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Evaluation of Mn-V Steel Tendency to Hydrogen Embrittlement

Ocjena sklonosti Mn-V čelika prema vodikovoj krtosti

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Recently great attention is given to investigations related to oil - and natural gas exploitation, especially from the aspect of material selection used for production of tubular equipment. In these conditions tubes destructions caused by mechanical damages are less frequent than destructions caused by various corrosion crack forms and especially corrosion cracks in sulphide conditions, with H_2S *as a dominant component. Results of mechanical properties and evaluation of tendency of seamless tubes in as rolled and heat treated condition, produced from medium-carbon Mn-V steel to hydrogen embrittlement by method of cathode polarization at the constant current density of 4.0 mA/cm*^{2} *are presented in this paper besides the above stated possible tube destruction forms in the conditions of oil - and natural gas exploitation. The fractographic analysis of fractured samples surfaces after cathode polarization was also performed by scanning electron microscope. It was found that tubes in the as rolled condition (no heat treatment) show great tendency to hydrogen embrittlement with the values of the calculated embrittlement index of 86.4%. By normalization (900° C/30 min. air) of tubes, resistance to hydrogen embrittlement was not improved compared with the as rolled condition. The heat treatment (quenching + tempering) resulted in a great resistance of tubes to hydrogen embrittlement with the calculated embrittlement index of 25.1%. The stated results are proved by the fractographic analysis of morphology of fractures that are explicitly brittle for tubes without heat treatment, but tough for quenched and tempered tubes. Therefore it can be concluded that from the aspect of mechanical properties and corrosion resistance the most suitable tubes for use in the oil - and gas wells are those quenched and tempered at high temperatures (700° C).*

Danas se u svijetu velika pažnja poklanja istraživanjima vezanim uz problematiku eksploatacije nafte i zemnog plina, posebno s aspekta izbora materijala koji se koriste za izradu cijevne opreme. Propadanja cijevi u tim uvjetima uslijed mehaničkih oštećenja su manje često nego propadanja uslijed različitih oblika korozijskih raspucavanja, a posebno korozijskog raspucavanja u sulfidnim uvjetima gdje je H_2S *dominantna komponenta. U radu su pored navedenih mogućih oblika oštećenja cijevi u uvjetima eksploatacije nafte i zemnog plina prikazani rezultati mehaničkih svojstava kao i ocjena sklonosti valjanih i toplinski obrađenih bešavnih cijevi iz srednjeugljičnog Mn-V čelika prema vodikovoj krtosti metodom katodne polarizacije kod konstantne gustoće struje od 4.0 mA/cm*^{2}*. Također je provedena na scanning elektronskom mikroskopu i fraktografska analiza prelomnih površina uzoraka nakon katodne polarizacije. Utvrđeno je da cijevi u valjanom stanju (bez toplinske obrade) pokazuju veliku sklonost prema vodikovoj krtosti s vrijednostima izračunatog indeksa krtosti od 86.4%. Normalizacijom (900° C/30 zrak) cijevi otpornost na vodikovu krtost nije se poboljšala u usporedbi s valjanim stanjem. Međutim toplinskom obradom (kaljenje + popušatnje) postignuta je velika otpornost cijevi prema vodikovoj krtosti s izračunatim indeksom krtosti od 25.1%. Navedene spoznaje dokazuje i fraktografska analiza morfologije preloma koji su za cijevi bez toplinske obrade izrazito krti cijepajući dok su žilavi za zakaljene i popuštene cijevi. Prema tome, ovaj rad dokazuje da su s aspekta mehaničkih svojstava i korozijske otpornosti za primjenu u naftnim i plinskim bušotinama najpogodnije cijevi koje su zakaljene i popuštene na visokim temperaturama (700° C).*

1 Introduction

Due to ever increasing demand for energy a great attention is given to investigations related to problems connected to oil and natural gas exploitation, especially to the selection of material for tubular equipment. Thirty five years ago medium quality steels having 400 MPa yield strength were used for tubes and pipes in natural gas and oil exploitation from 1000–3000 meters depths. Nowadays the exploitation proceeds not only in higher depths (10 000 m) but in more severe conditions also because of the presence of highly corrosive acidic gas (H_2S, CO_2), chlorides, high pressure and temperature, etc. Therefore, material for tubular ware have to satisfy high requirements for both mechanical and corrosion properties.

Cracking of tubular equipment in the presence of sulphide is particularly frequent corrosion phenomenon. The selection of appropriate steel and the heat treatment of final goods to obtain optimal compromise of mechanical and corrosion properties are used as countermeasure[1-6].

Different possible tube damage in oil and natural gas exploitation with special emphasis on SSCC (sulphide stress corrosion cracking) as a form of hydrogen embrittlement is described.

Samples made from hot rolled seamless tube manufactured from medium carbon low alloyed Mn-V steel were investigated. Cathodic polarization following heat treatment carried out under laboratory conditions was used to determine susceptibility to hydrogen embrittlement and evaluate corrosion properties.

2 Forms of oil pipe damage

Tubes and pipes used in natural gas and oil exploitation are known as Oil Country Tubular Goods (OCTG). OCTG is divided into tubing, casing and drill tube used in vertical direction for pumping, external protection and drilling, respectively. In a wider sense OCTG includes also pipe line used for transport purposes mainly in horizontal direction.

Despite complex stresses pure mechanical failure is less frequent as compared to corrosion failure. Economic operation of oil wells is often dependent on proper selection of tube material. The control of corrosion has become one of main factors in the production of energy from geoenergetic sources. Corrosion failure of natural gas and oil exploitation equipment is very serious problem from safety as well as economic viewpoint since the costs in oil industry amount to several hundreds millions of US$ per year. Material failure due to corrosion is also associated with production breaks. Corrosion problems in oil and gas explotation equipment[7-10] can appear in several forms:

- weight loss due to corrosion,
- localized corrosion known as pitting,
- corrosion fatigue,
- galvanic corrosion,
- stress corrosion and
- sulphide stress corrosion cracking (SSCC)

Stress corrosion cracking caused by sulphide is very frequent since typical oil and gas exploitation environment besides chlorides, sulphates, carbonates, CO_2 and moisture contains considerable amount of H_2S also which can reach up to 30%. Hydrogen sulphide attack increases general corrosion, erosion corrosion in turbulent media, stress corrosion cracking, corrosion fatigue of tubes and equipment at bottom of drilled wells etc. Stress corrosion cracking in the presence of sulphide may appear in two forms:

- hydrogen induced cracking (HIC)
- sulphide stress corrosion cracking (SSCC)

Hydrogen induced cracking is characteristic for OCTG equipment made from low alloyed steel with ferrite—perlite microstructure and 700 MPa tensile strength. It can occur even in the absence of external stress. This form of corrosion results from atomic hydrogen absorbed on microstructural defects (hydrogen traps) which recombines into molecular hydrogen.

Sulphide stress corrosion cracking occurs in OCTG equipment made from high strength steel as a form of hydrogen embrittlement. Hydrogen embrittlement has been well known and frequently observed in metals for quite a long time. It is caused mostly by corrosion, galvanisation or leaching associated with the generation of atomic hydrogen which under certain conditions can diffuse into crystalline lattice resulting in the hydrogenization of metal.

In the beginning the effect of hydrogen was attributed to stress corrosion. Recently the similarity between hydrogen embrittlement and certain types of stress corrosion, particularly SSCC[8-10] has been pointed out.

There is no unique theory capable of explaining all phenomena associated with hydrogen attack because it depends on a number of factors e.g. type of steel, its microstructure, electrolyte, etc. At present, the proposed mechanisms of hydrogen attack are based on increase in the inner pressure, surface adsorption, decohesion, increase or decrease in plasticity and the formation of hydride[11]. Acidic environment in natural gas and oil exploitation enhances hydrogen embrittlement and SSCC as its particular form because of

- the presence of H_2S at low pH value of media,
- sulphides which increase the amount of hydrogen diffusing into the crystalline lattice of metal and
- tendency for the localization of anodic part of corrosion reaction which promotes initial cracks.

There are two sources of atomic hydrogen; the inner generated by manufacture and heat treatment of steel and the exterior resulting from the effect of definite environment. During application of material hydrogen may be adsorbed from gaseous phase in molecular form with subsequent dissociation into atoms or by electrochemical dissolving of liquid phase i.e. surrounding corrosive media which takes place during the exploitation. In this case hydrogen is formed in molecular or atomic form. The overall reaction of hydrogen formation is

in acidic solutions:

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O \quad (1)$$

in caustic solutions:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

The transport of H_3O^+ ion (from now on H^+) or H_2O molecule to electrode surface and subsequent formation of adsorbed hydrogen atoms can be described by (3) and (4):

$$H^+ + e^- \rightarrow H_{ads} \quad (3)$$

$$H_2O + e^- \rightarrow H_{ads} + OH^- \quad (4)$$

Irrespective on the nature of solution, hydrogen is adsorbed on metal electrode surface. To be continuous the electrochemical process requires permanent presence of H_{ads} on electrode surface from where it can be removed in one among three ways[12,13]:

- by catalytic recombination (Volmer-Tafel's mechanism) where both the adsorption and desorption take place simultaneously:

$$H^+ + e^- \rightarrow H_{ads} \quad (5)$$

$$H_{ads} + H_{ads} \rightarrow H_2 \quad (6)$$

- by Volmer-Heyrowski's mechanism of electrochemical desorption where desorption results from the reduction

Table 1. Chemical composition of the Heat (T) and billet (K)

Steel	Sample	Composition in wt. %								
		C	Mn	P	S	Si	V	Mo	Al	Cr
Mn-V	T	0.33	1.10	0.017	0.004	0.23	0.21	-	0.027	-
	K	0.33	1.14	0.025	0.005	0.29	0.23	0.02	0.04	0.08

of H^+ ion or H_2O molecule according to (7), (8) and (9):

$$H^+ + e^- \rightarrow H_{ads} \quad (7)$$
$$H^+ + H_{ads} + e^- \rightarrow H_2 \quad (8)$$
$$H_2O + H_{ads} + e^- \rightarrow H_2 + OH^- \quad (9)$$

- by emission mechanism where adsorbed hydrogen atoms vaporize from electrode surface:

$$H_{ads} \rightarrow H \quad (10)$$

Consequently, hydrogen atoms adsorbed on the surface (H_{ads}) can recombine into either harmless gaseous hydrogen through (6) which is bubbled out of solution or diffuse into metal and enhance embrittlement:

$$H_{ads} \rightarrow H_{abs}$$

It can be concluded that sulphide stress corrosion cracking is caused by absorbed hydrogen. The dissolving of iron and the presence of H_2S in water solution create conditions for increase in hydrogen content of steel[14]. Usually, only a small part of hydrogen generated on cathode diffuses into metal. Diffusion rate depends on numerous factors, e.g. the type of steel or alloy, its composition and previous thermo-mechanical treatment, nature of electrode surface, type of electrolyte, its composition, cathode current density, etc.

Hydrogen embrittlement is often used in evaluation of the effect of hydrogen on steel at room temperature which results in a loss of ductility (reduction in elongation and contraction), decrease in tensile strength and enhanced brittleness.

3 Experimental

Mn-V steel billet of ⌑ 135 · 420 mm dimensions was produced under laboratory conditions on Metallurgical Institute Hasan Brkić, Zenica. The billet was hot rolled into ϕ60.3 · 4.83 mm pumping oil tube (tubing) under industrial conditions in Seamless Tube Mill of Željezara (Iron and Steelworks) Sisak. **Table 1** presents Heat (T) and a control (K) analysis of the steel.

Samples cut from rolled tube were subjected to heat treatment (annealing, annealing + tempering, quenching + tempering) in electric resistance chamber furnace. Investigation of mechanical properties were carried out on INSTRON type 1196 machine using samples prepared according to ASTM standard. Brinell or Rockwell C hardness was determined depending on the sample hardness.

Corrosion resistance was measured by the method of cathodic polarization which is known as one among the most appropriate for determination of relative susceptibility to hydrogen embrittlement. After cleansing with acetone the samples for cathodic polarization were put in the electrochemical cell of ZWICK 50 kN tensile machine (**fig. 1**) and subjected to static load of 80% of yield stress.

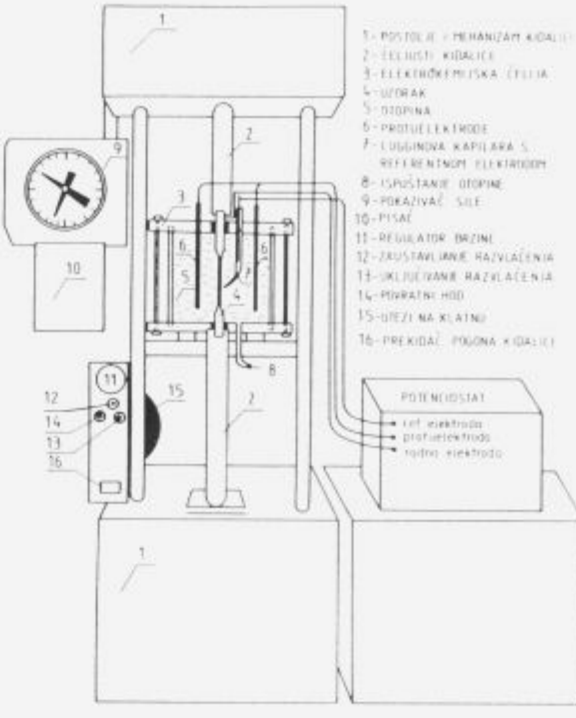


Figure 1. Schematic illustration of equipment for hydrogen embrittlement evaluation by cathodic polarization method.
Slika 1. Shematski prikaz aparature za ocjenu vodikove krtosti metodom katodne polarizacije.

Sample of Mn-V steel was used for working electrode and saturated calomel electrode (SCE) situated in Luggin's capillary tube as a reference. Two graphite Johnson Matthey electrode of 6.5 mm diameter were used as counter electrode.

The solution used was 1N H_2SO_4 with addition of 10 mg/l As_2O_3 used to activate the generation of H_{ads}. The solution was deaerated by nitrogen blowing for 30 min.

For cathodic polarization WENKING potentiostat modell 68 FR 0.5 was used and constant 4 mA/cm^2 current density was applied. After 2 hours of polarization samples were taken out of the cell and immediately tested on INSTRON machine at very low deformation rate of $2.4 \cdot 10^{-4} s^{-1}$. The overall tensile test lasted for 3–4 mins. Afterward the cross section of fractured surface was measured to determine the contraction. Due to the loss of ductility (contraction) embrittlement index F was calculated from:

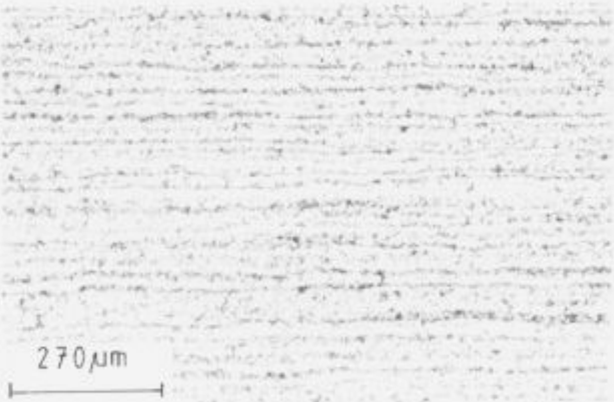
$$F = \frac{Z_0 - Z_1}{Z_0} \cdot 100$$

where:

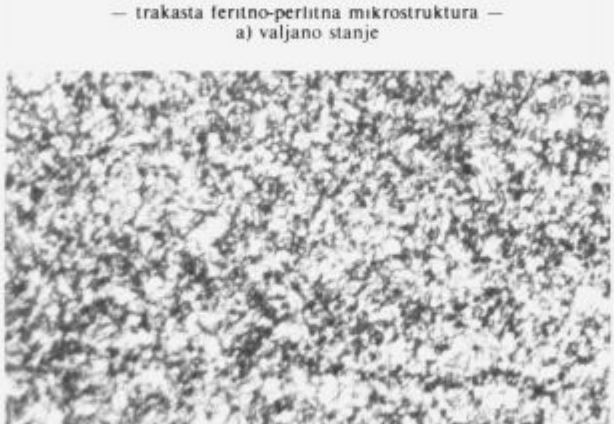
Z_0 contraction before polarization
Z_1 contraction after polarization

Table 2. Results of mechanical testing of Mn-V steel tube samples in as rolled and heat treated state.

Sample	Heat treatment	R_e MPa	R_m MPa	A_2" %	Hardness, HB; I	II	III	IV	API grade
2	-	605.5	759.5	25.5	216	216	211	213	L-80
20	900°C/30' air + 670°C/60' air	535.0	657.0	24.6	222	215	229	235	J-55
21	870°C/30' water + 640°C/60' air	794.0	836.0	21.2	276	278	276	278	P-105
23	870°/30' water + 700°/60' air	692.0	723.0	23.4	232	234	255	231	C-90



— trakasta feritno-perlitna mikrostruktura —
a) valjano stanje



— popušteni martenzit —
b) K: 870°C/30 voda + P: 700°C/60 zrak

Figure 2. Microstructure of tubing Mn-V steel in rolled (a) and heat treated (b) condition.
Slika 2. Mikrostruktura cijevi iz Mn-V čelika u valjanom (a) i toplinsko obrađenom (b) stanju.

4 Results

Results of mechanical and metallographic investigation

Investigation of mechanical properties (tensile strength, yield stress and strain) were carried out on two tube samples in as rolled state and another two in heat treated state. Ring-like $\phi 60.3 \cdot 4.83 \cdot 30$ mm samples were used for Brinell or Rockwell C (for quenched samples) hardness measurement using three impressions per quadrant (in the middle of sample wall). Average values of mechanical properties for as rolled and different heat treated state are seen in **table 2**.

Mechanical properties of Mn-V steel tubes in as rolled state i.e. without heat treatment correspond to L-80 API grade of corrosion resistant OCTG wares. Annealing treatment (900°C/30' in air) followed by tempering at 670°C produces lower quality OCTG wares with mechanical properties correponding to J-55 API grade. Quenching in water coupled with subsequent tempering at 640°C yields OCTG wares of higher mechanical properties (P-105 grade) which are not desired because of poor resistance to SSCC, i.e. a high susceptibility to hydrogen embrittlement. However, tempering at 700°C results in API C-90 grade corresponding to corrosion resistant OCTG wares.

Mechanical properties measured are in accordance with corresponding microstructures as can be seen on **fig. 2.**

Results of cathodic polarization tests

Since the determination of susceptibility to hydrogen embrittlement by catodhic polarization is based on the loss of ductility caused by absorbed hydrogen, samples were subjected to tensile test with $2.4 \cdot 10^{-4} s^{-1}$ deformation rate immediately after the polarization. Embrittlement index F was calculated from equation (11) taking into account contraction measured before (Z_0) and after (Z_1) polarization. The results are given in **table 3.**

Histograms given on **figs. 3** and **4** present the change in contraction and embrittlement index, respectively for as rolled and heat treated Mn-V steel sample caused by cathodic polarization. Samples in as rolled state and that in annealed state show high susceptibility to hydrogen embrittlement i.e. a great decrease in contraction (**fig. 3**) and high index of embrittlement (**fig. 4**). Samples annealed and subsequently tempered at 670°C have significantly lower embrittlement ($F = 28.1\%$ only).

The best resistance to hydrogen embrittlement ($F = 25.1\%$) have samples which were quenched and tempered at 700°C because of highly tempered martensite microstructure as seen in **fig. 2b.** Fracture surface of samples after cathodic polarization was analysed by electron scanning microscope as seen in **fig. 5.** Fracture surface of Mn-V steel samples in as rolled state after cathodic polarization

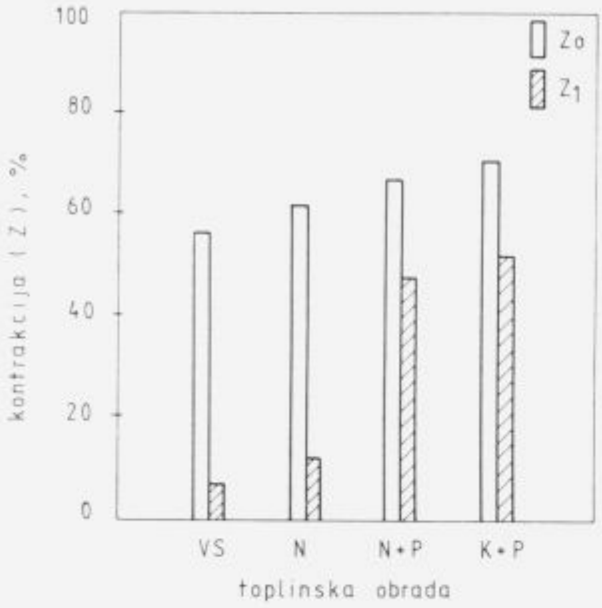


Figure 3. Concentration change resulting from cathodic polarization of Mn-V steel in different heat treatment conditions VS-rolled. Heat treatment

- N: 900°/30' air
- N + P 900°/30' air + 670°/60' air
- K + P: 870°/30' water + 700°/60' air

Slika 3. Promjena kontrakcije uslijed katedne polarizacije za različita stanja toplinske obrade Mn-V čelika. VS—valjano stanje. Toplinska obrada

- N: 900°/30' zrak
- N + P 900°/30' zrak + 670°/60' zrak
- K + P: 870°/30' voda + 700°/60' zrak

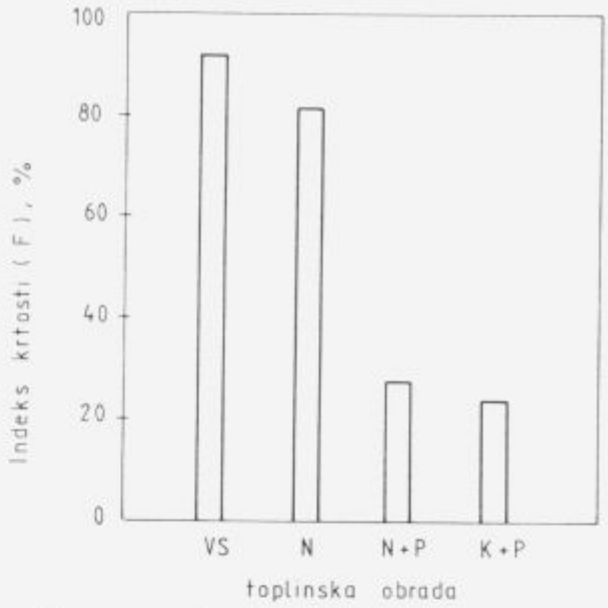


Figure 4. Embrittlement index change resulting from cathodic polarization of Mn-V steel in different heat treatment conditions VS—rolled. Heat treatment

- N: 900°/30' air
- N + P 900°/30' air + 670°/60' air
- K + P: 870°/30' water + 700°/60' air

Slika 4. Promjena indeksa krtosti uslijed katodne polarizacije za različita stanja toplinske obrade Mn-V čelika. VS—valjano stanje. Toplinska obrada

- N: 900°/30' zrak
- N + P 900°/30' zrak + 670°/60' zrak
- K + P: 870°/30' voda + 700°/60' zrak

shows typical brittle fracture (**fig. 5a**) whereas quenched and highly (700°C) tempered samples show ductile fracture (**fig. 5b**) corresponding to a low index of embrittlement (**fig.** 4).

5 Discussion

Despite the fact that mechanical properties of Mn-V steel seamless tube samples in as rolled state correspond to API L-80 grade of corrosion resistant OCTG wares, the cathodic polarization at 4.0 mA/cm^2 current density displayed great susceptibility to hydrogen embrittlement. As a result of cathodic polarization the contraction dropped from initial (as rolled state) 56.9% to 7.7% corresponding to embrittlement index $F = 86.4\%$ (figs. 3 and 4). The susceptibility to hydrogen embrittlement of Mn-V steel tubes in as rolled state is also seen (fig. 5a) from brittle fracture surface. It results from strip like ferrite-perlite microstructure with elongated inclusions (fig. 2a) which is favorable for accumulation of the critical amount of hydrogen required for the initiation of cracking. From the viewpoint of resistance to SSCC viz. hydrogen embrittlement, elongated sulphide inclusions (especially MnS which act as hydrogen trap) and high tendency for segregation of manganese (martensite and bainite islands observed in microstructure) are unfavorable and have a dominant influence on corrosion resistance of Mn-V steel in as rolled state.

The annealing treatment carried out (900°C/30' air) on tested tubes did not improve the resistance to hydrogen embrittlement since strip like ferrite-perlite structure with prevailing influence of MnS inclusions acting as hydrogen traps was preserved. On the contrary, tempering (670°C/60' air) of annealed tubes resulted in considerable increase of the resistance to hydrogen embrittlement since martensite and bainite islands were removed. In respect to mechanical properties the heat treatment combined of quenching and tempering at temperatures within 640–700°C range yielded J-55, P-105 and C-90 (table 2) API grades. Cathodic polarization test of tubes corresponding to API C-90 grade showed high resistance to hydrogen embrittlement with only 25.1% reduction in contraction. The obtained high resistance to hydrogen embrittlement is illustrated also by fig. 5b showing ductile nature of fracture surface.

As compared to samples in as rolled state the microstructure of heat treated sample tubes of Mn-V steel instead of bands of ferrite-perlite was composed of homogeneous highly tempered martensite marked by high ductility and capacity for accumulation of higher amounts of energy generated e.g. by Zappfe's mechanism[11] of hydrogen embrittlement. Since MnS was observed in heat treated samples also, it is evident that highly tempered martensite reduces harmful influence of MnS on corrosion properties of OCTG wares.

Table 3. Loss of ductility of Mn-V steel as determined by the method of cathodic polarization.

Sample	Heat treatment	R_e MPa	Applied stress	Z_0 %	Z_1 %	i mA/cm^2	F %
2-3	-	599.1	0.8 R_e	56.9	7.7	4.0	86.4
20N-4	900°C/30'air	594.5	0.8 R_e	61.1	10.9	4.0	82.0
20-5	900°C/30' air + 670°C/60' air	519.4	0.8 R_e	67.2	48.3	4.0	28.1
23-4	870°C/30' water + 700°C/60' air	681.8	0.8 R_e	70.1	52.5	4.0	25.1

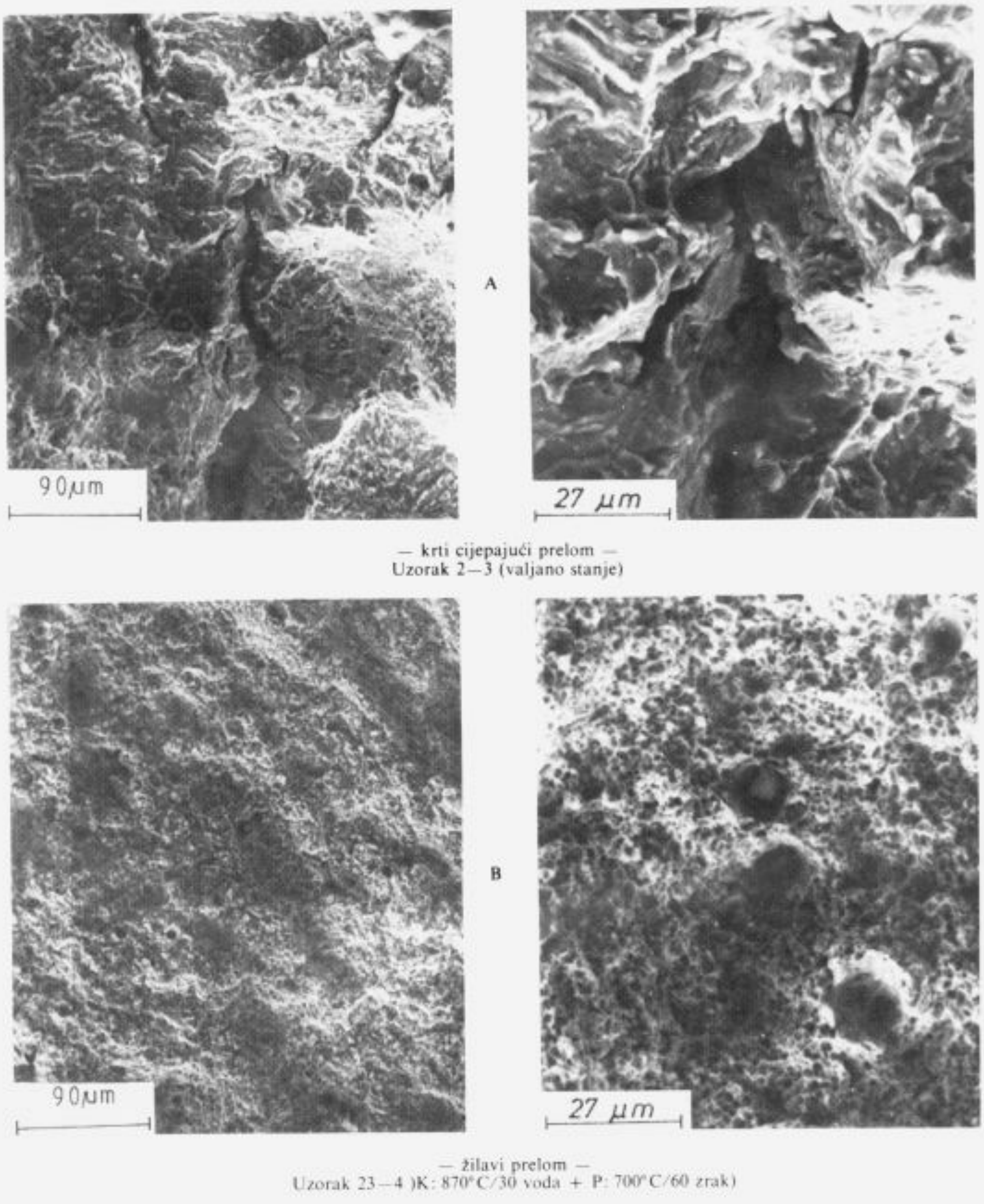


Figure 5. Fracture morphology of specimens form Mn-V steel in rolled (a) and heat treated (b) condition after cathodic polarization.

Slika 5. Morfologija preloma uzoraka iz Mn-V čelika u valjanom (a) i toplinsko obrađenom (b) stanju nakon katodne polarizacije.

Summary

Based on the investigation of susceptibility to hydrogen embrittlement of seamless Mn-V steel tubes utilized in natural gas and oil industry the following conclusions can be derived.

- Mechanical properties of Mn-V steel tubes in as rolled state with higly oriented ferrite-perlite microstructure correspond to L-80 API grade.
- Beside J-55 and P-105, C-90 API grade conforming to corrosion resistant OCTG wares was also attained by heat treatment (annealing + tempering, quenchung + tempering) of tubes.
- Cathodic polarization of tubes in as rolled state showed small resistance to hydrogen embrittlement since embrittlement index F was 86.4%.
- The resistance to hydrogen embrittlement was not improved by annealing (900°C/30' air) ($F = 82.0\%$) as compared to as rolled state.
- Based on brittle fracture surface revealed by fractographic analysis of samples subjected to cathodic polarization it was established that Mn-V steel tubes in annealed or as rolled state are not suitable for the use in oil industry.
- High resistance to hydrogen embrittlement proven by comparatively small embrittlement index ($F = 25.1\%$) and ductile nature of fracture surface was acquired by quenching and tempering at a high temperature (700°C).
- In respect to both mechanical and corrosion properties Mn-V steel tubes quenched and temepered at a high temperature are suitable for the use in natural gas and oil wells.