HYDROGEN EMBRITTLEMENT OF METALS IN THERMAL POWER STATION WATER-STEAM CIRCUITS

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ABSTRACT

This paper presents the basic results from examinations of metal components in thermal power station water-steam circuits experienced non-deformed fractures by hydrogen embrittlement (evaporating pipes, supercritical/high pressure boiler superheater pipes, nonheated piping bends involved in boiler circuit, live steam pipes, steam turbine components, feedwater heater components). A number of factors favouring hydrogen embrittlement of metals is established. An important part of oxide film condition in prevention of hydrogen embrittlement is demonstrated. The paper gives some recommendations for the avoidance of hydrogen embrittlement of metal components in thermal power station water-steam circuits.

KEYWORDS

Hydrogen embrittlement, boiler, evaporating pipe, superheater, steam pipe, turbine, heater.

STEAM BOILERS

The major factors favouring hydrogen embrittlement of steam boiler components are: cycling; wide application of thermal power stations with industrial steam extraction using industrial recycle condensates; feed water contamination with corrosive impurities; high local temperatures; tendency of modern boiler manufacture to furnace size reduction at the expense of rapid heat transfer (Vainman and Filimonov, 1980; Vainman, 1985).

Evaporating Pipes. External appearance of evaporating pipes experienced hydrogen embrittlement is presented in Fig. 1, metal structure and crack mode in the fracture region are presented in Fig. 2. Metal hydrogen charging (steel - 20 or 12 Cr 1 Mo V steel) usually runs in the localized areas of "vapor phase delaying". These are:
1. vertical pipes in the burner region with relatively clean inside surfaces exposed to strong

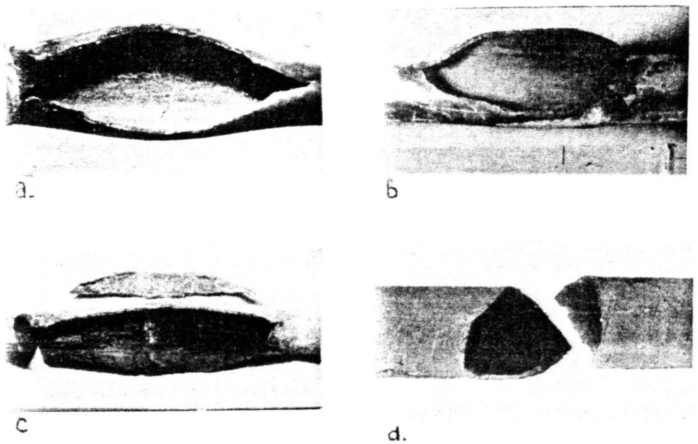

Fig.1 Typical fractures (external appearance) of 15,5 MPa boiler evaporating pipes exposed to hydrogen embrittlement; operation time: a – 12.000 hours; b – 19.000 hours; c – 22.000 hours; d – 46.000 hours.

heat flows, q;
2. similar pipes with porous inside deposits of low heat conduction hence "vapor phase delaying" is observed at the lower values of q;
3. inclined and bent pipes (bottom waterwall tubes, burner bypass pipes, etc.); vertical pipes in the economizer-evaporating pipe transition region (Vainman and Melehov, 1988; Vainman et al.,);

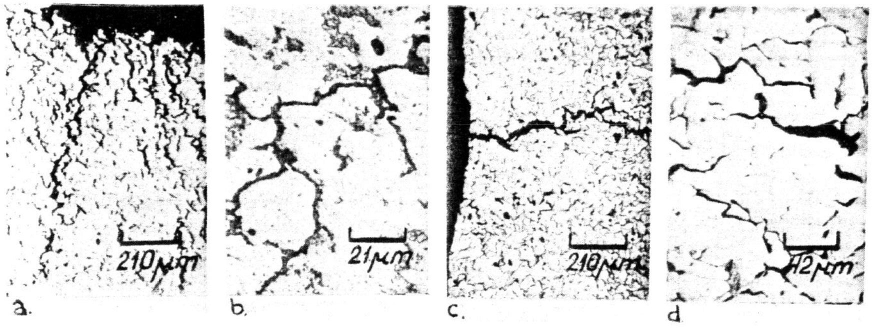

Fig.2 Crack propagation and metal structure in the hydrogen embrittlement region: a, b – the pipe is shown in Fig. 1, a; c, d – the pipe is shown in Fig. 1, b.

4. waterwall tubes severely attacked by burner flares; evaporating pipes exposed to furnace gases (with reductive conditions). Besides, the hydrogen embrittlement can occur both on the inside (i. i. 1, 2, 3) and on the outside (i. 4) of the pipes. The boiler water pH value lowering (pH < 7) at operating parameters results in the hydrogen embrittlement, in particular with the ingress of potentially acid organic compounds into the thermal power station feed circuit (inflows, make-up water, industrial recycle condensates). As a rule the potentially acid organic compounds fail to show its properties before entering the evaporating pipes but at increased temperatures in the evaporating pipes they decompose (thermolysis) with the formation of organic and mineral acids.

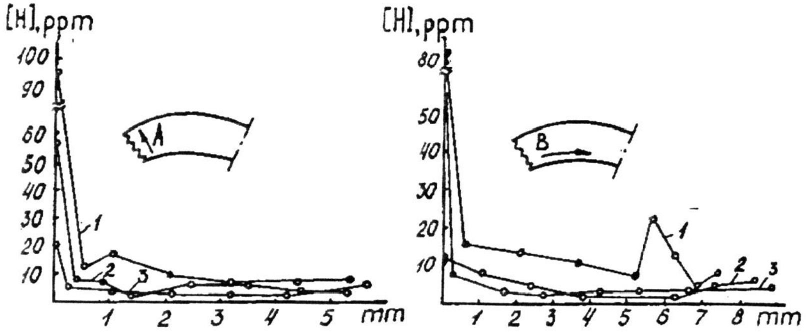

Fig. 3 Hydrogen distribution in metal of 14,0 – 16,0 MPa boiler evaporating pipes (1, 2, 3): A – in pipe wall thickness (near the area of fracture); B – in perimeter (on the inside of pipe)

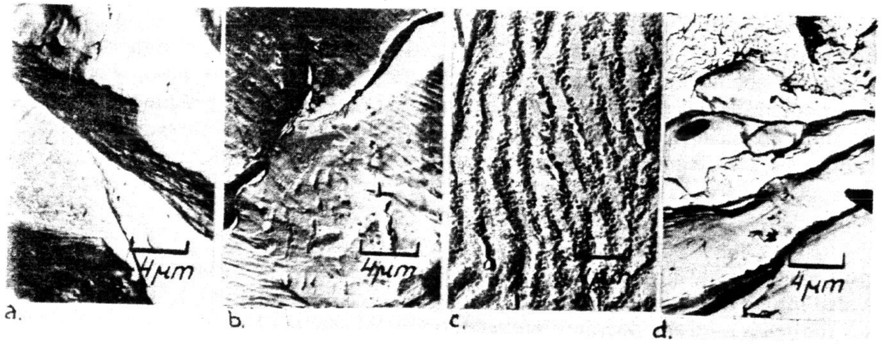

Fig. 4 Evaporating pipe fractography: a – area of intergranular crack (embrittlement region); b – area of pearlite grains (crack region); c – area of pearlite grains (region perpendicular to cementite platelets); d – mechanical failure region.

As a rule the pipe edges in the fracture region are blunt, torn and laminated, the pipe wall thinning is slight. Often and often two regions can be distinctly observed: the wide (50 - 90% of pipe wall thickness), rough and dark-coloured region of hydrogen embrittlement on the inside of the pipe and the smooth, light-coloured region of mechanical ductile failure on the

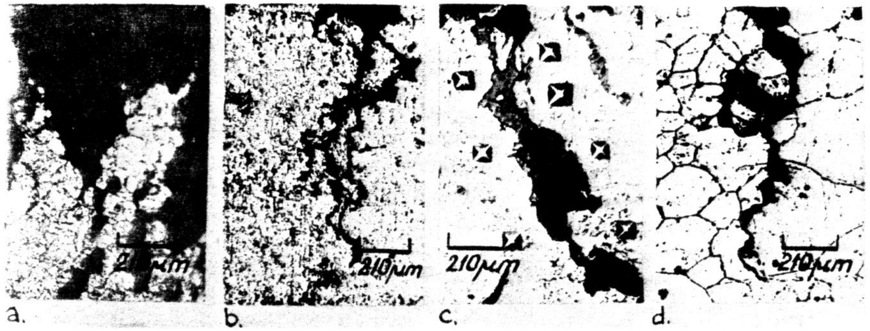

Fig. 5 Mode of pits (a) and cracks (b,c,d) on the inside of superheater pipes (a,b,c–12 Cr1 Mo V steel, d –12 Cr 18 Ni10 Ti steel)

for the superheater pipes of austenitic steel (1 Cr 18 Ni 12 Ti, 12 Cr 18 Ni 10 Ti, 12 Cr 18 Ni 12 Ti) in the fracture regions. Under gas corrosion the intensive hydrogen charging and embrittlement of metal (pearlitic and austenitic steels) can also occur on the outside of the superheater pipes, especially when firing liquid vanadium-and sulfur-containing fuels, and with incomplete combustion products in flue gases including hydrogen sulphide. Besides, the principal causes of damages of the protective oxide films on metal surface for the superheater pipes are: accelerated steam boiler cooling after its shutdown; shutdown boiler filling with relatively cold water by the non-cooled superheater pipes; downtime corrosion of the undrainable superheater coils, especially with acid organic compounds in steam condensate; thermal shocks in forcing out the condensate from the vertical (undrainable) superheater coils during starting up the steam boiler, and also at the ingress of boiler water into the superheaters; temperature variations of the flue gases and the superheater pipe metal at the steam boiler starting and cycling; unstable operation of the automatic injection vapor coolers, damage of their jackets or condensate injection pipes; scale growth at load operation. Hence it is necessary to take account of correlation of metal damage processes at all stages, i. e. steam boiler shutdown, downtime, starting up and load operation, with reference to hydrogen embrittlement and brittle fractures of the superheater pipes.

Steam Boiler Nonheated Pipe Bends. With reference to fracture mechanism the bends are divided into two categories:
1st. - the bends used at moderate temperatures - less than 673 K (water downcomer tubes, water-circulating tubes, vapor tubes - steel - 20); 2nd. - the bends used at creep temperatures - more than 773 K (steam-circulating tubes - 12 Cr 1 Mo V). The principal causes of fractures: for the 1st. category bends - corrosion fatigue and steel hydrogen charging (the fractures on the inside of the tubes, along a neutral); for the 2nd. category bends - development of creep cracks or creep - and corrosion cracks accompanied with steel hydrogen charging (the cracks on the outside of the tubes, tension region). The most active development of corrosion is observed along the bends neutrals on the inside of the tubes. The development of the 2nd. category bend corrosion is caused by wetting of the insulation containing the corrosive agents. The cracks along the 1st. category bends‘ neutrals differ from those ones at the 2nd. category bend damages by intergranular development, branching and by the presence of cavities, widenings, narrowings. Usually the hydrogen content of metal in the fracture regions of the bends is between 15 and 50 ppm but in some cases (the 2nd. category) it reaches 120 -210 ppm. Sometimes the hydrogen chemical effect on steel followed by its decarburization is not observed (Vainman and Melehov, 1988; Vainman et al.,1990). Evidently hydrogen degrades the plastic and strength properties of steel in the region of the original source of stresses and at the microcrack tip, lowers the threshold level of bursting stress, and facilitates the development of crack forming the molecules on grain boundaries. The fracture along the bends‘ neutrals is caused by metal hydrogen fatigue.

HIGH PRESSURE STEAM PIPES

In a number of cases, especially at thermal power stations using industrial recycle condensates we can observe the steam pipe brittle fractures which are not related to metal creep. More often than not the bending sections of the steam pipes are damaged in that way, rarely, the straight sections. Unlike metal creep, the above fractures develop on the inside

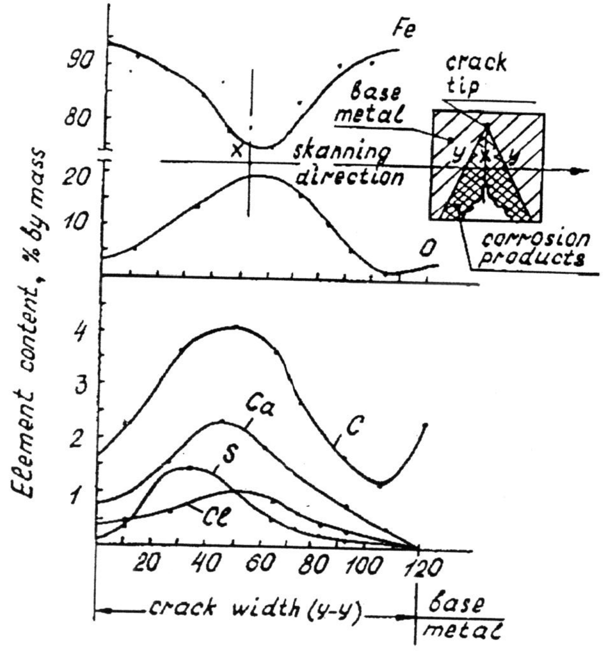

Fig. 6 Element distribution in section perpendicular to microcrack axis (Auger spectrometer linear scanning, crack is shown straight).

outside of the pipe. The characteristics of metal on the undamaged side of the pipe comply with the codes. As concerns the metal characteristics in the fracture region, they are as follows:

a. considerable degradation of strength and plastic properties of steel (2 - 3 times and more);
b. a lot of intergranular cracks side by side with the main one;
c. partial or complete steel decarburization (Fig. 2);
d. no metal overheating;
e. high concentrations of residual hydrogen exceeding the initial ones for the given steel quality by 1 - 2 order (Vainman, 1985; Vainman and Melehov, 1988; Vainman et al., 1990).

The volume hydrogen content has been determined by inert gas specimen melting (Leco RH-1 gas analyzer). The hydrogen distribution in the fracture region has been measured by Echo 4 M lazer mass spectrometer (Ukrainian Institute of Electric Welding) (Fig. 3). The fractography of metal exposed to hydrogen embrittlement confirms the brittle nature of intercrystalline cracks, the partial or complete dissolution of cementite platelets in pearlite grains (Fig. 4, a-b). The mechanical failure region shows the ductile fracture with the cup-shaped and comb-shaped profiles (Fig. 4, d): The essential recommendations for the prevention of the evaporating pipe hydrogen embrittlement: steam boiler design should provide for its service with heat flows far from critical over a wide range of loads; decrease in maximum heat flows (q) and their even distribution; potentially acid organic compound detection and prevention of their ingress into the feed circuit; use of nonvolatile alkali (sodium hydroxide) for correction of boiler water conditions and for boiler water pH maintenance (if necessary); application of internally spiral-finned tubes in the regions of very high heat flows (q) and in the areas of "vapor phase delaying".

Superheater Pipes. Hydrogen embrittlement of superheater pipes may be caused only by metal hydrogen charging on the one hand, and by the joint action of hydrogen embrittlement and creep on the other hand. Besides, the damage of oxide films on steel surface and the presence of corrosive impurities in working medium are the principal causes of the indicated fractures. The signs of diameter widening and superheater pipe wall thinning usually taking place in other cases are not observed. The corrosion-fatigue intercrystalline cracks uncommon for working medium (superheated steam) develop on the inside of the pipe. The abovesaid cracks differ essentially from those ones under thermal fatigue or creep by winding, branching, and by the presence of cavities, narrowings, widenings, blunt or rounded tips. Pearlitic steel (12 Cr 1 Mo V, 12 Cr 2 Mo V Si B) was decarburized in the crack propagation regions (Fig. 5). In many cases in the main crack region on the inside of the pipes we can observe the damage of oxide films,the development of point and pitting corrosion and the propagation of intergranular microcracks in numbers. The internal corrosion and hydrogen embrittlement of superheater pipes mostly take place at thermal power stations where the industrial or natural organic impurities (including potentially acid organic compounds) together with feed water enter the steam boiler and decompose. In particular, the following agents have been found in the boiler circuit: acetic, formic, propionic, butyric and citric acids; humic compounds, CCl_4, dichloroethane, cleaning and conserving agents, a number of film - formers. The residual hydrogen content of metal in the fracture regions of the superheater pipes (pearlitic steel) varies between 10 and 80 ppm. The high concentrations of residual hydrogen of metal (12-60 ppm) are also determined of the pipe as the corrosion or corrosion - fatigue intergranular cracks. The characteristic pores or pore chains of creep cannot be observed. The residual deformation is slight (3-10 times less of allowable). The strength and especially plastic properties of metal (12 Cr 1 Mo V steel) in the fracture region are essentially degraded, metal is partially decarburized. The residual hydrogen concentration is 13-60 ppm. In the area of fracture two regions are distinctly observed with the naked eye: the wide (70-95% of pipe wall thickness), rough and dark-coloured region of hydrogen embrittlement; the smooth region of mechanical failure on the outside of the pipe. The investigations performed by Auger spectrometer (Riber LAS-2000) have shown the presence of carbon, calcium, sulphur and chlorine (Fig.6) in the microcrack cavity on the inside of the steam pipe side by side with the oxides having the different phase composition. The content of the above elements in base metal beyond the borders of the microcrack is below the threshold of Auger spectrometer sensitivity (0,01%). Thus there is the ingress of the impurity elements into the microcrack cavity from the working medium during its growth. The fracture on the working medium side is evidently caused by the joint action of chemical and hydrogen corrosion.

STEAM TURBINES

The relation between hydrogen charging and metal brittle fractures has been revealed for the turbine casing components as well as the rotating blades in the phase transition region (Wilson region). The examinations of K-200-130 MP turbine metal (15 Cr 1 Mo 1 V steel) in the cracking region (inside) have shown the following :

1.uneven distribution of residual hydrogen (5-44 ppm) with a maximum value at a distance of 1-2 mm from crack tip;
2.presence of interdendritic shrinkage porosity in metal with inclusions in the form of silicon oxide globules in "manganous sulphide casing" (inclusion-matrix interfaces stand duty as "traps" and regions where absorbed hydrogen accumulates and turnes into molecules).

The brittle fractures of the turbine rotating blades in Wilson region are associated with corrosiveness and low pH values (4,5-6,5) of the primary condensate.The examinations of K-160-130 LP turbine 5th stage blade metal (12 Cr 13 steel) have shown the following:presence of pitting under deposits on the concave surface of a blade; degradation of steel properties in the above region; presence of pores, mainly on grain boundaries, the sizes of which diminish in the direction from surface deep into metal (from 20 to 5 μm); macrofatigue fracture having the traces of stopping in the development of the intergranular cracks; residual hydrogen content in the embrittlement region is 12-15 ppm, and 0,8-1,5 ppm in the mechanical failure region. The formation of pores is only observed in the hydrogen charging region and caused by high hydrogen pressure after its turning into molecules.

FEEDWATER HEATERS

In the high pressure heaters the vapor cooler tubes contacting with heater condensate are exposed to active hydrogen embrittlement. This applies to the last high pressure heaters (by feed water movement) at bad ventilation of their vapor space in case of application of the oxygen water treatment. In the fracture region on the outside of the vapor cooler tubes

(Ø 32 x 5, steel - 20, steam parameters - 6,24 MPa, 650 K) metal is exposed to deep decarburization (ferrite structure) and complete embrittlement (goes to pieces at slight mechanical loads). The residual hydrogen content is 35-120 ppm.

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