MECHANICAL PROPERTIES AND MICROSTRUCTURE OF STEEL PIPES FOR GAS BOTTLES

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In this paper mechanical and microstructural results of laboratory heat treatment (quenching and tempering) of seven various heats made of low-alloyed manganese steels are shown. The effect of vanadium and nitrogen contents on the yield/tensile strength ratio of pipes in quenched and tempered state was analysed. The linear relationship between the total amount of vanadium and nitrogen contents and the yield/tensile strength ratio was found. The obtained results are suitable for various heats of following chemical composition: 0.32–0.35 wt.% C, 1.13–1.37 wt.% Mn, 0.15–0.22 wt.% V, and 0.0070–0.0127 wt.% N. Quenching the pipes in oil from 850 °C, tempering them at 650 °C and cooling them in air, the required mechanical properties are obtained. In order to obtain the yield/tensile strength ratio below 0.95, the total amount of vanadium and nitrogen should be lower than 2200 ppm.

Key words: low-alloy steel, mechanical properties, micro-alloying, microstructure, vanadium, nitrogen, precipitation

MECHANICKÉ VLASTNOSTI A MIKROŠTRUKTÚRA OCEĽOVÝCH RÚR PRE PLYNOVÉ FĽAŠE

V príspevku uvádzame mechanické vlastnosti a mikroštruktúru siedmich laboratórne tepelne spracovaných (kalených a popúšťaných) vsádzok z nízkolegovaných mangánových ocelí. Analyzovali sme vplyv obsahu vanádu a dusíka na pomer medze sklzu a medze pevnosti rúr v zakalenom a popustenom stave. Našli sme lineárny vzťah medzi celkovým obsahom vanádu a dusíka a pomerom medze sklzu a medze pevnosti. Získané výsledky sú vhodné pre rôzne vsádzky s nasledujúcim chemickým zložením: 0,32 – 0,35 hm. % C, 1,13 – 1,37 hm. % Mn, 0,15 – 0,22 hm. % V a 0,0070 – 0,0127 hm. % N. Požadované mechanické vlastnosti sme dosiahli kalením rúr z teploty 850 °C do oleja, popúšťaním pri

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teplote 650 °C a chladením na vzduchu. Na získanie pomeru medze sklzu a medze pevnosti menšieho ako 0,95 by malo celkové množstvo vanádu a dusíka byť nižšie ako 2200 ppm.

1. Introduction

Addition of a small amount of micro-alloying elements such as vanadium, niobium and titanium plays an important role in the grain refinement of micro-alloyed steels [1, 2]. These elements increase strength of steels by means of precipitation hardening (as carbides, nitrides, or carbonitrides). For vanadium micro-alloyed steels the size and distribution of precipitates depend on both the transformation temperature and presence of certain elements, particularly nitrogen [3]. The ratio of yield/tensile strength of pipes made of this steel in quenched and tempered state should be smaller than 0.95 [4]. Data available for the heat treatment of micro-alloyed steels has been reviewed by Engineer et al. [5]. Most investigations on the tempering of steels containing vanadium were carried out at much larger additions (0.5–2 wt.%) [6–8]. It was found that the addition of 0.01–0.10 wt.% vanadium to 0.2 wt.% carbon steel resulted in a much higher hardness after tempering at 600 °C [9].

The purpose of this work is to obtain the desirable mechanical properties of steel pipes for gas bottles made of low-alloyed manganese steel micro-alloyed with vanadium (0.15–0.22 wt.%) using quenching and tempering procedure [10] as well as to determine the total amount of vanadium and nitrogen in order to obtain the yield/tensile strength ratio below 0.95.

2. Experimental

Seven different heats of low-alloyed manganese steels micro-alloyed with vanadium were melted in the electric arc furnace followed by continuous casting in billets. The billets were hot-rolled into pipes with 140 mm in diameter and 4.3 mm of wall thickness. The chemical composition of steels is given in Table 1. The reheating temperatures at hot-rolling were selected between 1250 and 1280 °C. The finish-rolling temperatures after pipe-reducing mill were between 850 and 920 °C.

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

Heat	C	Mn	P	S	Si	Cu	V	Al	Cr	N
1	0.32	1.13	0.009	0.018	0.30	0.26	0.15	0.026	0.12	0.0085
2	0.32	1.15	0.008	0.014	0.25	0.23	0.16	0.023	0.08	0.0100
3	0.32	1.22	0.016	0.022	0.26	0.22	0.17	0.022	0.11	0.0073
4	0.34	1.25	0.015	0.018	0.28	0.12	0.18	0.020	0.12	0.0094
5	0.34	1.35	0.018	0.021	0.27	0.21	0.18	0.020	0.16	0.0112
6	0.35	1.37	0.014	0.017	0.35	0.13	0.19	0.032	0.10	0.0127
7	0.32	1.34	0.020	0.023	0.36	0.23	0.22	0.047	0.17	0.0070

The procedure of dilatometric measurements for determination of transformation temperature was as follows: the specimens with 4 mm in diameter and 50 mm in length were heated from room temperature up to 930 ℃ at the reheating rate of 0.08 ℃/s. The specimens were cooled continuously from the austenitization temperature at a cooling rate of 0.08 ℃/s. The heat treatment of specimens with 140 mm in diameter and 300 mm in length was carried out in the electric resistance furnace without protective atmosphere. First, the normalization of specimens at 870 ℃ for 20 minutes was performed followed by air cooling. After that the specimens were austenitized at 850 ℃ for 20 minutes and quenched in oil. Immediately after quenching, the tempering of specimens at 650 ℃ was carried out for 45 minutes.

Mechanical properties of three specimens were tested on tensile testing machine in accordance with ASTM procedures [11]. The average hardness was measured by the Brinell method (HB). The toughness of pipes was evaluated at −20 ℃ by the Charpy method. Before and after heat treatment, the microstructure was observed using light microscopy (LM). Specimens for LM were mechanically ground down by 1000 grit SiC papers, and finally polished with 0.5 μm alumina powder to obtain a mirror surface. Specimens for LM were etched in nital solution. Thin foils for transmission electron microscopy (TEM) observation were prepared by mechanical grinding to 0.2 mm thickness followed by chemical thinning in a mixed solution of hydrofluoric acid and hydrogen peroxide. Subsequently the foils were examined by TEM Jeol JEM-2000 FX operated at 200 kV equipped with a facility for energy dispersive X-ray spectrometry (EDXS). During TEM testing of the foils, the Cu-grid was used. The phase identification of the specimens in tempered state was carried out by X-ray diffraction (XRD) method using Co$K\alpha$ radiation. The obtained diffraction spectra were analyzed by the comparison method using JCPDS data [12].

3. Results and discussion

The transformation start and finish temperature at the cooling rate of 0.08 ℃/s are shown in Table 2. In order to ensure the uniformity of microstructure and to remove residual stresses, the specimens were normalized at 870 ℃ before quenching. It is well known that during continuous cooling of low-alloyed steels, the austenite transforms into ferrite-pearlite, bainite and/or martensite, depending on the cooling rate and the chemical composition [13]. A coarse elongated ferrite-pearlite microstructure after cooling of pipes from the finish-rolling temperature at 900 ℃ was observed, as shown in Fig. 1. The nucleation of ferrite probably occurred at the γ/γ boundaries, and an occasional growth proceeded along these boundaries [14]. Pearlite is formed from the parent austenite phase by cooperative growth of ferrite and cementite [15]. On the other hand, uniformly distributed ferrite-pearlite grains were observed in Fig. 2 for the pipe normalized at 870 ℃. For all the heats a similar

Table 2. Results of dilatometric testing

Heat	Ac_1 [°C]	Ac_3 [°C]	Ar_3 [°C]	Ar_1 [°C]
7	745	800	720	620

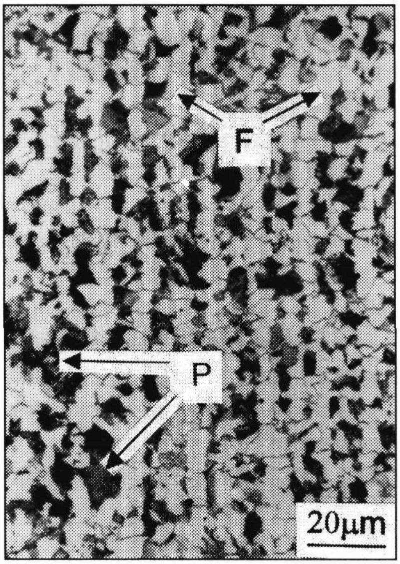

Fig. 1. Light microscope micrograph of the pipe specimen after hot-rolling. F – ferrite, P – pearlite.

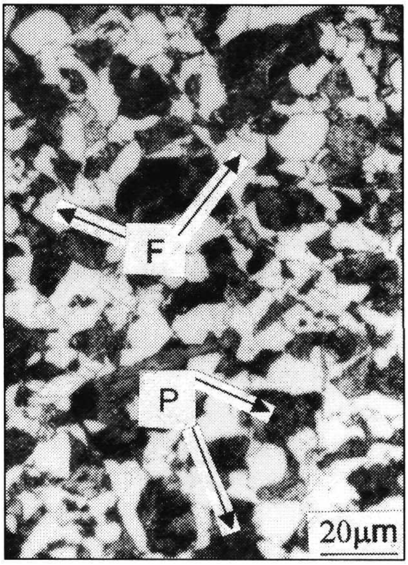

Fig. 2. Light microscope micrograph of the pipe specimen after normalization at 870 °C. F – ferrite, P – pearlite.

microstructure was observed. Therefore only microstructure for the heat 7 is shown. During the rapid oil cooling the austenite was transformed to the lath martensite (Fig. 3). Martensite is reported to be formed by shear mechanism, where many atoms move cooperatively and almost simultaneously in contrast to atom-to-atom movements during diffusion-controlled transformation [16]. The tempering of pipes at 650 °C resulted in the tempered martensite microstructure shown in Fig. 4.

TEM analysis of foils made from the heats 1 and 7 was carried out. The obtained bright-field images and EDX spectra for both heats are similar. Fig. 5 shows TEM-bright micrograph of the heat 7 tempered at 650 °C with its corresponding X-ray energy dispersive spectrum. As it can be seen, only the cementite carbides are visible. Vanadium nitrides and carbonitrides have not beeen observed. Fig. 6 shows X-ray diffraction spectrum of the heat 7 which was tempered at 650 °C. Fe_3C and $VC_{0.88}$ precipitates were identified.

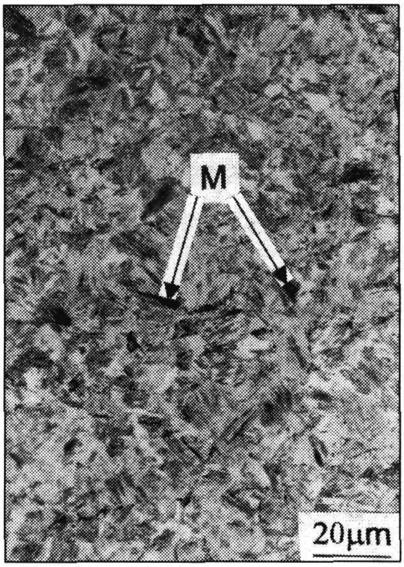

Fig. 3. Light microscope micrograph of the pipe specimen quenched in oil from 850 °C. M – lath martensite.

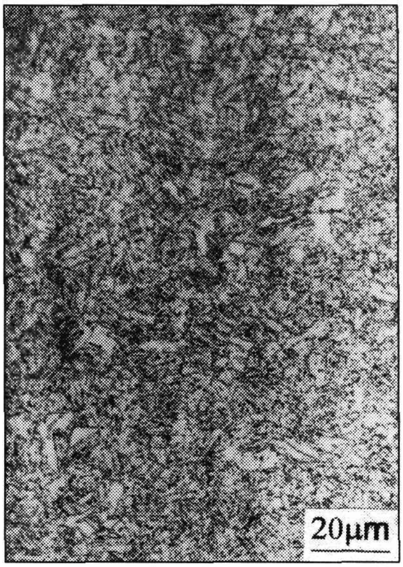

Fig. 4. Light microscope micrograph of the pipe quenched in oil from 850 °C and tempered at 650 °C in air.

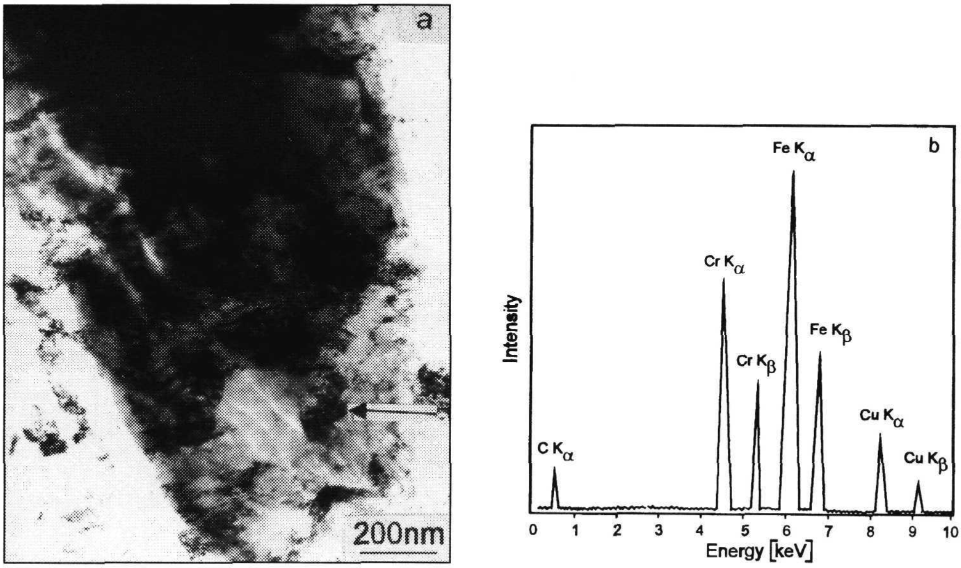

Fig. 5. TEM bright-field image (a) of the heat 7 after tempering at 650 °C with its corresponding X-ray energy dispersive spectrum of carbide (b) shown with arrow on Fig. 5a.

Mechanical properties of pipes after hot-rolling are given in Table 3. The yield strength of pipes increases with the increase in vanadium and nitrogen contents. Hot-rolled pipes had the yield strength from 568 to 689 MPa and a poor impact toughness at −20 °C (from 18 to 23 J/cm^2). To ensure a good combination of strength and toughness, the pipes were quenched and tempered. Mechanical properties of pipes after quenching and tempering are given in Table 4. As shown in Table 4, the desirable mechanical properties were obtained. Values of impact toughness from 47 to 82 J/cm^2 for these pipes probably ensure the resistance to the initiation of brittle fracture.

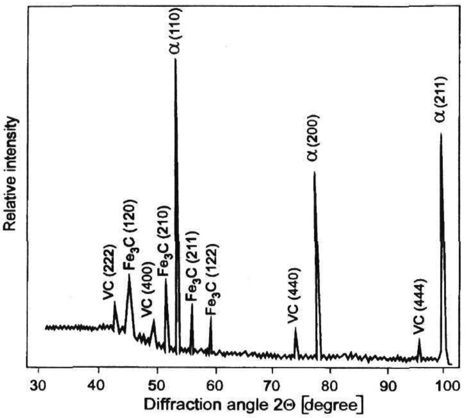

Fig. 6. X-ray diffraction spectrum of the heat 7 after tempering at 650 °C.

It is known that required mechanical properties can be obtained by modification of the chemical composition of steel, by rolling or controlled cooling of steel from finish-rolling temperature. Micro-alloying of steel is one of the acceptable ways to reach the aimed yield strength. In this work, a particular emphasis has been laid on the utilization of the effect of vanadium in combination with nitrogen. For the sake of complex evaluation of the results and especially for the evaluation of the effect of vanadium in association with nitrogen on the yield strength of the steels, it was necessary to eliminate the effect of other hardening factors. As seen in Table 1, the contents of carbon, manganese and silicon were within a narrow range. Thus, the effect of manganese and silicon can be neglected. The optimum utilization of vanadium and nitrogen

Table 3. Mechanical properties of pipes after hot rolling

Heat	Yield strength [MPa]	Tensile strength [MPa]	Elongation [%]	Impact toughness [J/cm^2]
1	568	721	23.4	27.1
2	582	755	20.7	23.7
3	598	773	20.1	20.7
4	631	759	23.4	23.0
5	650	821	19.6	21.4
6	676	831	21.8	20.0
7	689	839	16.4	18.7

can be ensured by correctly selected dissolution temperature of precipitates. The solubility of VN in austenite can be expressed by the following equation [16]:

$$\log[\mathrm{V}][\mathrm{N}] = -(8330/T) + 3.46. \qquad (1)$$

According to Eq. (1) vanadium nitride is fully soluble at the reheating temperature from 1250 to 1280 °C. The finish-rolling temperatures at the production of pipes for gas bottles varied from 850 to 920 °C. The temperature was not less than 850 °C during rolling of pipes, i.e. it was significantly above Ar_3-temperature (Table 2). The vanadium nitride and vanadium carbonitride were not present according to TEM observation (Fig. 5). Analysis of X-ray energy dispersive spectrum (Fig. 5b) showed that the carbides were rich in iron and chromium. Thus, only the cementite carbide (M_3C) was present. However, X-ray analysis (Fig. 6) showed that the Fe_3C and vanadium carbides ($VC_{0.88}$) were present in the ferrite matrix. It corresponded to the results achieved by Amin [17] who found out that for the steels with content of V above 0.14 wt.%, vanadium carbide was the main contributor to the precipitation hardening.

The precipitation hardening is strongly dependent on the contents of vanadium and nitrogen in the steels. The contribution of the precipitation hardening to yield strength of pipes in the hot-rolled state in relation with the total amount of vanadium and nitrogen is shown in Fig. 7. From the linear regression it can be concluded that for each 0.0150 wt.% (V+N) the yield strength of pipes increased

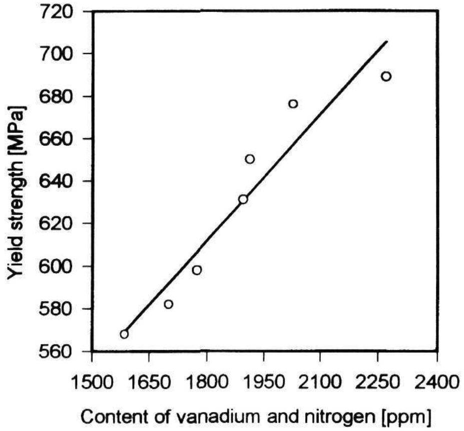

Fig. 7. The effect of vanadium and nitrogen contents on yield strength of pipes in hot-rolled state.

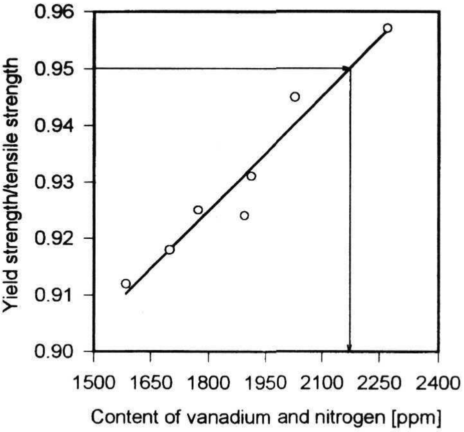

Fig. 8. The effect of vanadium and nitrogen contents on the yield /tensile strength ratio of pipes in quenched and tempered state.

Table 4. Mechanical properties of pipes after heat treatment

Heat	Yield strength > 630 MPa	Tensile strength 730–880 MPa	Ratio YS/TS < 0.950	Elongation > 14 %	Hardness HB	Impact toughness > 45 J/cm^2
1	720	789	0.912	17.5	239	79.6
2	741	807	0.918	17.6	234	74.1
3	765	827	0.925	17.5	255	67.0
4	775	838	0.924	17.3	249	79.8
5	769	826	0.931	18.5	255	82.5
6	770	815	0.945	18.0	249	79.3
7	783	818	0.957	17.3	255	47.0

YS/TS – the ratio of yield strength and tensile strength

by 30 MPa. As seen from the data of the pipes quenched from 850 °C in oil and tempered at 650 °C followed by cooling in air, the required mechanical properties were obtained (Table 4). The strong effect of the total amount of vanadium and nitrogen on the yield/tensile strength ratio was recognized. A regression analysis carried out over the composition range of the seven different heats indicates that for an yield/tensile strength ratio lower than 0.95, the total amount of vanadium and nitrogen should be below 2200 ppm (Fig. 8).

5. Conclusion

The results of the investigation of low-alloyed manganese steels with different amounts of vanadium and nitrogen can be summarized as follows:

1. Analysis of the seven various heats of steel pipes in hot-rolled state has shown that for each 0.0150 wt.% (V+N) the yield strength increased by 30 MPa.
2. The lath martensite microstructure was obtained by quenching steel pipes in oil.
3. Tempering of steel pipes at 650 °C for 45 minutes followed by air cooling resulted in the tempered martensite microstructure. In this case, Fe_3C and VC particles in the ferrite matrix were identified.
4. After quenching of pipes in oil from 850 °C and tempering at 650 °C followed by cooling in air, the desirable mechanical properties were obtained.
5. To obtain the aimed yield/tensile strength ratio lower than 0.95 in quenched and tempered state, the total amount of vanadium and nitrogen should be below 2200 ppm.

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