

COMPARISON OF CORROSION PROPERTIES OF AUSTENITIC STEEL X50MnAlNiCu27-7 AFTER ROLLING AND AGING

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Abstract

Austenitic steels with 20-30% Mn and 5-10% Al have a high level of ductility and toughness in comparison to carbon steels with similar strength level. The corrosion behavior of these steels can be negatively affected by high manganese content. The paper compares the corrosion properties of the two heats of high-alloy steels (X50MnAlNiCu27-7) developed in conditions after hot rolling and subsequent aging at 450°C for 20 and 60 minutes. Carbon steel (C10) sheet for comparative purposes was also tested. The corrosion resistance of steels and heat treatment effects were compared and assessed on the basis of potentiodynamic polarization measurements in NaCl water solution, setting parameters of pitting and uniform corrosion, and determining the corrosion potential and polarization resistance in a dilute sulfuric acid solution. Comparative neutral salt spray test and a gravimetric method were also used. Types of corrosion attack were assessed by microscopic observations. Small differences in chemical composition of melts or modification of steels (in tenths of % wt.) practically have not shown differences in their corrosion resistance. After aging, a slight decrease in corrosion mass losses compared to the state after hot rolling there was observed. In an acidic environment significantly lower values of the polarization resistance of X50MnAlNiCu27-7 steel compared with carbon one and a slightly lower corrosion potential were measured. It was confirmed a negative effect of manganese and a positive of aluminum on changes of corrosion resistance of said steels.

Keywords: high manganese steel, aging, corrosion resistance, polarization method, salt spray test

1. INTRODUCTION

The new high manganese (TRIPLEX) steels are perspective materials for vehicles structures and cryogenic temperature applications. These steels contain 0.5-1,0 % C, 20-30 % Mn and 5-15 % Al (wt.%) and their structure consist of austenitic phase with higher stacking fault energy and very fine coherent k-carbides, according to treatment. [1]. Small volume fraction of δ -ferrite in structure after rolling can be also formed. The advantage of stated steels is higher absorption energy and slightly lower density in comparison with commercial carbon steel. Higher corrosion rate of high manganese steels is connected with a lower value standard potential and without the ability of Mn to form protective layer. Manganese is often contained in sulfides and/or carbides, favoring certain types of localized corrosion. The corrosion resistance of high manganese steel (e.g. Fe-25Mn, Fe-25Mn-3Al) is a low and for protection Ni coating can be used [2]. The decisive influence on corrosion resistance of Mn steels (X7MnSiAlNbTi26-3-3, X5MnSiAlNbTi24-3-2) has their chemical composition, which determines the type and rate of dissolution in acidic media, i.e. general corrosion and formation of pitting [3]. Alloying with aluminium (5-12%) can improves corrosion resistance in some media, especially in oxidizing type, by formation of protective quasi-passive layer. On the other side, relatively higher aluminium content supports formation of inclusions (oxides Al_2O_3 , nitrides AlN) that reduce the plastic properties and toughness [4] and probably corrosion resistance.

Addition of Cu or Ni could contribute to corrosion resistance of high Mn steels in certain environments (e.g. non-oxidizing solutions).

The aim of this contribution is evaluation and comparison of corrosion resistance of steel X50MnAlNiCu27-7 after hot rolling and aging on the bases of electrochemical methods and exposure standard tests. For comparison purposes low carbon steel (C10) was also used.

2. MATERIAL AND TESTING METHODS

2.1 Manganese steel X50MnAlNiCu27-7

For corrosion tests samples of austenitic steel containing 0.50% C, 27% Mn, 7 % Al, 1% Ni and 0.5-1% Cu were prepared, see **Table 1**. Dimensions of samples were approximately 41 x 22 mm, thickness 1.5 mm. List of the samples and their identification is shown in **Table 2**. Commercial carbon steel C10 (CSN 411321, C ≤ 0,10 %, Mn ≤ 0,45 %, sheet 1,0 mm) was also tested as a reference material.

Table 1 Chemical composition of X50MnAlNiCu27-7 steel (wt. %)

steel No.	C	Mn	Al	Si	P	S	Cu	Ni	Fe	heat No.
S 4	0.50	27.0	7.0	0.4	0.015	0.017	1.03	0.90	Bal.	1074
S 6	0.50	26.8	7.1	0.33	0.012	0.022	0.50	1.0	Bal.	1076

The samples of steel plate were prepared in the state after hot rolling (cca 1 100°C ~ 900°C) and after aging at temperature 450 °C for 20 min. and 60 min. with subsequent cooling on the air. The scaled and rough surfaces of samples were then wet ground by SiC paper (up to No. 1200 grain size), cleaned in alcohol and drayed. Surfaces of reference samples of low carbon steel C10 were prepared in a similar manner as in case of the Mn-Al steel.

Table 2 Marking and treatment of samples

steel	Rolling state	Aging 450°C / 20 min	Aging 450°C / 60 min	note
S 4	A 4, B 4	A42, B42	A44, B44	sample
S 6	A 6, B 6	A62, B62	A64, B64	sample

The structure of steel consists of austenitic matrix with small islands of ferrite and submicroscopic k- carbides (FeMn)₃AlC that are larger after aging and contribute to increasing of hardness and strength. These carbides could cause initiation of pitting. More details about structure and properties of related Mn-Al steels are published in research papers [4-6].

2.2 Corrosion tests

The corrosion potential (E_{cor}) values were determined firstly and then polarization measurement was started from approx. 50 mV below value E_{cor} .

Potenciodynamic cyclic polarization tests of pitting corrosion were carried out according to standard [7] in aqueous solutions of 0.1 mol/l NaCl at room temperature and scanning rate 0.5 mV/s Polarization measurements were performed (using the potentiostat PGP201) in a special corrosion cell (flushed port cell for elimination of crevice corrosion) with three-electrode connection: the working electrode as sample with exposed surface 0.5-1 cm², reference saturated calomel electrode (SCE) and platinum auxiliary electrode. Polarization resistance measurement was also performed in solution of 0.1 mol/l H₂SO₄ [8] under the same conditions as the previous test. The Stern method was applied for determination of polarization resistance (R_p).

Exposure tests were performed according to standard [9] in the salt spray cabinet LIEBISH S400 M-TR, where samples were placed on inert plastic racks (the largest samples area under the angle of 20° to the vertical)

and then exposed for 12 hours in neutral salt spray at 35°C, made of 5% neutral NaCl water solution. Gravimetric method was applied for the corrosion extent evaluation.

Note: Aqueous solutions of sodium chloride are used for testing and comparing the corrosion resistance of metallic materials and different coatings (layers) applied in the automotive industry.

After performed tests the photos of exposed surfaces were made using digital camera Canon A700, stereomicroscopy and metallography technique.

3. RESULTS AND DISCUSSION

3.1 Polarization methods

On the basis of the potentiodynamic polarization method [7, 8] the polarization curves were recorded (**Fig. 1**) and following parameters of pitting and/or uniform corrosion were determined:

E_d - depassivation potential set at current density $J_d = 100 \mu\text{A}/\text{cm}^2$ (conventional value)

E_r - repassivation potential at current density $J_r = 10 \mu\text{A}/\text{cm}^2$,

E_{cor} - corrosion potential, J_{cor} - corrosion current density,

R_p - polarization resistance (inversely proportional to the uniform corrosion rate $r_c = B/R_p$)

The values of potentials are related to a saturated calomel electrode (SCE).

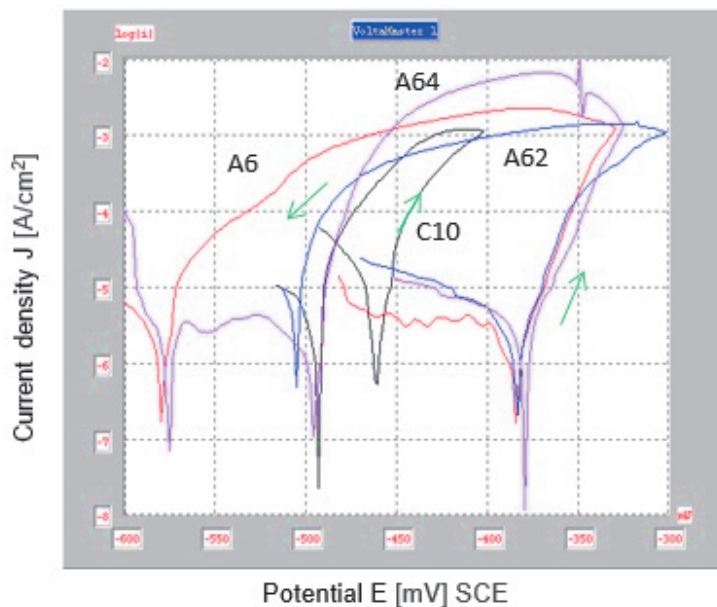


Fig. 1 Cyclic potentiodynamic polarization curves of tested samples - X50MnAlNiCu27-7

A6 - after hot rolling (red)
A62 - aging 450°C/20' (blue)
A64 - aging 450°C/60' (violet)
C10 - rolling (black, ref. 11 321)

Fig. 1 Comparison of corrosion parameters of tested and compared steels

Generally, the higher are the values of potentials (E_d , E_r) the higher is the resistance to pitting corrosion. It is also necessary to consider the differences between these potentials and corrosion one, i.e. the higher $E_d - E_{\text{cor}}$ and/or $E_r - E_{\text{cor}}$ values, the better resistance. Further parameters (E_{cor} , J_{cor} , R_p , r_c) are related to uniform corrosion (before pitting initiation). The uniform corrosion is lower, if parameters J_{cor} and r_c have smaller values or R_p is higher.

The results of pitting resistance measurements are compared in **Fig. 2**. Slightly higher values of E_{cor} and E_r were found out on steel after aging, compared to hot rolling. The E_d values were approximately at the same level. For steel C10 the lower values of E_{cor} and E_d potential were measured. Polarization resistance was

determined in the range $R_p = 1\text{-}5 \text{ k}\Omega\cdot\text{cm}^2$, and higher mean values were calculated for steel in rolling state. Corresponding corrosion rates were estimated in the range 0.01 - 0.1 mm/a.

Significantly higher corrosion resistance of X100MnAl28-12 steel compared with X70Mn22 was proved in paper [10]. The significant increase in depassivation E_d and/or repassivation E_r potential values (**Fig. 2**) and the order of magnitude increase in the polarization resistance was explained by a passivation effect of aluminum (~10%) on the high Mn-Al steels. The difference of 0.5 % Cu between heats (S4, S6) has no practical influence on mean values of measured potentials (E_{cor} , E_d , E_r).

Note: For comparison, X10Cr12 stainless steel under similar conditions (25°C; 0.1 M NaCl) has potential values: $E_{cor} = -200 \text{ mV}$, $E_d = +10 \text{ mV}$, $E_r = -270 \text{ mV}$. Chromium is better passivation element than Al (at the same concentration).

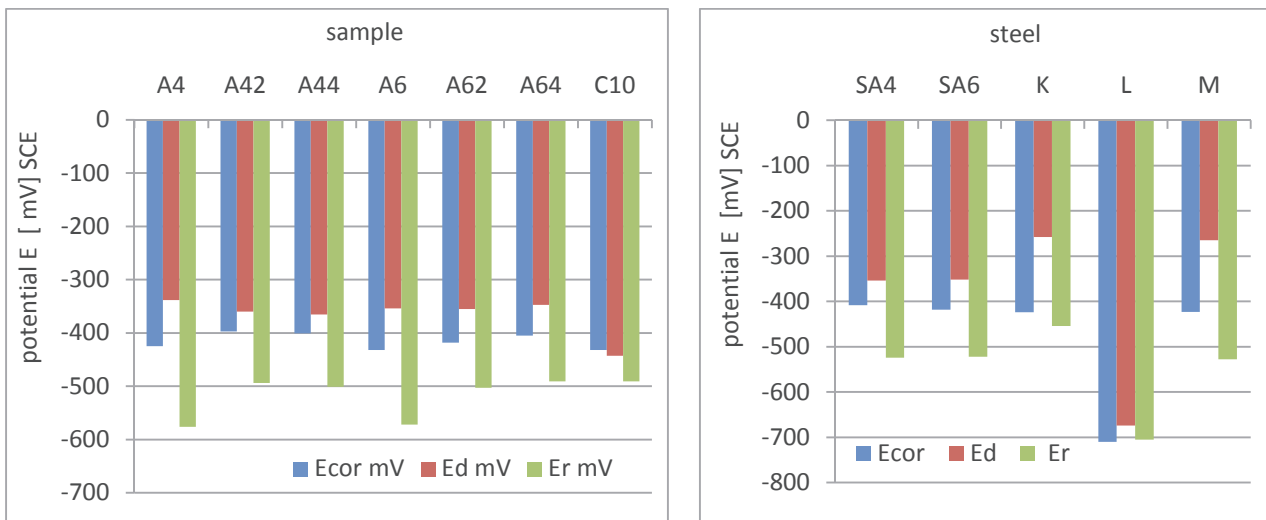


Fig. 2 Parameters of pitting corrosion of tested samples in 0,1 M NaCl. Comparison of different steels: X50MnAlNiCu27-7 (S 4, S 6), K - X100MnAl28-12, L - X70Mn22, M - X70MnAl28-9

Using a stereo- and metallographic microscope on Mn-Al steel after corrosion test the different and elongated spots with microscopic pits ($\varnothing 20\text{-}100 \mu\text{m}$) and several smaller clusters of corrosion pits ($\varnothing 20\text{-}40 \mu\text{m}$) were observed, **Fig. 3**.

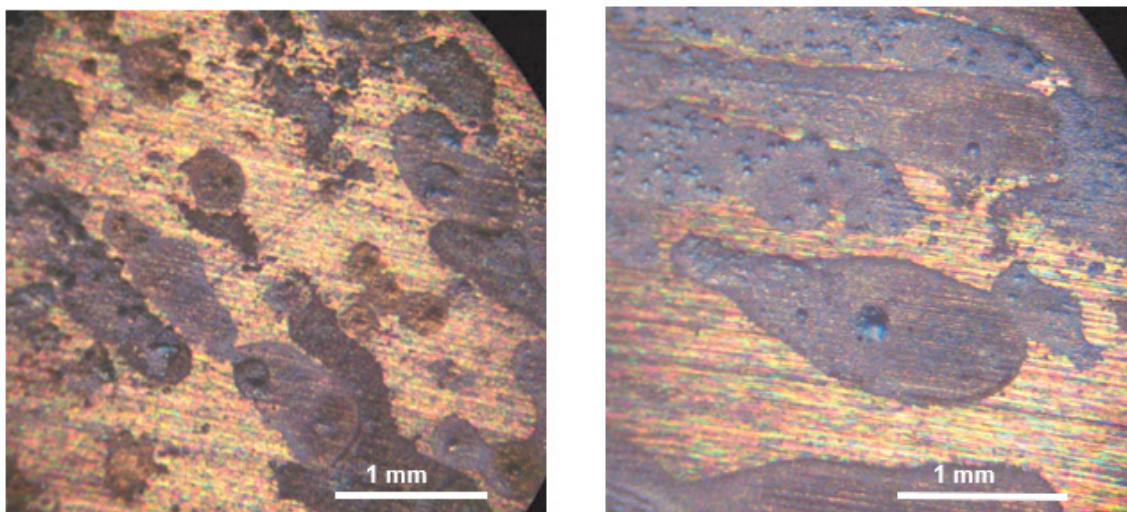


Fig. 3 Pitting corrosion and spots (sample A4, A42) after testing in 0.1 M NaCl

In acidic solution mean values of E_{cor} were nearly the same for heats S4 and S6 (-500 and -508 mV) and similar to steel C10 (-490 mV). Polarization resistance values were on average slightly higher for melting S4 ($R_p=18,3 \Omega.cm^2$, S6: $R_p=17,2 \Omega.cm^2$, C10: $389 \Omega.cm^2$). When comparing the effect of processing, slightly higher values of R_p were measured after rolling in comparison with aging of both heats (Fig. 4). Two values E_{cor} are relative to the time of 10 min. and approximately 50 min.

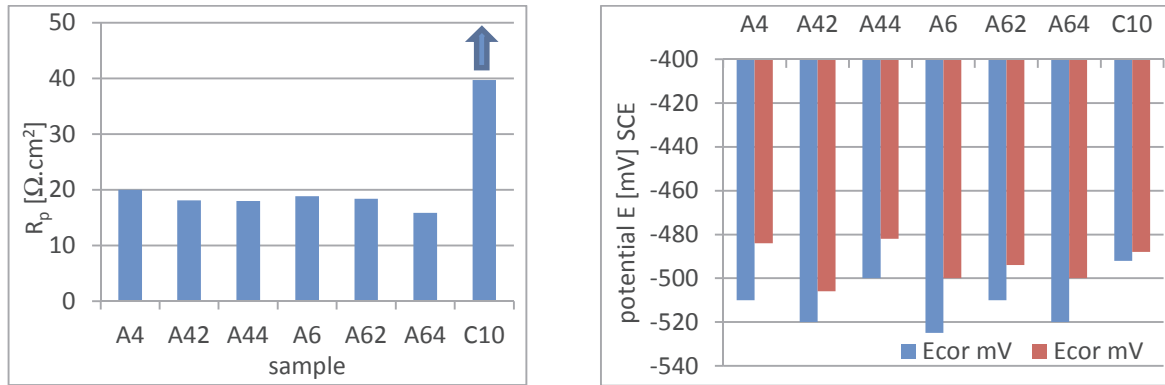


Fig. 4 The polarization resistance and corrosion potential of tested samples in 0.1 M H_2SO_4

Higher corrosion rate or small polarization resistance of X50MnAlNiCu27-7 steel in acidic solution can be explained by high content of Mn and Al because both elements have a low equilibrium (standard) potential compared to Fe. The standard potential for Al, Mn and Fe has the following value: $E_o = -1.66$ V, -1.18 V and -0.44 V SHE (Standard Hydrogen Electrode).

Note: Testing in acidic solutions can be useful in terms of dissolution in steel pickling [3] and also in assessing the impact of polluted industrial atmosphere due to SO_2 or action of acid rain. The corrosion rates of X50MnAlNiCu27-7 steel in acidic solution are significantly higher (2 orders of magnitude, according to the polarization resistance values) than in neutral NaCl solution.

3.2 Salt spray test

The results of accelerated salt spray test are shown in Fig. 5 and 6. Non-uniform type corrosion, rusty stains (spots, points) are shown in Fig. 5, where silver-white background is initial clean metal surface. Macroscopic differences of corrosion products on tested samples after rolling and aging have not been found. Mean mass gain was almost identical for both heats (S4: 14.2 g/m² and S6: 14.1 g/m²).

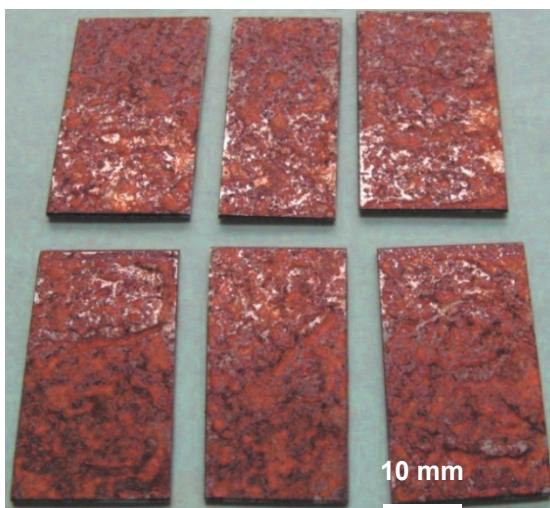


Fig. 5 Samples of Mn-Al steel, salt spray test

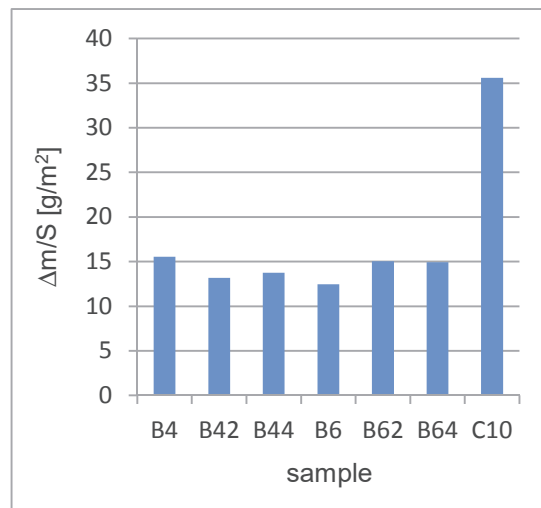


Fig. 6 Corrosion mass gains of compared samples

Little changes were measured among samples after hot rolling and aging. Measured average corrosion mass gains were approximately 2.5x lower for X50MnAl27-7 steel compared to C10 steel, **Fig. 6**. Small differences in corrosion mass losses were also observed after removing of corrosion products (rust) by acidic HCl solution with inhibitor ($C_6H_{12}N_4$), i.e. for heat S4 (25.4 g/m²) and S6 (27 g/m²). After removing of corrosion products (**Fig. 5**), the similar type of corrosion was observed after salt spray test as **Fig. 3** demonstrates.

CONCLUSION

The corrosion properties of high manganese steels X50MnAlNiCu27-7 were tested and compared with carbon steel (C10). Based on the polarization tests in water solutions with sodium chloride there small differences in corrosion resistance after hot rolling and aging were observed. Positive effect of aluminum for corrosion resistance increase was also demonstrated by values of measured parameters. Small differences in chemical composition of tested heats have not been observed in neutral sodium chloride solutions, slightly higher corrosion resistance of heat with 1.0 % Cu was found out in acidic solution (0.1 M H₂SO₄). After salt spray test on Mn-Al steel the non-uniform corrosion was observed in the form of spots and small pits. High uniform corrosion of manganese steels was confirmed in the sulfuric acid solution.

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