

TESTING ADSORBENTS FOR HEAT TREATMENT OF PIPES

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Abstract

Heat treatment of pipes was performed under industrial conditions at 580°C in a dry protective gas containing a CO₂–CO–H₂–N₂ mixture. A commercial adsorbent (733 kg) used for production of the gas removed 52.7 l of water in five h and 22.5 min. During the annealing of pipes oxidation and decarburization were not observed. The results were confirmed by metallographic analysis. The values of enthalpy of water desorption (36.4–40.5 kJ mol⁻¹) obtained by DSC and TG measurements were close to those of water evaporation (44.1 kJ mol⁻¹). This suggests that the bonds between the water molecules and adsorbents were not of chemical but of physical nature.

Keywords: adsorbent, heat treatment, thermal analysis, water adsorption, water desorption

Introduction

For heat treatment of pipes the protective atmosphere including both its technical and economical aspects is very important. This is particularly true of industrial conditions. The gas is made in a separate device, whence it is led into the furnace which must be gas-tight to prevent leakage. To avoid the oxidation and decarburization of pipes during heat treatment various protective atmospheres (hydrogen, nitrogen, argon, nitrogen-hydrogen mixture, CO₂–CO–H₂–N₂ and CO₂–CO–CH₄–H₂–H₂O–N₂ mixtures) are used [1–3]. Since the protective gas contains large volumes of CO₂ and H₂O the greater part of these must be removed by chemical adsorption and drying [4]. To obtain a dry protective gas different adsorbents can be used. The gas mixture passes through the layer of adsorbent which is placed into the dryer. There are no literature data concerning systematic characterization of adsorbents used for drying of the protective gas during heat treatment of pipes in industrial conditions. Likewise, there is no information about the effect of the dry protective gas and heat treatment on the surface properties (oxidation and decarburization) of cold rolled pipes. In this

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work the results of characterization of commercial adsorbents for the production of a dry protective gas in industrial heat treatment of cold rolled pipes made from St. 52.3 are presented. The behaviour of adsorbents in industrial and laboratory conditions is also compared.

Experimental

The commercial adsorbents used in this work for adsorption of water vapour from a moisture protective gas were assigned A and B (grains 3–4 mm in diameter). They were used for drying the protective gas during heat treatment of cold rolled pipes (outer diameter 75 mm and wall thickness 7.5 mm) made from St. 52.3 steel (Table 1). The pipes were annealed at 580°C by passing at a rate of 10 m h⁻¹. The annealing was performed in industrial conditions. A long horizontal RoDr 3300/4200 furnace equipped with a GW-200 device for the production of a dry protective gas by incomplete combustion of natural gas and air (air factor $\lambda=0.9$) was used. The results of chromatographic analysis of natural gas are given in Table 2. The contents of CO₂, H₂ and CO₂+CO+H₂ in a mixture of the dry protective gas were determined continuously during their production by means of a triplex monoanalyzer type E49092.

Table 1 Chemical composition of heat treated pipes, mass%

C	Mn	P	S	Si	Cu	Ni	Mo	Al	Cr
0.19	1.22	0.017	0.017	0.33	0.21	0.16	0.02	0.04	0.20

Table 2 Composition of natural gas, vol.%

CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C _n H _m	N ₂	CO ₂
96.77	1.88	0.06	0.01	0.01	1.21	0.06

The investigation of microstructure on polished and etched (in initial solution) specimens made from pipes before and after annealing was carried out with an optical microscope at 100× magnification.

Thermal analysis of adsorbents was performed by a differential scanning calorimetry (TA Instruments, DSC Model 2910) and simultaneous TG-DTA measurements (TA Instruments SDT Model 2960). Samples (20 mg) were tested in an open aluminum DSC pan at the heating rate of 10°C min⁻¹ in a nitrogen flow of 100 (DSC measurements) and 50 ml min⁻¹ (TG measurements). Both apparatuses were calibrated by means of indium. To determine water adsorption in adsorbents for each sample three measurements were performed. Firstly, the samples were subjected to DSC and TG analyses in the temperature range from 20 to 300°C. After that the samples were cooled to room temperature and then subjected to thermal analysis in the same temperature range. To obtain qualitative and quantitative information about water adsorption the same samples were moistened in water for one h. After that they were subjected to DSC and TG analyses up to 300°C at heating rate of 10°C min⁻¹.

Results and discussion

Figure 1 shows a GW-200 device for drying of the protective gas in industrial conditions. During the flow of the protective gas through adsorbents placed in dryer 1, the adsorbents in dryer 2 were on regeneration. The mass of adsorbents in each dryer (166 kg of adsorbent A and 566 kg of adsorbent B) was chosen to ensure proper drying of the moisture protective gas within 8 h. After drying the dry protective gas was led into the furnace. Table 3 shows that the time regeneration of the dryer was from 5 to 6 h by the average water desorption of 52.7 l. A mixture of adsorbents A and B lost water during heating up to 200°C. This behaviour agrees quite well with what was expected.

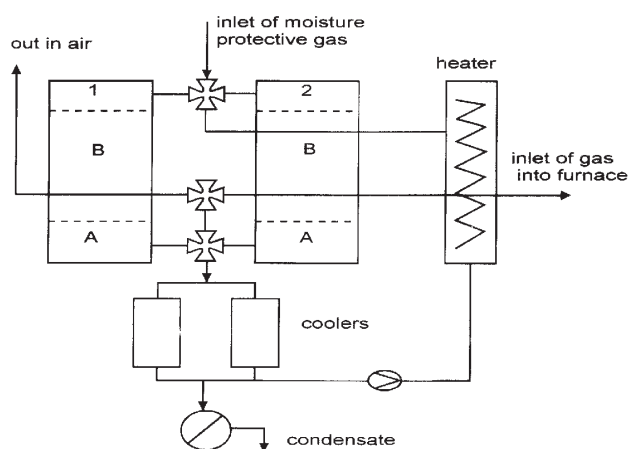


Fig. 1 Schematic illustration of GW-200 device for production of a dry protective gas. 1 and 2 – dryers, A – adsorbent A, B – adsorbent B

Table 3 Volume of water condensed during regeneration in dryers

Dryers	Time heating of dryers/h and min	Volume condensated of water/L
I	5 h and 15 min	51
II	5 h and 15 min	53
I	5 h and 30 min	53
II	5 h and 45 min	54
I	5 h and 15 min	53
II	5 h	51
I	5 h and 30 min	53
II	6 h	53
I	5 h and 15 min	53
II	5 h and 15 min	53
Average	5 h and 22.5 min	52.7

The amount of air (V_{oi}) for the complete combustion of natural gas and air (air factor $\lambda=1$) was:

$$V_{oi}=9.52 \text{ vol.\% CH}_4+16.7 \text{ vol.\% C}_2\text{H}_6+23.8 \text{ vol.\% C}_3\text{H}_8+ \\ 31 \text{ vol.\% C}_4\text{H}_{10}+17.7 \text{ vol.\% C}_n\text{H}_m \quad (1)$$

The composition of the protective gas at incomplete combustion (air factor $\lambda=0.9$) determined by the water-gas reaction:



Figure 2 shows the content of gas components in a dry protective gas as determined by an industrial monoanalyzer. The CO_2 content was 1.5 vol.%, that of H_2 6.5 vol.% and the content of the $\text{CO}_2+\text{H}_2+\text{CO}$ mixture was 9 vol.%. The contents of CO'_2 , CO' and H'_2 were confirmed by calculation according to a procedure described in literature [5].

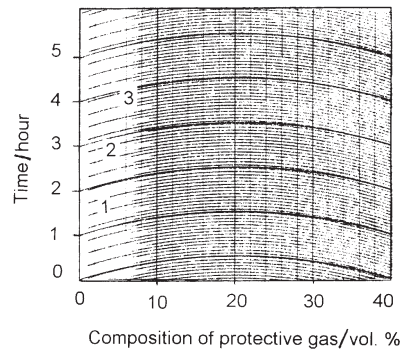
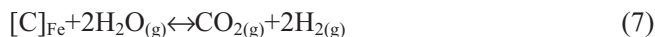


Fig. 2 Content of gas components in a dry protective gas obtained using an industrial monoanalyzer. 1 – CO_2 ; 2 – H_2 ; 3 – $\text{CO}_2+\text{H}_2+\text{CO}$ mixture

The microstructure of pipes shown in Fig. 3b is an example of good heat treatment of pipes with a dry protective gas. For comparison, Fig. 3a shows the microstructure of pipes before heat treatment. This is an elongated ferrite-pearlite microstructure as a result of cooling with the finishing temperature of rolling bringing about the diffusionless phase transformation during the decomposition of austenite [6]. As shown by Fig. 3b oxidation and decarburization were not observed. Obviously, the elongated ferrite-pearlite microstructure was due to tempering stresses occurring at 580°C without any phase transformation. The mayor chemical reactions of decarburization of steel are [7]:





where $[\text{C}]_{\text{Fe}}$ is the solid solution of carbon in austenite. Reactions (3), (6) and (7) were avoided for our annealing conditions at 580°C because O_2 and H_2O were not present in the protective gas. Oxygen was not present because the protective gas was produced by incomplete combustion of natural gas and air (air factor $\lambda=0.9$). Water vapour in the form of condensed water was completely removed during the regeneration of adsorbents in the dryer (Table 3). Reactions (4) and (5) were not possible due to two reasons: (i) low content of CO_2 and H_2 in the dry protective gas (Fig. 2), and (ii) low diffusion coefficient of carbon at 580°C [4].

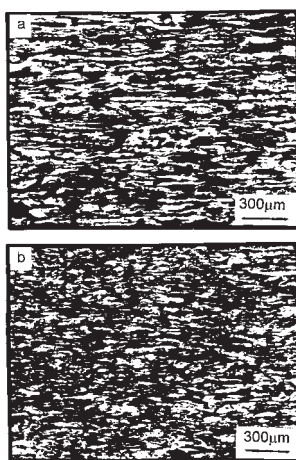


Fig. 3 Microstructure of St. 52.3 steel pipes before (a) and after annealing (b) near the outside steel surface. Passing rate of pipes 10 m h^{-1}

The TG curve of non-treated adsorbent A (curve 0 in Fig. 4a) shows a mass loss (25.0 mass%) occurring in the temperature range from 20 to 150°C. The loss was caused by the storage conditions of the adsorbent. After the same sample was cooled to room temperature, the TG analysis in the same temperature range showed a mass loss of 9.4 mass% (curve 1). This indicates that during cooling from 300 to 20°C a certain amount of water was adsorbed on the adsorbent. The TG analysis of samples moistened in water during 1 h showed a mass loss of 33.8 mass%. Similar results were obtained for adsorbent B (Fig. 4b). The mass loss of the non-treated sample was 26.9 mass%. Heating to 300 and then cooling to 20°C resulted in a loss of 14.6 mass%, while for the sample moistened in water during 1 h the mass loss was 27.9 mass%.

From the DSC curves for both adsorbents an intensive endothermic DSC peak in the range from 20 to 150°C was observed. It suggests that the mass loss registered by TG measurements may be attributed to water desorption. The onset of desorption immediately followed the start of the programmed heating of the sample. Thus at the be-

gining of heating the specific heat capacity of the samples changed considerably resulting in the non-existence of the baseline (the initial part of DSC curves).

The enthalpy of water desorption was determined (ΔH_{sample}) on the basis of DSC measurements (the peak area under the endothermic peaks). By combining TG and DSC data the molar enthalpy of water desorption was calculated ($\Delta H_{\text{des H}_2\text{O}}$) according to the equation:

$$\Delta H_{\text{des H}_2\text{O}} = (\Delta H_{\text{sample}} \cdot 100) \cdot 18.01 / \% \text{H}_2\text{O} \quad (8)$$

where $\% \text{H}_2\text{O}$ is the percentage of water desorbed as determined by TG measurements, and 18.01 is the relative molar mass of water. Results of molar heat water desorption (Table 4) are very close to the values of the molar enthalpy of water vaporization (44.1 kJ mol^{-1}) [8]. This indicates that the water molecules are adsorbed on the active surface of adsorbents not in a chemical but in a physical way. Thermal analysis of samples moistened in water for 1 h indicates that they are capable of adsorbing water. On the basis of the results of TG analysis the ability of adsorbents was determined. Adsorbent A adsorbed 33.8 mass% of water (percentage in relation to mass), while adsorbent B adsorbed 27.9 mass% of water.

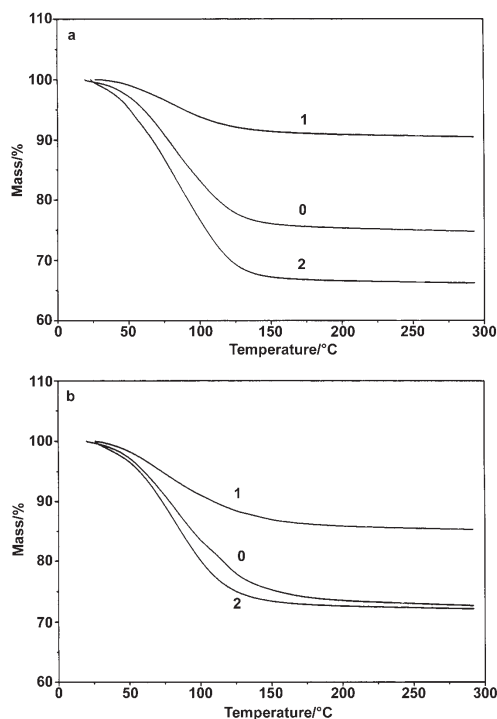


Fig. 4 TG curves of adsorbents A (a) and B (b) for the different states of samples. Heating rate $10^\circ\text{C min}^{-1}$ and nitrogen flow 50 ml min^{-1} . 0 – non-treated sample; 1 – sample after cooling from 300 to 20°C and repeated heating to 300°C ; 2 – sample moistened in water for 1 h

Table 4 Percentage of mass loss, enthalpy of water desorption and molar enthalpy of water desorption for different states of adsorbents

Adsorbent	State of sample	H ₂ O/%	$\Delta H_{\text{sample}}/\text{J g}^{-1}$	$\Delta H_{\text{des,H}_2\text{O}}/\text{kJ mol}^{-1}$
A	non-treated	25.0	614.8	44.3
	cooled to 20°C	9.4	157.6	30.2
	moistened	33.8	759.8	40.5
B	non-treated	26.9	586.0	39.2
	cooled to 20°C	14.6	213.3	26.3
	moistened	27.9	565.1	36.4

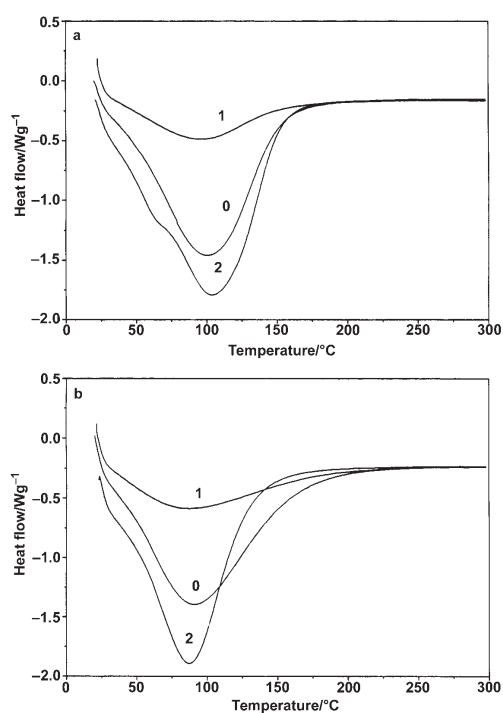


Fig. 5 DSC curves of adsorbents A (a) and B (b) for the different states of samples. Heating rate $10^\circ\text{C min}^{-1}$ and nitrogen flow 100 ml min^{-1} . 0 – non-treated sample; 1 – sample after cooling from 300 to 20°C and repeated heating to 300°C ; 2 – sample moistened in water for 1 h

Conclusions

The protective gas which contained the $\text{CO}+\text{H}_2$ mixture of 7.5 vol.% was produced by incomplete combustion of natural gas and air (air factor = 0.9).

By heat treatment of cold rolled pipes at 580°C in the protective gas containing the CO₂-CO-H₂-N₂ mixture the steel surface without oxidation and decarburization was obtained. It was probably the result of the low CO₂ content in the dry protective gas and the low diffusion coefficient of carbon at 580°C. The results were confirmed by metallographic analysis.

The measurements of condensed water in GW-200 dryers showed that heating of 733 kg of adsorbents for 5 h and 22.5 min up to 200°C yielded 57.2 l.

The techniques of thermal analysis proved to be suitable for the determination of adsorption and desorption i.e. the activity of adsorbents. TG measurements of non-treated adsorbents showed a mass loss of 25–26.9 mass% in the temperature range from 20 to 150°C. The loss was probably caused by the preliminary storage conditions of the adsorbent. The results were confirmed by DSC measurements. DSC and TG measurements of adsorbents moistened in water for 1 h showed that the enthalpy of water desorption (36.4–40.5 kJ mol⁻¹) was close to that of its evaporation (44.1 kJ mol⁻¹). This suggests that the bonds between the water molecules and the adsorbent were not of chemical but of physical nature.

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