

THE EFFECT OF PROTECTIVE GAS ON ANNEALING OF 42CrMo4 STEEL PIPES

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In this work the effect of protective gas on annealing of cold-rolled 42CrMo4 steel pipes was analysed. The production of protective gas (CO₂-CO-H₂-N₂ mixture) and the annealing of pipes at the different temperatures are discussed. By annealing of pipes in industrial conditions at 920 °C a bright steel surface was obtained. Decarburization of pipes at depth of 0.09–0.12 mm was observed. However, annealing the pipes at 700 °C the decarburization did not occur. The process of decarburization is explained by means of diffusion of carbon and surface reactions of solid solution of carbon in austenite and some components of protective gas.

Key words: protective gas, annealing, cold rolling, steel, decarburization, microstructure

VPLYV OCHRANNÉHO PLYNU NA ŽIHANIE RÚR Z OCELE 42CrMo4

V práci analyzujeme vplyv ochranného plynu na rúry z ocele 42CrMo4 valcované za studena. Zaoberáme sa výrobou ochranného plynu (zmes CO₂-CO-H₂-N₂) a žiňaním rúr pri rôznych teplotách. Žiňaním rúr v priemyselných podmienkach pri teplote 920 °C sa získal lesklý povrch ocele. Pozorovali sme oduhlíčenie rúr do hĺbky 0,09–0,12 mm, avšak pri žiňaní rúr pri teplote 700 °C sme oduhlíčenie nepozorovali. Proces oduhlíčenia sa vysvetľuje pomocou difúzie uhlíka a povrchových reakcií tuhého roztoku uhlíka v austenite a niektorých zložiek ochranného plynu.

1. Introduction

The general purpose of an annealing treatment is to reduce the hardness of the steel or to produce a microstructure that facilitates the progress of subsequent

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working operations. The annealing involves heating of the steel to a specific temperature, holding it at that temperature for a defined period of time, and cooling it at a controlled rate. The annealing temperature, holding time, and cooling rate depend on the chemical composition, required properties, and the type of equipment used. Today for a large volume production of steel pipes continuous annealing furnaces with a controlled atmosphere are required. To obtain the protective atmosphere for annealing of steels the hydrogen, nitrogen, argon, nitrogen-hydrogen mixture, vacuum, and $\text{CO}_2\text{-CO-H}_2\text{-N}_2$ and $\text{CO}_2\text{-CO-CH}_4\text{-H}_2\text{-H}_2\text{O-N}_2$ mixtures are used [1–9]. The protective atmosphere has to provide one or more of the following requirements: (i) to protect the steel surface from oxidation, (ii) to avoid decarburization, (iii) to counteract effects of leaking of air (oxygen and water vapor) into the furnace during annealing, and (iv) to supply necessary reducing gases to obtain a bright steel surface [10].

It is known that during a heat treatment of steel its oxidation or decarburization may occur [11]. Both processes are undesirable. The decarburization is specially harmful due to a complete modification of steel surface chemistry. As a result of the decarburization both the mechanical and technological performances of the steel surface layer are decreased. The effect of protective gas on the modification of steel surface is not well defined [12, 13]. It is specially related to using $\text{CO}_2\text{-CO-H}_2\text{-N}_2$ mixture as a protective gas. The low alloy CrMo steel (42CrMo4) was chosen for consideration in this investigation programme. In this work the effect of protective gas on annealing of steel pipes was investigated using a chromatographic analysis, as well as an optical microscopy technique before and after an industrial annealing in $\text{CO}_2\text{-CO-H}_2\text{-N}_2$ protective atmosphere.

2. Experimental

The seamless hot-rolled pipes (outer diameter 159 mm and wall thickness of 8 mm) are cold-rolled (outer diameter 130 mm and wall thickness of 6.5 mm) using the KPW-150 cold-pilger process. Table 1 gives the chemical composition of steel pipes. The annealing of cold-rolled pipes was performed in industrial conditions using a long horizontal furnace, type RoDr 3300/4200 (Nassheuer) equipped with a device for production of the protective gas, type GW-200. The pipes are annealed at 920°C by passing rate of 20 m/h, as well as at 700°C by passing rate of 10 m/h. During the annealing of pipes the protective atmosphere is used. A dry protective gas was produced by means of GW-200 device. An incomplete combustion of natural gas and air is used (air factor $\lambda < 1$). For annealing at 920°C

Table 1. Chemical composition of steel investigated [wt.%]

C	Mn	P	S	Si	Cu	V	Mo	Al	Cr	Ni	Sn
0.43	0.75	0.015	0.018	0.23	0.15	0.02	0.29	0.036	1.18	0.06	0.017

the ratio of natural gas vs. air was 195:31.5 N·m³/h ($\lambda = 0.6370$). At the annealing temperature of 700°C the ratio natural gas vs. air was 150:17 N·m³/h ($\lambda = 0.908$). During annealing in the furnace a dry protective gas was inserted. In the combustion chamber of natural gas and air the temperature was measured using an optical pyrometer Hartmann & Braun. Determination of H₂, CO, and CO₂ content in the protective gas was performed according to ASTM standard [14]. The composition both of the natural gas and the protective gas was determined by chromatographic technique using normalizing method. The chromatographic system was calibrated with mixed Supleco gases (Scot Specialty Gases). The accuracy of chromatographic measurements was $\pm 2\%$. The investigation of microstructure on polished and etched (in nital solution) specimens before and after annealing was carried out by an optical microscope at magnification of 500 \times and 1000 \times .

3. Results and discussion

The results of chromatographic analysis of natural gas are given in Table 2. The theoretical amount of air (V_{01}) for the complete combustion of natural gas and air (air factor $\lambda = 1$) is:

$$V_{01} = 9.52 \text{ vol.}\% \text{ CH}_4 + 16.7 \text{ vol.}\% \text{ C}_2\text{H}_6 + 23.8 \text{ vol.}\% \text{ C}_3\text{H}_8 + \\ + 31 \text{ vol.}\% \text{ C}_4\text{H}_{10} + 17.7 \text{ vol.}\% \text{ C}_n\text{H}_m. \quad (1)$$

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
96.82	2.59	0.21	0.05	0.01	0.01	0.26

The composition of the protective gas at an incomplete combustion ($\lambda < 1$) can be determined by water-gas reaction:



The ratio of CO', H₂O', CO'₂, and H'₂ contents in the combustion product was determined with constant equilibrium (K_w):

$$K_w = \text{H}_2\text{O}' \cdot \text{CO}' / \text{H}'_2 \cdot \text{CO}'_2. \quad (3)$$

The relationship between K_w and temperature is given in the following equation [15]:

$$K_w = 0.00398 \vartheta - 2.26, \quad (4)$$

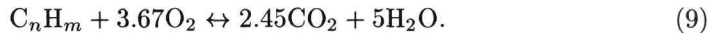
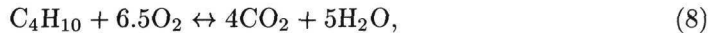
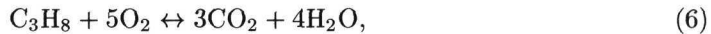
where ϑ [°C] is temperature of combustion products of natural gas.

The results both of the measuring temperature of the products natural gas combustion and the equilibrium constant are given in Table 3.

Table 3. Measured temperature of products of natural gas combustion for the different air factors and the values of K_w

Ratio natural gas vs. air		Air factor, λ	Measured temperature [°C]	K_w
$N \cdot m^3/h$ natural gas:	$N \cdot m^3/h$ air			
31.5:	190	0.6370	1090	2.47
17:	150	0.908	1190	2.08

For combustion of natural gas the following reactions are important:



To obtain final combustion products, both the material balance and the total of combustion products were used.

Balance of carbon:

$$C'' = CO_2' + CO' = CO_2 + CO + 2C_2H_6 + 3C_3H_8 + CH_4 + 4C_4H_{10} + 2.45C_nH_m. \quad (10)$$

Balance of hydrogen:

$$H'' = H_2' + H_2O' = 3C_2H_6 + 4C_3H_8 + 2CH_4 + 5C_4H_{10} + 2.45C_nH_m. \quad (11)$$

Balance of oxygen:

$$O'' = CO_2' + 0.5(CO' + H_2O') = CO_2 + 0.5(CO + H_2O) + O_2 + 0.209 \lambda V_{ol}. \quad (12)$$

Balance of nitrogen:

$$N_2'' = N_2 + 0.791 \lambda V_{ol}. \quad (13)$$

Obtained amount of a real protective gas (V_z) is: $V_z = C'' + H'' + N_2''$.

Calculation of value C'' , H'' and O'' for $1 \text{ N} \cdot \text{m}^3$ of protective gas was performed using following equations:

$$C' = C''/V_z, \quad H' = H''/V_z, \quad O' = O''/V_z. \quad (14)$$

From equations

$$\text{CO}'_2 + \text{CO}' = C', \quad (15)$$

$$\text{H}_2\text{O}' + \text{H}'_2 = H', \quad (16)$$

$$\text{CO}'_2 + 0.5(\text{CO}' + \text{H}_2\text{O}') = O', \quad (17)$$

inserting Eqs. (15), (16) and (17) into Eq. (3) the following solution can be obtained:

$$K_w = [\text{CO}' + 2(\text{O}' - \text{C}')] \text{CO}' / (\text{CO}' - \text{C}') [\text{CO}' + 2(\text{O}' - \text{C}') - \text{H}']. \quad (18)$$

With known K_w (Table 3), the CO' content was determined by means of Eq. (18). Other gas components in the protective gas were calculated from the following equations:

$$\text{CO}'_2 = C' - \text{CO}', \quad \text{H}_2\text{O}' = \text{CO}' + 2(\text{O}' - \text{C}'), \quad \text{H}_2 = H' - \text{H}_2\text{O}'. \quad (19)$$

Table 4 gives the calculated values of gas components in the protective gas at various air factors, as well as the results of chromatographic analysis of the protective gas. The results of chromatography represent an average of five measurements. As seen from Table 4, the results of chromatographic analysis of the protective gas at $\lambda = 0.637$ are similar to the values calculated taking into account Eqs. (18) and (19).

Figure 1 shows the microstructure of 42CrMo4 steel after cold-rolling (before annealing). As it can be seen, the steel has a fine bainite microstructure across the whole wall thickness without any changes observed near the outer and inner steel surface. Figures 2 and 3 show the microstructure of steel after heat treatment.

Table 4. Composition of protective gas vs. air factor [vol.%]

Air factor λ	Moist protective gas (Calculated values)					Dry protective gas (Calculated values)				Chromatographic analysis of dry protective gas			
	CO'_2	CO'	H'_2	$\text{H}_2\text{O}'$	N'_2	CO'_2	CO'	H'_2	N'_2	CO_2	CO	H_2	N_2
0.6370	4.7	8.2	10.6	14.8	61.7	5.5	9.6	12.4	72.5	5.2	12.0	11.5	71.3
0.9080	8.4	1.9	2.0	18.2	69.5	10.2	2.3	2.4	85.1	-	-	-	-

Figure 2 shows the microstructure of the steel after annealing at 920 °C with passing rate of 20 m/h where the protective gas with the contents of 12.0 vol.% CO, 11.5 vol.% H₂ and 5.2 vol.% CO₂ was used. After annealing at these conditions a bright steel surface was obtained. As it can be seen from Fig. 2a, a decarburization near the outer steel surface occurred (in the depth of 0.12 mm). The decarburization occurred also near the inside steel surface but in the depth of 0.09 mm (Fig. 2b). In

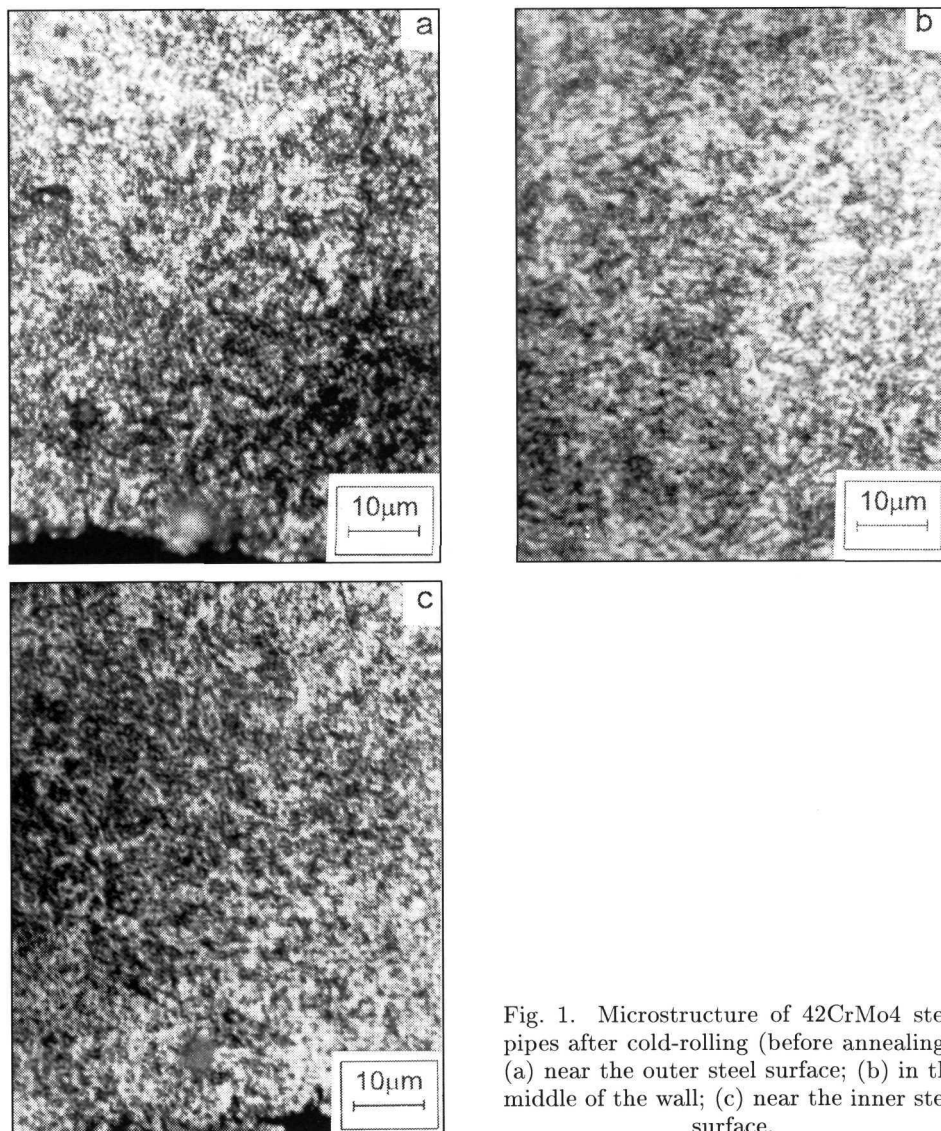


Fig. 1. Microstructure of 42CrMo4 steel pipes after cold-rolling (before annealing): (a) near the outer steel surface; (b) in the middle of the wall; (c) near the inner steel surface.

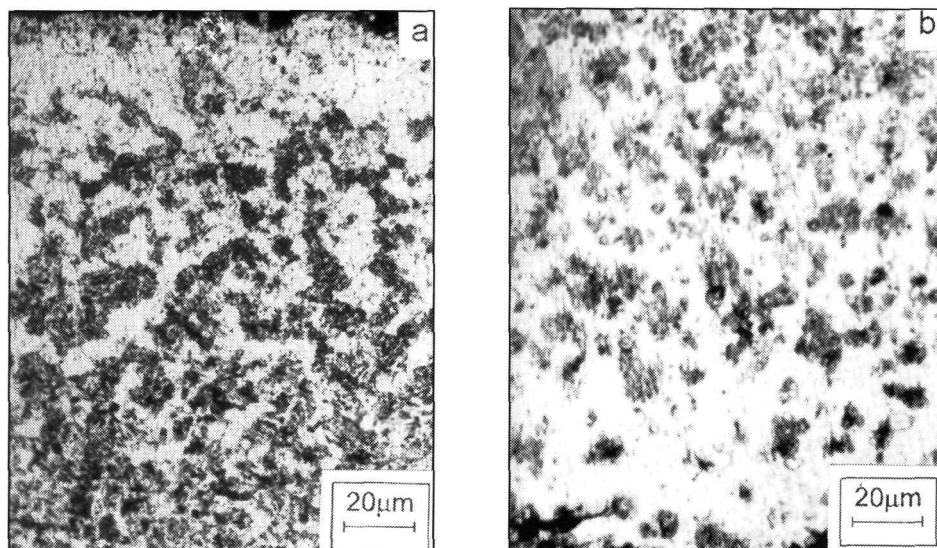
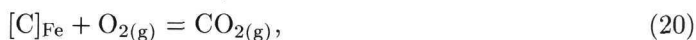


Fig. 2. Microstructure of 42CrMo4 steel pipes after annealing at 920°C in RoDr 3300/4200 furnace. Passing rate of pipes is 20 m/h. Protective gas: 12.0 vol.% CO + 11.5 vol.% H₂. (a) near the outer steel surface; (b) near the inner steel surface.

the middle of the wall the microstructure consists of a fine bainite. Figure 3 shows the microstructure of the steel after annealing at 700°C with passing rate of 10 m/h where the protective gas contains 2.3 vol.% CO and 2.4 vol.% H₂ used. After this annealing the traces of oxidation on steel surface were not observed. As it can be seen from Figs. 3a–b, the decarburization was present neither near to the outer (Fig. 3a) nor inner steel surface (Fig. 3b). Simultaneously, the microstructure in the middle of the wall is tempered bainite with spheroidized carbides.

It is known that during the heat treatment of steels, interaction between the steel surface and the protective atmosphere can occur [11]. Two processes are possible: oxidation and decarburization. Oxidation of the steel surface is due to the presence of O₂, CO₂, and H₂O. In this case an oxide film was obtained. The composition and structure of the oxide film depend on annealing temperature. In this investigation at annealing of 42CrMo4 steel the oxidation did not occur. However, the decarburization of steel was present. Decarburization of the steels represents a selective oxidation of carbon [16]. The major chemical reactions of decarburization of steel are [17]:



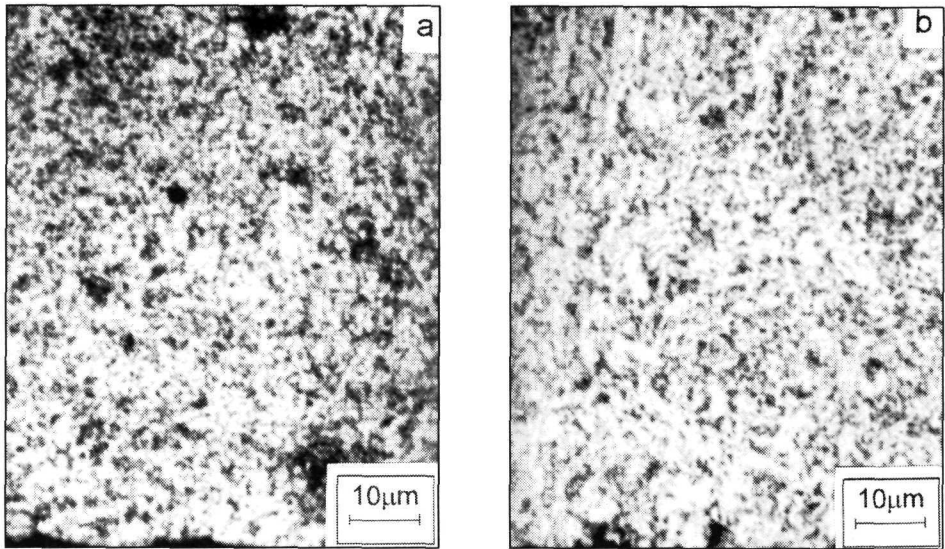
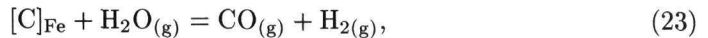


Fig. 3. Microstructure of 42CrMo4 steel pipes after annealing at 700 °C in RoDr 3300/4200 furnace. Passing rate of pipes is 10 m/h. Protective gas: 2.3 vol.% CO + 2.4 vol.% H₂.
(a) near the outer steel surface; (b) near the inner steel surface.



where $[C]_{Fe}$ is the solid solution of carbon in austenite.

In our annealing conditions at 920 °C the reactions (20), (23) and (24) do not take place as O₂ and H₂O are not present in the protective gas. It is confirmed by the results of chromatographic analysis (Table 4). Oxygen is not present because the protective gas was produced during an incomplete combustion of natural gas ($\lambda < 1$). Before entering the furnace the water vapor was removed by drying in GW-200 device. The reactions (21) and (22) are possible because the protective gas contains 5.2 vol.% CO₂ and 11.5 vol.% H₂. At temperature of 920 °C the carbon diffuses out of the steel surface and reacts with CO₂ and H₂ from protective gas. Possible explanation for the observed decarburization at 920 °C is based on diffusion of carbon out of the steel surface. Diffusion takes place due to a concentration gradient which produces the driving force required for the diffusion process. The diffusion coefficient D is very strongly influenced by temperature. The temperature

dependence of D is given by the following equation:

$$D = D_0 \exp(-Q/RT), \quad (25)$$

where D_0 is a frequency factor [m^2/s], Q is the energy of activation [kJ/mol], T is the absolute temperature [K] and R is the gas constant [$\text{kJ}/\text{K}\cdot\text{mol}$]. Approximate values of D_0 and Q for carbon in γ -iron are $0.21 \times 10^{-4} \text{ m}^2/\text{s}$ and $141.51 \text{ kJ}/\text{mol}$, respectively [18]. Provided that the graph representing decarburization has the appearance shown in Fig. 4, it is possible, using equation (26), to calculate the depth from which the carbon has diffused [11]:

$$C = C_0 \text{erf} [x/2(Dt)^{1/2}], \quad (26)$$

where C is carbon concentration at the depth x below the surface, C_0 is the basic carbon content of the steel, x is the depth below the surface [mm], t is time (s) and erf is the error function. Assuming that the carbon content of the outermost layer was reduced practically to zero, we can calculate the carbon concentration at certain depth. Since the 42CrMo4 steel with 0.43 wt.% C (Table 1) was annealed in the furnace for 49.5 min at 920°C , using Eq. (26), the carbon concentration in the outer layer, which was removed from the depth of $x = 0.10 \text{ mm}$ from the surface, is 0.12 wt.%.

However, at annealing temperature of 700°C , the decarburization of 42CrMo4 steel did not occur (Fig. 3). At this temperature the steel is in the α -range, and the diffusion process is slow. Diffusion coefficient of carbon at 700°C is $6.7 \times 10^{-3} \text{ m}^2/\text{s}$. Simultaneously, the carbon reactions with gas component (Eqs. 21 and 22) are also suppressed due to the lower annealing temperature. Results obtained are different of that by Aljamovskaja et al. [12]. They found that during annealing of steel containing 0.46–0.54 wt.% C, 0.8–1.1 wt.% Cr, and 0.1–0.2 wt.% V in the temperature range from 720 to 740°C in the nitrogen-hydrogen mixture gas with increased moisture, the decarburization

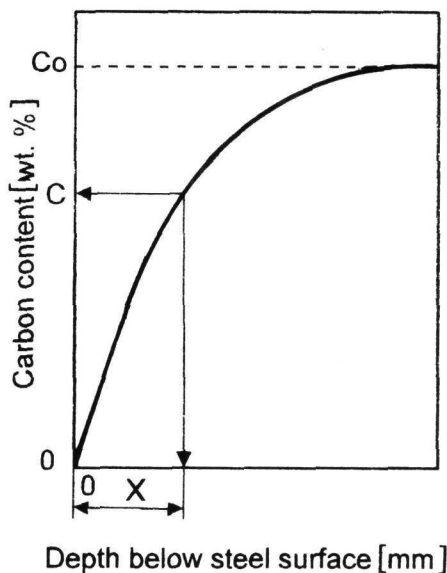


Fig. 4. Schematic illustration of decarburization diagram.

at depth of 0.23 mm was observed [12]. Probably in this case the conditions for reactions (23) and (24) took place. Thus, the protective gas may influence the decarburization. However, in our case the decarburization did not occur because the protective gas was dried and the annealing temperature was lower.

4. Conclusion

By an incomplete combustion of natural gas and air (air factor $\lambda = 0.637$) in the GW-200 device, the protective gas containing $\text{CO}_2\text{-CO-H}_2\text{-N}_2$ mixture was obtained. The results are confirmed by chromatographic analysis. By annealing cold-rolled pipes from 42CrMo4 steel in RoDr 3300/4200 furnace at 920 °C under the protective gas the bright steel surface was obtained. However, the decarburization of pipes was observed at the depth of 0.09–0.12 mm from the surface. The carbon concentration at the decarburization depth of 0.10 mm was calculated (0.12 wt.% C). The process of decarburization of pipes was explained by higher diffusion of carbon out of the steel towards the surface and by the surface reactions of the solid solution of carbon in austenite with CO_2 and H_2 from the protective gas. At annealing temperature of 700 °C in the protective gas containing $\text{CO} + \text{H}_2 = 4.7$ vol.% the decarburization and/or the oxidation of pipes was not observed what corresponds to the lower carbon diffusion at the lower applied annealing temperature. The obtained results for annealing of pipes at 900 °C and 700 °C are confirmed by metallographic analysis of specimens near the outer and inner steel surface.

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