

## INFLUENCE OF THERMAL TREATMENT ON STRUCTURE AND CORROSION PROPERTIES OF HIGH MANGANESE TRIPLEX STEELS

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In this paper corrosion properties of X70MnAl28-9 TRIPLEX steel were tested after hot rolling and subsequent aging at 500 °C for 6, 30 and 60 min. and at 600 °C for the same times. For comparison related steels (X100MnAl28-12, X70Mn22, C20) were also used. The microstructure was characterized by light microscopy, SEM, energy dispersive X-ray microanalysis. The corrosion behaviour of steels was examined by light and scanning electron microscopy, electrochemical techniques (potentiodynamic polarization method, linear polarization, using NaCl and H<sub>2</sub>SO<sub>4</sub> water solutions), salt spray test and gravimetric method. Aging has relatively small influence on corrosion resistance of X70MnAl28-9 steel. The localized corrosion in relation to structure and phases is discussed and compared in terms of dissolution, pitting and changes in chemical composition.

*Key words:* triplex steels, structure, corrosion, polarization tests

### INTRODUCTION

The increasing requirements of automotive (transport) industry have resulted in development of steels with a higher strength properties and high plastic deformability. Several types of steels have been developed and recommended for different part of cars with high energy absorption capability in case of accident [1,2]. From Hadfield and TWIP (twinning-induced plasticity) steels have been developed high manganese TRIPLEX steels.

The advanced TRIPLEX steels contain 25-30 % Mn, 6 – 12 % Al and 0,6-1,2 % C (wt. %). The structure of triplex is characterized by stable austenitic phase with higher stacking fault energy (100-120 mJ/m<sup>2</sup>) and very fine coherent  $\epsilon$ -carbides (FeMn)<sub>3</sub>AlC with fcc L1<sub>2</sub> type structure, dispersed in matrix [3]. Small volume fraction (5 – 10 %) of  $\delta$ -ferrite can be also formed in structure after rolling. High manganese steels show higher strength values ( $R_m=1100$  MPa) and simultaneously high plasticity ( $A=60$  %). The advantage of stated steels is higher absorption energy ( $E_s=0,4-0,5$  J/mm<sup>3</sup>) and lower density (6,5-7,5 Mg/m<sup>3</sup>) as compared with commercial carbon steel.

The mechanical properties and corrosion resistance of X50Mn22 (TWIP) steel after heat treatment and forging has been studied in work [4]. After exposition in 3,5 % NaCl water solution the corrosion was revealed primarily in deformation twins interfaces. The fine grain size and the boundaries of deformation twins, acting as numerous

trapping sites, are favourable for a lower local corrosion penetration and better corrosion resistance.

The corrosion resistance tests were carried out on two similar high-manganese steels X7MnSiAlNbTi26-3-3 and X5MnSiAlNbTi24-3-2 with a different structure in aqueous sulphur acid solution [5]. The steel of higher aluminium concentration has a single-phase austenitic structure with many annealing twins and the second contains some fraction of martensitic phases of lamellar morphology. Higher mass decrement of first steel is probably a result of the lower aluminium content compared to second steel. The decisive influence on corrosion resistance of examined steels has their chemical composition, which determines high rate of Mn and Fe dissolution in acidic media, i.e. general corrosion and formation of pitting [5].

The electroless coating Ni-P were used to enhance the corrosion resistance of TWIP (Fe-25Mn, Fe-25Mn-3Al) steels. The potentiodynamic polarization tests in 3,5 % NaCl and 0,1 M H<sub>2</sub>SO<sub>4</sub> showed that Ni-P coating significantly improved the corrosion resistance in both media [6]. The local galvanic corrosion is possible between base material and more noble coating. There is possibility of application of new coatings (Ni-Cr, Cr<sub>3</sub>C<sub>2</sub>) resistant to corrosion and wear of parts [7].

The aim of the work is comparison of structure and corrosion resistance of TRIPLEX steel X70MnAl28-9 after aging.

### STEELS AND EXPERIMENTAL METHODS

For corrosion tests TRIPLEX steel of composition (wt. %): 0,70 % C, 28 % Mn, 8,6 % Al (at. %: 2,9 % C,

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25,4 % Mn, 15,9 % Al) was used. The samples of steel plate were prepared in the state after hot rolling (1 100 °C – 920 °C) and after aging at temperature 500 °C for 6 min., 30 min and 60 min, as well as at 600 °C for the same holding times (i.e. 5, 30 and 60 min.) with subsequent water cooling each sample. The scaled and rough surfaces of samples were wet ground by SiC paper (up to No. 1000 grain size), then cleaned and dried. The nominal dimensions of samples were 43 × 28 × 1,8 mm. For comparison purposes related steels (0,7 % C, 22 % Mn; 1,0 % C, 28 % Mn) and commercial carbon steels (C20, CSN 11 375, 11 523) were chosen. Surfaces of samples were prepared in a similar manner as in case of the first steel.

Potentiodynamic cyclic polarization test for pitting was performed according to standard [8] using 0,1 mol/l NaCl water solution at room temperature. Polarization measurements were performed using a potentiostat-galvanostat PGP201 and special corrosion cell with three-electrode connection. The corrosion potential values ( $E_{cor}$  or open circuit potential OCP) were measured before potentiodynamic test. Linear polarization test of uniform corrosion was conducted in 0,1 mol/l  $H_2SO_4$  under similar conditions as for NaCl solution.

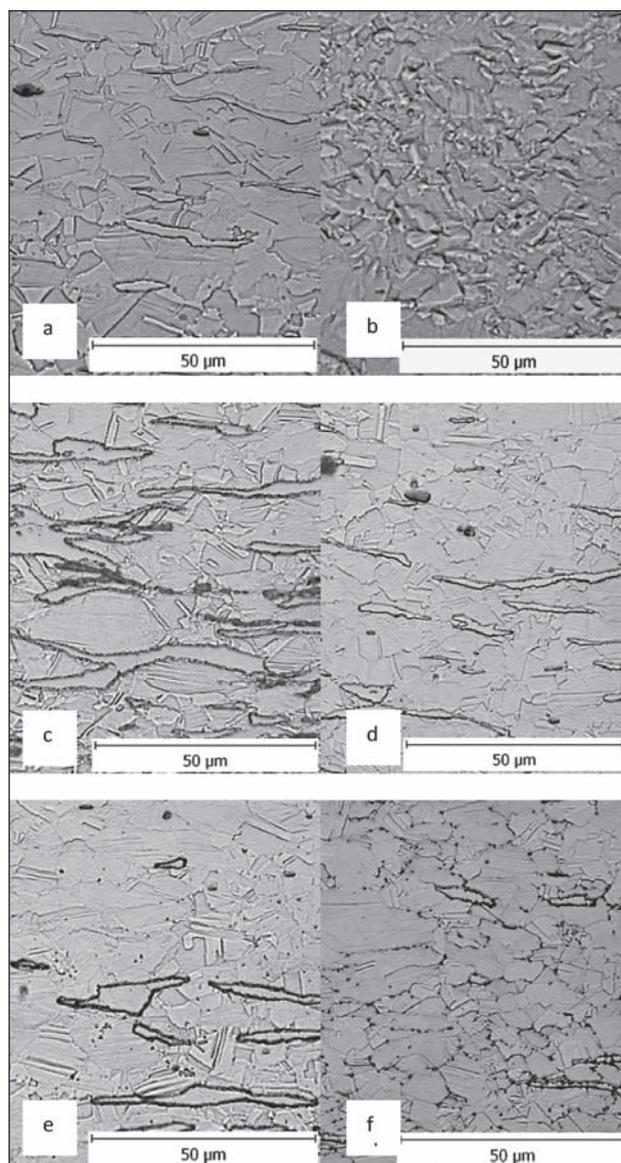
Sodium chloride containing water solutions are prescribed for corrosion testing of materials and surface layers for automotive parts. Neutral salt spray test was performed according to standard [9] in corrosion testing system LIEBISH S400 M-TR, where the samples were exposed for 6 and 12 hours. Gravimetric method was applied for comparison of corrosion rate. The surfaces and crosssections of specimens were observed after corrosion tests using light microscopy, scanning electron microscopy (SEM) and energy dispersed X-ray micro-analysis.

## RESULTS AND DISCUSSION

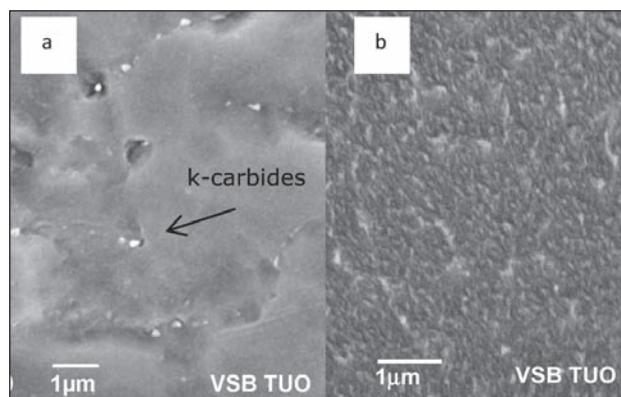
The structures of tested TRIPLEX steel are documented in Figure 1 (a-f), where after aging small particles (k-carbides) are preferentially found along the boundaries of ferrite and austenite. At higher aging temperature and/or for longer holding time,  $\delta$ -ferrite local content was lower and k-carbides had larger size (coarsening).

At very high magnification the carbides of dimension 10-100 nm dispersed in matrix were observed using electron microscope (Figure 2), probably along the border or edges of stacking faults and slip bands [10].

Based on measured polarization measurements and recorded curves (Figure 3) values of electrochemical corrosion parameters were determined:  $E_{cor}$  – corrosion potential,  $R_p$  – polarization resistance, which is inversely proportional to corrosion rate ( $r_c = B/R_p$ , B – constant),  $E_d$  – depassivation potential (for current density  $J_d = 100 \mu A/cm^2$ ),  $E_r$  – repassivation potential ( $J_r = 10 \mu A/cm^2$ ). In general, the higher values of pitting potentials ( $E_p$ ,  $E_r$ ) were found, the greater resistance to pitting corrosion was revealed. It is also necessary to consider the differ-



**Figure 1** Structure X70MnAl28-9 steel: a, b) after rolling, c) aging 500°C/6', d) aging 600°C/6', e) 500°C/60', 600°C/60'



**Figure 2** Structure after aging: a) 500°C/30', b) 500°C/60', k-carbides are white, light

ences between pitting potentials and corrosion ones that are  $E_d - E_{cor}$  and  $E_r - E_{cor}$ .

The differences in values of corrosion potential and polarization resistance are relatively small for tested samples with respect to dispersion, Table 1.

Table 1 Aging temperature and times of samples. Values of selected parameters

Sam. / No.	State Aging	$E_{cor}/$ mV	$R_p/$ k $\Omega$ cm <sup>2</sup>	$E_{cor}/$ mV	$R_p/$ $\Omega$ cm <sup>2</sup>
7	Rolled	-355	10,3	-611	31,0
11	500°C/6'	-447	16,7	-617	32,0
12	500°C/30'	-393	13,4	-616	29,8
13	500°C/60'	-362	4,55	-617	29,5
14	600°C/6'	-442	2,61	-611	29,6
15	600°C/30'	-472	4,99	-610	26,6
16	600°C/60'	-469	3,63	-624	22,1
	Solution	0,1 M NaCl		0,1 M H <sub>2</sub> SO <sub>4</sub>	

At aging conditions 600 °C/30-60 min, lowered  $R_p$  values were found out (at passive state in NaCl solution or active state in H<sub>2</sub>SO<sub>4</sub> one). Similar decreasing trend was registered in values of pitting potentials  $E_d$ ,  $E_p$ , see Figure 4, i.e. lowered resistance to pitting. Weight loss may characterize total extent of pitting corrosion.

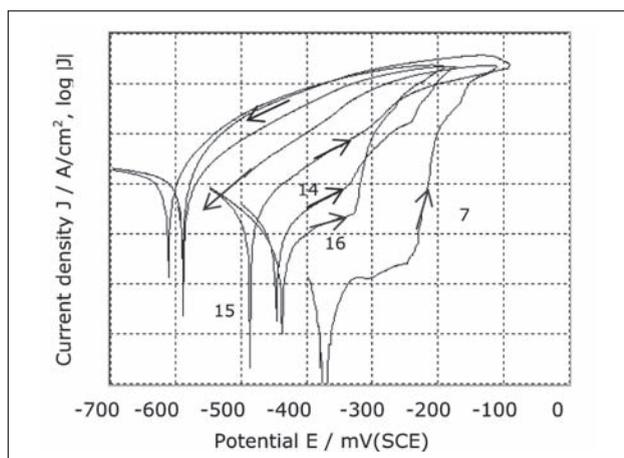


Figure 3 Typical potentiodynamic polarization curves of samples 7, 14-16, see Table 1

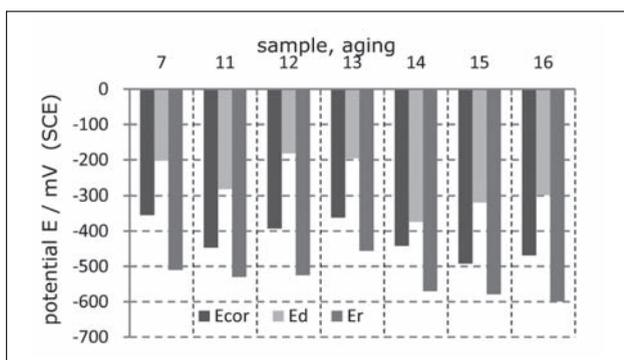


Figure 4 Comparison of pitting corrosion resistance

After 6 and 12 hours exposition in saline mist, the mass changes of TRIPLEX steel is 2-3 times lower as compared to carbon steels (Figure 5), which is explained by protective effect of aluminium.

Positive effect of Al and rather negative influence of Mn on corrosion is confirmed by comparative test with reference steels, Table 2. In this table compared steels are marked:

A - X70MnAl28-9, B - X100MnAl28-12, C - C20, D - X70Mn22.

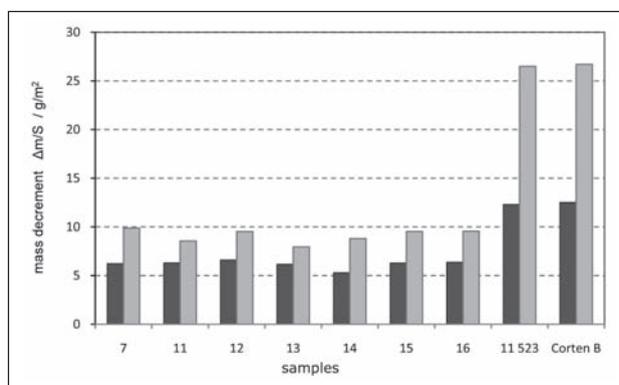


Figure 5 Comparison of general corrosion of tested steels by gravimetric method

The high manganese content and heterogeneous structure may reduce corrosion resistance in many environments. Aluminium can contribute to passivation of tested steel, but less than chromium. From testing is confirmed that primary are changes in chemical composition, secondary are changes in structure for corrosion behaviour, depending on redistribution of Mn, Al and C.

Table 2 Comparison of corrosion parameters of steels in solutions

steel	$\Delta m/S$ / g/m <sup>2</sup>	$-E_{cor}$ / mV	$-E_d$ / mV	$-E_r$ / mV	$-E_{cor}$ / mV	$R_p$ $\Omega^*$ cm <sup>2</sup>
A	9,1	423	265	538	613	31,2
B	7,8	424	258	454	614	38,3
C	15,3	493	431	528	515	-
D	16,1	710	674	705	557	23,7
	salt mist and NaCl solution			H <sub>2</sub> SO <sub>4</sub> solution		

Oval dimples were typically formed in all samples tested in salt mist, Figure 6. They mainly contain Al (20 – 30 %) and O (50-70 %), lower Fe and Mn amount ( $\leq 10$  %). The lighter upper layers contain Fe (30 – 50 %), O (30 – 40 %) and lower Mn, Al portion. In corrosion products were also detected Cl, Si, S, Ca, Na ( $\leq 5$  wt.). Similar chemical composition was confirmed by surface microanalysis of corrosion products.

The relation between aging parameters and maximum depth of pitting was difficult to find out on the

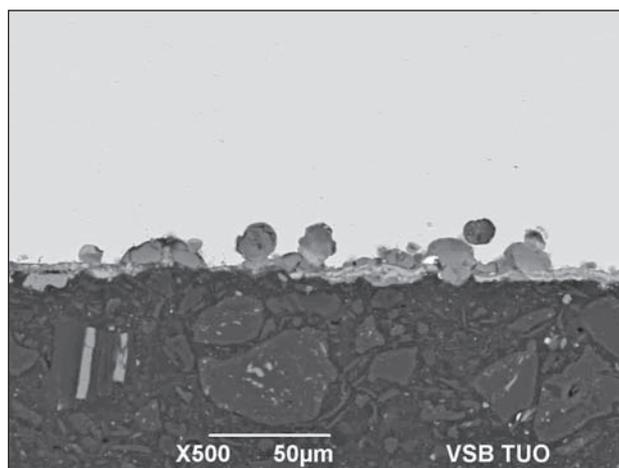


Figure 6 Corrosion of steel X70MnAl28-9, 500°C/6min, after salt spray test (SEM, signal BEC)

base of metallography sections. Local maximal pit depths were measured in the range of 20-120  $\mu\text{m}$  after salt spray test.

## CONCLUSION

Advanced TRIPLEX steels have higher strength and plastic properties and are perspective material for some automotive parts. Metallographic study and standard corrosion tests were performed on X70MnAl28-9TRIPLEX steel after aging (500 – 600  $^{\circ}\text{C}/6-60$  min). The differences in structure after aging have small influence on corrosion resistance changes in tested solutions (0,1 M NaCl, salt mist, and 0,1 M  $\text{H}_2\text{SO}_4$ ). Manganese shows detrimental influence on corrosion, aluminium increases corrosion resistance. The carbides or Al-depleted phases or areas are local places for initiation of pitting corrosion. TRIPLEX steel has higher corrosion resistance than compared TWIP (X70Mn22) or commercial steel (C20).

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**Note:** The translator for English language is Zdeněk Friedrich, Ostrava, Czech Republic