in the forthcoming period of the power plant operation.

EXPERIMENTAL RESEARCH

The chemical composition of brass condenser tubes is determined in the Copper Mill at Sevojno. The chemical composition is given in Table 1.

Table 1. Chemical composition of CuZn28Sn1 (mass %).

Sample	Cu	Zn	Sn	Sb	As
New tube	70.0	28.9	1.00	0.001	0.035
Undamaged tube	71.4	27.5	1.02	0.001	0.027
Fractured tube	71.6	27.4	0.98	0.001	0.027

Tensile characteristics of brass condenser tubes are determined in the Copper Mill, Sevojno, and are listed in Table 2 ($R_{p0.2}$–yield strength; R_m–ultimate tensile stress; A–elongation). Grain size was also determined in the Copper Mill, in accordance with standards ISO 643 and ASTM E112. The grain size was found to be G9-G10, which means 4000 to 8000 grains per 1 mm^2.

Fractured surfaces of the brass condenser tubes are examined using SEM. The chemical composition of deposits on the fractured surfaces in the inner side of tubes and in the vicinity of the fractured location are determined by FTIR.

Table 2. Tensile characteristics of CuZn28Sn1.

Sample	$R_{p0.2}$ (MPa)	R_m (MPa)	A (%)
New tube	218	425	57
Undamaged tube	197	403	62
Fractured tube	200	408	46

Data on cooling water that flowed through the brass condenser tubes, i.e. conductivity (λ), pH value and chemical composition of the water, are obtained from the technical personnel of the power plant.

RESULTS

Brass condenser tubes are mechanically joined to the backing plate of carbon steel. The cooling water (roughly filtered river water) flows through the tubes, while the hot steam flows around the tubes. It was noted that the failure of the brass condenser tubes occurred in the region of ~ 4-5 mm from the joining place with the backing plate (Fig. 1).

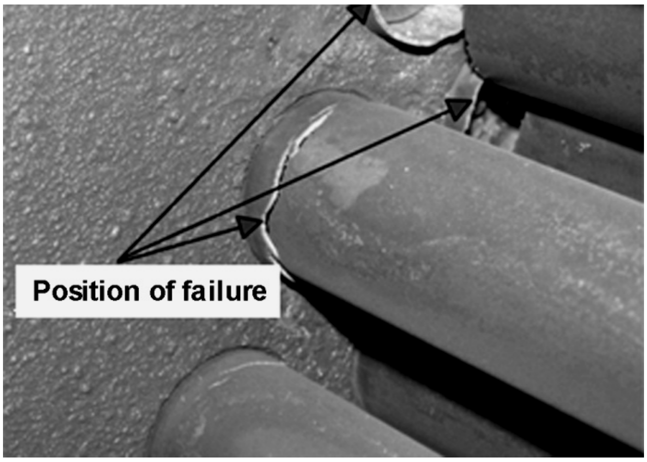

Figure 1. Failure of brass condenser tubes near joining location with backing plate.

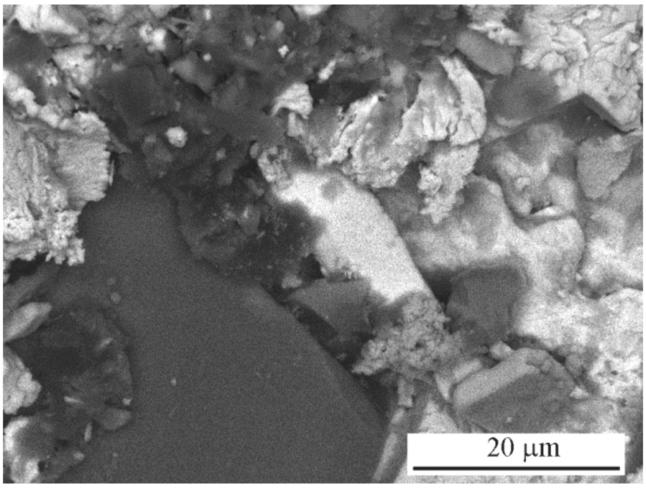

Figure 2. SEM micrograph of deposits on fractured surface.

Organic and inorganic deposits are present on the inner side of brass condenser tubes, in the vicinity of fracture, as well as on fractured surfaces. Figure 2 shows the SEM micrograph of the deposit on the fractured surface. FTIR analysis of the deposits on the tube inner side in the vicinity of fracture shows that deposits contain ammonia and nitrate compounds (Fig. 3). Ammonia and nitrate compounds are the specific agents that cause stress corrosion cracking (SCC) of brass. The results of FTIR analysis are direct evidence of the presence of compounds in condenser tubes. A SEM micrograph of the condenser tube fractured surface is shown in Fig. 4.

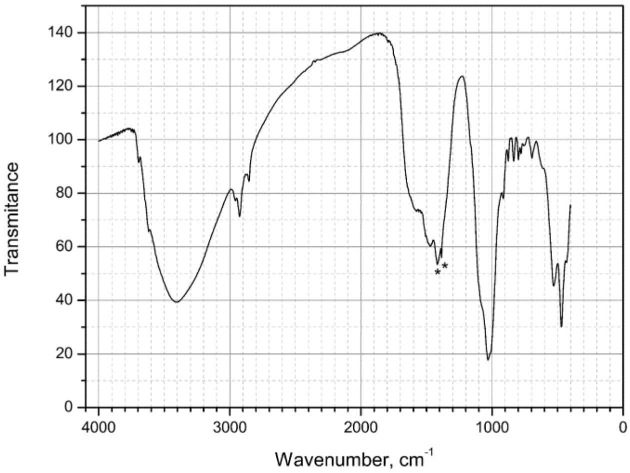

Figure 3. Results of FTIR analysis of deposits on inner side of condenser tube near fracture site. Wave-number peak at 1417 cm^{-1} corresponds to ammonia compounds, while wave-number peak of 1385 cm^{-1} corresponds to nitrate compounds.

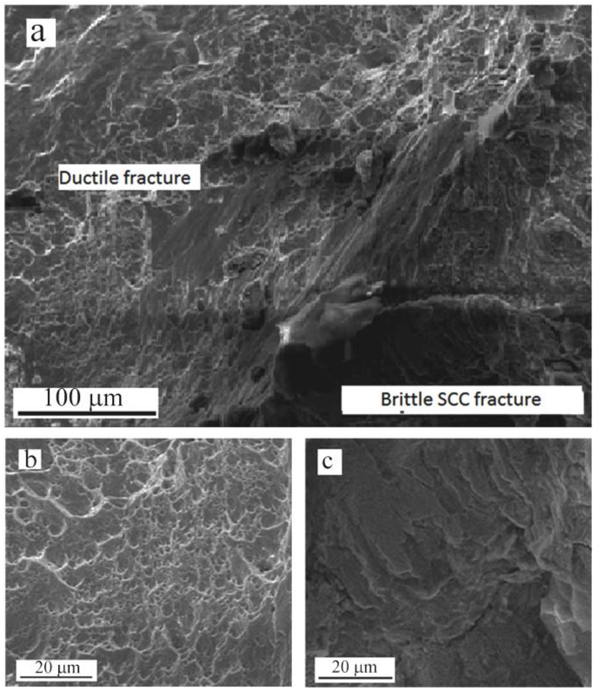

Figure 4. a) Fractured surface of brass condenser tube, b) ductile fracture is a result of mechanical action, c) brittle transgranular fracture is a result of SCC.

Chemical composition and mechanical properties (Tables 1 and 2) of brass condenser tubes are in accordance with prescribed values. Elongation of the test sample in the region of mechanical joining of the tube with the backing plate is slightly less than in other parts of the tube. Crystal grains in brass are very small (4000 to 8000 grains per mm^2) which is favourable in terms of mechanical properties and the resistance to SCC. The brass with smaller grain size shows greater resistance to SCC, /1-5/.

After the flood in May 2014, the pH value of the cooling water was within optimal values. However, the conductivity of the water was several times higher than permitted values, according to the report of technical personnel at the power plant. Data relating to the quality of the cooling water after the flood are presented in Table 3. Higher conductivity (λ) of the cooling water indicates the presence of various inorganic compounds such as ammonia, nitrate compounds, etc. Also, it can be seen in Table 3 that the concentration of SiO_2 is 5 times higher than allowed.

Table 3. Quality of cooling water, immediately after flood.

Sample	pH	λ (μS/cm)	SiO_2 (ppb)
Feed water	9.2	0.88	102
Fresh steam	9.2	0.72	11
Condensate	8.9	2.2	41
Permitted values	8.8-9.3	< 0.2	< 20

The flow rate of the cooling water through brass condenser tubes is determined indirectly. According to the technical personnel at the thermal power plant, the flow rate was within permitted limits. The permitted flow rate value of the cooling water through condenser tubes of brass CuZn28Sn1 is lower than the permitted value through the tubes made of CuNi90-10.

DISCUSSION

The failure of brass condenser tubes is caused by SCC. Brass CuZn28Sn1 is very susceptible to SCC /2, 5, 6/. Also there are residual stresses in the joining region of brass condenser tubes to backing plate (where the failure of tubes occurred). Results of FTIR analysis (Fig. 3) have shown that ammonia and other nitrogen compounds are present in the cooling water flowing through condenser tubes. These substances reached the condenser tubes from the river feed water. A significant increase in conductivity of river cooling water is observed (Table 3). During the flood in May 2014, river water has dissolved a certain amount of ammonia and other nitrogen compounds that are present e.g. in fertilizers and in the manure on the overflowed soil, which resulted in increased conductivity of river cooling water. Ammonia and nitrogen compounds could also have been formed due to the decomposition of organic compounds in condenser tube deposits, during several months of operating delay of the thermal power plant, after the May 2014 flood.

Heavier corrosion damages in thermal power plants are usually observed during the operating delay. During the delay it is not possible to remove oxygen from condenser tubes. In the presence of ammonia, moisture and oxygen SCC occurs and also other forms of corrosion, which can lead to a reduction in the wall thickness of condenser tubes. Due to the evaporation of water during the operating delay there is an increase in concentration of corrosive substances in condensers tubes. On the surface of the tubes below the deposits, corrosion of brass occurs according to the mechanism of differential aeration. In this way the aggressivity of the corrosive environment further increases.

For the occurrence of SCC, it is necessary that these following four requirements are fulfilled, /2/:
1. the metal/alloy is susceptible to SCC
2. tensile stresses (residual or applied) are present
3. a specific corrosive environment is present
4. required time, long enough for SCC occurrence.

If any of these conditions are not fulfilled, SCC will not occur, i.e. the condenser tubes will not fail. Several SCC mechanisms in brass and other copper alloys have been proposed, /7-9/.

Brass CuZn28Sn1 is susceptible to SCC. There are residual tensile stresses in the region of mechanical joining of the condenser tubes to the backing plate, ammonia and other nitrogen compounds are present in the cooling water, as well as oxygen and carbon dioxide from air. Ammonia and nitrogen compounds are specific corrosion agents for the SCC of copper alloys, /1-6/. Presence of oxygen and carbon dioxide in cooling water is not necessary for SCC occurrence in brass, but influences the growth rate of the stress corrosion crack, /2/. When a higher concentration of specific substances that cause SCC is present in the corrosive environment, a lower level of tensile stress is required for SCC. In the ammonia environment, SCC of brass CuZn28Sn1 takes place at a low level of tensile stresses, and vice versa; at a higher level of tensile stresses, SCC occurs in the presence of very low concentrations of specific substances, such as ammonia, /1/.

Data on the relative susceptibility of copper and some copper alloys to SCC in the presence of ammonia are presented in Table 4.

Table 4. Relative susceptibility of copper and copper alloys to SCC in the presence of ammonia, /4/.

Very low susceptibility	Chemical composition (mass %)
CuNi90-10	88.7Cu+10Ni+1.3Fe
CuNi70-30	66.5Cu+31Ni+1Zn+1Mn+0.5Fe
ETP Copper	99.90Cu+0.04 O
Low susceptibility	
DLP Copper	-
DHP Copper	99.90Cu+0.02P
Intermediate susceptibility	
Red brass	85Cu+15Zn
Commercial bronze	90Cu+10Zn
Aluminium bronze	91Cu+7Al+2Fe
Silicon bronze	97Cu+3Si
Phosphor bronze	95Cu+5Sn
Nickel silver	65Cu+25Zn+10Ni
High susceptibility	
Naval brass	60Cu+39.25Zn+0.75Sn
Admiralty brass	71Cu+28Zn+1Sn
Yellow brass	65Cu+35Zn
Manganese bronze	58.5Cu+39Zn+1.4Fe+1Sn+0.1Mn
Aluminium brass	77.5Cu+20.5Zn+2Al+0.1As
Muntz metal	60Cu+40Zn
Cartridge brass	70Cu+30Zn

It can be seen that the copper alloys with nickel are the most resistant to SCC. Brass CuZn28Sn1 belongs to the class of copper alloys with the lowest resistance to SCC in the presence of ammonia.

Brass CuZn28Sn1 is resistant to selective corrosion (dezincification), as it is alloyed with Sn and As, which inhibit the process of dezincification, /1/. Dezincification is a form of selective corrosion of brass with selective dissolution of zinc (as a less noble metal in the alloy). A porous layer of copper which has poor mechanical properties remains at the brass surface. Sn and As do not improve the brass resistance to SCC. A certain reduction in resistance of brass to SCC is observed in the presence of Sn and As, /1/. Stress corrosion cracking of copper alloys is studied in /10-14/.

Brass CuZn28Sn1 is also susceptible to general corrosion and erosion corrosion, /6/. In the wet ammonia environment, in the presence of oxygen, brass CuZn28Sn1 shows the highest rate of general corrosion, while copper nickel alloys show the lowest rate of general corrosion. The presence of fine sand particles in the river cooling water (Table 3, concentration of SiO_2 is up to 5 times higher than permitted concentration) adversely affects the brass resistance to erosion corrosion. The presence of sand reduces the value of critical flow rate at which the corrosion rate of brass rapidly increases.

During the operating delay of the power plant, there are suitable conditions for SCC occurrence in the unclean brass condenser tubes, in the region of residual tensile stresses (the region of mechanical joining of condenser tubes to the backing plate). Initial cracks are formed in the inner wall of the tubes. The cracks started to grow at low rate through the tube wall, so that a relatively long time is needed for the cracks to reach critical size, when fast mechanical fracture has occurred. This phenomenon has been observed in a large number (several hundred) of brass condenser tubes. The fractured surface of the brass condenser tube is presented in Fig. 4. It can be seen that brittle transgranular fracture is a result of SCC. SCC fracture is always brittle (intergranular or transgranular) regardless of the level of alloy plasticity (brass), /3/. The final mechanical fracture is ductile type fracture in alloys with a higher degree of plasticity, such as brass.

It is likely that stress corrosion cracks exist in a number of condenser tubes, although these tubes did not fracture. During power plant operation, the formed SCC cracks can continue to grow by a combined mechanism of SCC and corrosion fatigue. Considering that conditions for SCC occurrence are less severe (lower concentration of specific corrosive substances in the cooling water) during the operation of the power plant, the process of corrosion fatigue also contributes to crack growth. Corrosion fatigue occurs as a result of cyclic stress in condenser tubes, near the place of mechanical joining of condenser tubes to the backing plate, where residual tensile stresses exist. It can be expected that failure in a certain number of the brass condenser tubes will happen in the forthcoming period.

The risk of SCC in brass condenser tubes can be reduced if specific substances for the SCC occurrence in brass can be removed. By cleaning, rinsing and drying of the tubes immediately after the operating delay, the existing deposits in the tubes will be removed. After such treatment, the tubes should be clean and dry, free of organic and inorganic impurities. The time for SCC occurrence in the presence of specific substances can be minimized, after regular cleaning and drying of brass condenser tubes.

The probability of condenser tube failure due to SCC occurrence can be significantly reduced if the tubes of brass CuZn28Sn1 (which is very susceptible to SCC) are replaced with tubes of alloys with a significantly higher resistance to SCC, such as copper nickel alloys. These alloys are much more resistant to general and erosion corrosion than brass CuZn28Sn1. Copper nickel alloys are also resistant to selective corrosion.

Residual tensile stresses exist in the joining region of condenser tubes with backing plates. In practice, the elimination or lowering of residual stresses are most frequently applied to prevent the risk of SCC. If residual stresses in brass condenser tubes are eliminated, the risk of SCC occurrence in the tubes is significantly reduced.

CONCLUSIONS

Condenser tubes in the thermal power plant are made of brass CuZn28Sn1. This alloy is very susceptible to SCC in the presence of ammonia and other nitrogen compounds. In the joining region of condenser tubes to backing plates there are residual tensile stresses. During the floods in May 2014, there was an increase in the concentration of ammonia and other nitrogen compounds in the river cooling water flowing through the condenser tubes. FTIR analysis of the deposits on the inner side of the condenser tubes confirmed the presence of ammonia and other nitrogen compounds in the deposits. Due to the increased concentration of ammonia and other nitrogen compounds in the river cooling water a significant increase in the conductivity of the water was noticed.

Failure of brass condenser tubes occurred due to SCC, because the necessary conditions for the SCC occurrence were fulfilled. Fractographic (SEM) analysis shows that the fracture of brass condenser tubes is a brittle transgranular fracture caused by SCC, while the final mechanical fracture is ductile fracture. It is possible that SCC cracks exist in a certain number of brass condenser tubes, although the failure of these tubes has not occurred in the previous period. It can be expected that some of these condenser tubes will fracture during further operation of the thermal power plant.

The risk of SCC in brass condenser tubes can be reduced if specific substances responsible for SCC occurrence are removed, as much as possible. This can be achieved by cleaning and drying the tubes immediately after the operation delay of the power plant. After such treatment, the condenser tubes should be free of organic and inorganic impurities, and dry. This will extend the lifetime of existing and new condenser tubes made of brass CuZn28Sn1.

Another way to reduce the risk of SCC occurrence in condenser tubes is the replacement of existing tubes (made of brass CuZn28Sn1, very susceptible to SCC) with tubes made of alloys of greater resistance to SCC, such as copper nickel alloys. These alloys are much more resistant to general and erosion corrosion than the brass CuZn28Sn1. Copper nickel alloys are also resistant to selective corrosion. Service life of condenser tubes of these alloys will be significantly extended.

Residual tensile stresses exist near the joining location of condenser tubes to the backing plates. In practice, the risk of SCC occurrence is usually reduced by eliminating or lowering residual tensile stresses. If residual stresses in brass condenser tubes are removed, the risk of SCC occurrence in the tubes will be significantly reduced.

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