

ORIGINAL STUDY

EFFECT OF THERMOCYCLIC ELECTROLYTE-PLASMA TREATMENT PARAMETERS ON THE STRUCTURAL-PHASE STATE AND TRIBOCORROSION BEHAVIOR OF 12KH1MF STEEL

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Abstract. In this work the influence of regimes of thermocyclic electrolyte-plasma treatment (TEPT) on structure-phase state, microhardness and tribocorrosion behavior of 12Kh1MF heat resistant low alloy steel for power plant steam pipelines and boilers is investigated. TEPT was performed in 10 % aqueous solution of Na₂CO₃. Voltage varied from 300 V (30 A) to 150 V (8 A) every 5 s. Three regimes were considered at maximum surface temperature from 800 to 900 °C. Samples were studied by SEM, X-ray phase analysis, Vickers microhardness test, ball-on-disk tribology test and neutral salt spray corrosion tests. TEPT has a layered structure - thermocyclic hardening zone, heat affected zone and base material. Hardened layer thickness is from 400 to 600 μm according to regimes. Ferrite pearlite initial structure transforms into martensite (α'-Fe) with Fe₃C carbides. Consequently, microhardness increases from 205 to 345-373 HV 0.1 (almost 1.7-1.8 times). Friction factor reduces from 0.627 to 0.596-0.617; wear intensity decreases up to 1.8-fold. Corrosion speed is reduced from 0.0024 to 0.0013-0.0019 mm / year. The optimal balance between friction and corrosion resistance was achieved in regime no 2. The maximum values of hardness and wear resistance were obtained for regime no 3. The obtained results indicate the effectiveness of TEPT on localized surface hardening of 12Kh1MF steel components working in abrasive and corrosive conditions.

Keywords: thermocyclic electrolyte-plasma treatment, 12Kh1MF steel, heat-resistant steel, martensite, microhardness, wear resistance, corrosion resistance.

1. Introduction

Heat-resistant structural steels are widely used in power engineering and other industries because they keep their properties at high temperatures and pressures. In thermal power plants, they are used for steam pipelines, turbine components and other parts. During long service, however, their structure gradually degrades and the steel loses strength [1]. Such steel is usually restored by conventional heat treatment, which acts on the whole volume of the part. However, many components need a hard, wear-resistant surface while the core stays ductile so that the assembly works reliably [2]. For this reason, researchers are developing hardening methods that change only the near-surface layer and keep the ductility of the bulk material. Electrolyte-plasma treatment, which is based on electric-discharge phenomena, is one such method [3]. The combination of them allows to increase strength, wear resistance and thermal stability of constructional steels, increase their operational lifetime in harsh environments.

The research on the electric-discharge techniques for materials processing progresses rapidly from theoretical to practical point of view. This resulted in development of highly effective and inexpensive technologies like: - Electrical discharge machining (EDM), [4, 5]; Electrospark machining (ESM), [6]; Electrolyte plasma hardening (EPH), [7]; Electrolyte plasma anodic treatment (EPAT), [8], Electrolyte plasma chemical thermal treatment (EPCTT) [9]. The mentioned technologies find wide application in different fields of industry, including power and mining industries.

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Garba et al. [10] showed that EDM is widely used in mould and die making, mechanical engineering, and the nuclear, aerospace and biomedical industries. Its main advantage is high precision in making complex parts. However, EDM has important drawbacks: a low material removal rate, poor surface quality, long processing times and high cost, and it can only process electrically conductive materials. These drawbacks limit its industrial use.

Korzhyk, Tyurin and Kolisnichenko [11]. Theoretical and experimental investigations of modification of metals by passing an electric current through a liquid - electrolyte electrode have been conducted in [11]. On its basis there were created complex hardening methods and devices for oxidation, alloying, structure changing of surface layer, not influencing on body part. Such technologies significantly increase the physical and mechanical characteristics of material - strength, resistance to wear and fatigue under friction.

Berladir et al. [12] compared nitrocarburising with cyclic heating and conventional isothermal nitrocarburising. They found that the thermocyclic process increases resistance to cavitation damage by 0.6–1.5 times. It also shortens treatment time, refines the grain structure and improves the mechanical properties of structural steel.

Among them, thermocyclic electrolyte-plasma treatment (TEPT) is one of the prospective technologies. The combination of thermal, electric and plasma actions on metal in an electrolyte – a current passing via the electrolyte into its surface; active components of the electrolyte are changing its surface - leads to high hardening of the surface layer. Repeated switching between heating and cooling results in substantial structure modification and enhancement of mechanical characteristics. This renders it suitable for industrial application.

Analysis of the literature revealed that electric discharge methods are able to substitute traditional thermal processing in order to enhance service characteristics of various steels. Process conditions for cathode electrolyte plasma treatment by means of thermocycling remain unexplored. The objective of this paper was investigation of influence of modes of thermocycle electrolyte plasma treatment on structure - phase composition and tribocorrosion behavior of 12Kh1MF construction steel.

2. Materials and methods

The investigated material was 12Kh1MF steel - heat resistant low alloy steel, which is used in power engineering as pipelines, boilers and other parts of high temperature operation under aggressive conditions. Composition by mass percent according to GOST 20072-74: C 0.10–0.15 %, Si 0.17–0.37 %; Mn 0.40–0.70 %; Cr 0.90–1.20 %; Mo 0.25–0.35 %; V 0.15–0.30 %, max. P 0.035 %; S 0.030 %; remainder – Fe.

Thermocyclic electrolyte-plasma treatment (TEPT) was performed in the electrolyte-plasma treatment device of the Surface Engineering and Tribology Research Center, Sarsen Amanzholov East Kazakhstan University. The device has a power source and an electrochemical cell (Fig. 1).

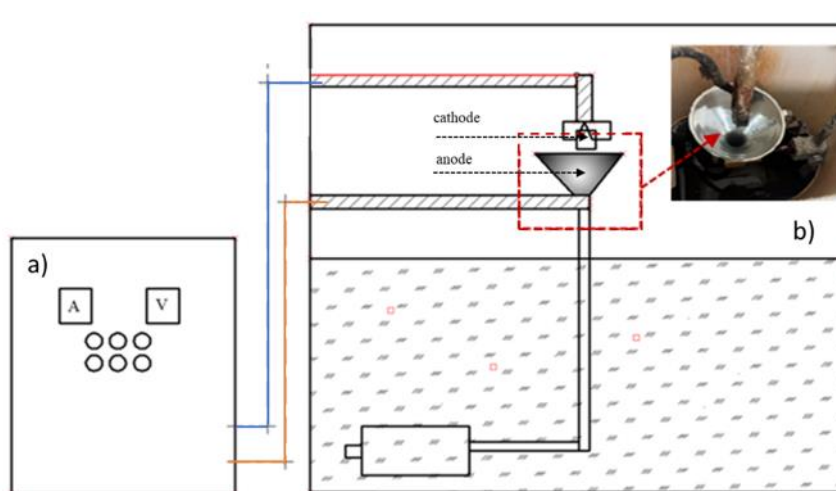


Fig. 1. Schematic diagram of the unit for thermocyclic electrolyte-plasma treatment: a) power supply; b) electrolytic cell.

The process works as follows. At a low voltage of about 150 V, ordinary electrolysis takes place in the cell. When the voltage is raised to 300 V, gas is released intensively at the electrode, and a vapour-gas envelope

forms around the sample surface. The electric field strength in this envelope reaches 10^4 – 10^5 V/cm. At a temperature of about 100 °C, this field ionises the vapour and causes emission of ions and electrons, which keeps a stable electric discharge going and produces an electrolyte plasma. The aqueous electrolyte serves as both the heating and the cooling medium.

An aqueous solution of sodium carbonate (Na_2CO_3) was used as the electrolyte. Our earlier studies [13, 14] showed that a higher Na_2CO_3 concentration increases the electrical conductivity of the electrolyte, which leads to high current density and intense heating. Compared with a 15% solution, a 10% solution gives a lower current density, so heating is smoother, the surface does not melt, and the heating process is easier to control. The electrolyte for the present study was thus 10 wt.% Na_2CO_3 in distilled water.

The TEPT regime parameters are given in Table 1. Each thermocycle consisted of four stages: heating at 300 V (30 A) for 5 s, holding at 150 V (8 A) for 5 s, heating at 300 V for 4 s and holding at 150 V for 5 s, giving 19 s per cycle. Regimes No. 1, No. 2 and No. 3 consisted of one, two and three cycles, respectively.

Table 1. Results of corrosion tests of samples before and after TEPT.

Stage within one cycle		Voltage U, V	Current I, A	Duration t, s
1 – heating		300	30	5
2 – holding		150	8	5
3 – heating		300	30	4
4 – holding		150	8	5
Regime	Number of cycles	Total treatment time, s	Max. surface temperature, °C	Electrolyte temperature, °C
No. 1	1	19	800	36
No. 2	2	38	850	37
No. 3	3	57	900	39

Metallographic analysis was performed after grinding and polishing on the Metapol - 2000 P device. Etching with a 4 % solution of HNO_3 in ethanol was used to show the structure. Structure of raw and processed specimens studied using TESCAN MIRA SEM at x60 and x1000 magnification.

The phase composition before and after TEPT was determined by X-ray phase analysis on an X'Pert Pro diffractometer. Scans were recorded in the 2θ range of 10–90° with a step of 0.02°.

Cross-sectional microhardness was determined using METOLAB 502 microhardness meter, Vickers diamond pyramid indenter (136° angle of opposite faces), by the method of GOST 9450-76. Load - 1 N (HV0.1), duration of holding under load - 10 s.

Tribological tests were carried out on a TRB3 tribometer using the ball-on-disk method. The load was 6 N, the sliding speed was 2 cm/s, the sliding distance was 60 m, and the wear track radius was 3 mm. The counterbody was a 6 mm ball of 100Cr6 steel (equivalent to ShKh15).

Resistance to corrosion was determined in HUD-E808 salt spray chamber according to GOST 34388-2023. Neutral 5 % NaCl solution; $T=35$ °C, $t=8$ h. Quantitative assessment of corrosion damage performed according to GOST 9.908-85 by determining the mass loss per unit surface area $\Delta m(\text{g}/\text{m}^2)$, which is calculated by formula (1).

$$\Delta m = \frac{m_0 - m_1}{S}, \quad (1)$$

where m_0 is the sample mass before testing, g; m_1 is the sample mass after testing and removal of corrosion products, g; S is the sample surface area, m^2 .

3. Results and discussion

Fig. 2 presents SEM micrographs of transversal sections from samples of 12Kh1MF steel after TEPT at a concentration of the 10 % Na_2CO_3 electrolyte in different modes (No. 1, No. 2 and No. 3) prior to treatment - the structure is ferrite - pearlite; after TEPT - the surface layer is predominantly martensitic, as a result of rapid cooling of the heated surface with an electrolyte solution. The transformation into martensite accounts for increased microhardness values and improved tribocorrosion behavior (Table 3).

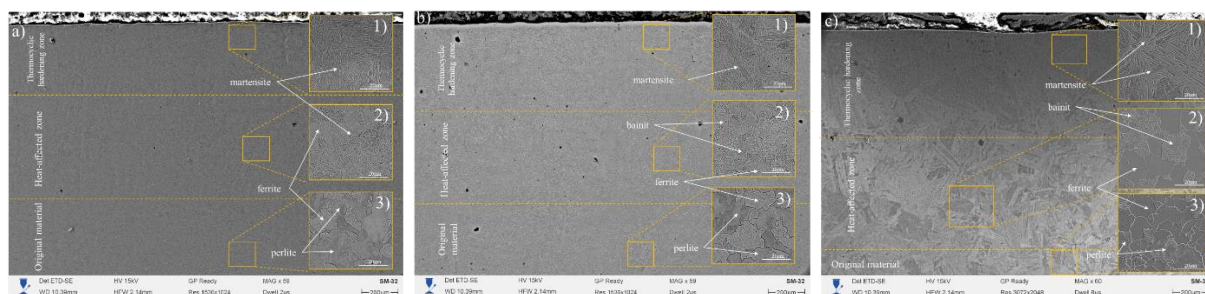


Fig. 2. SEM images of cross-sections of 12Kh1MF steel after TEPT in regimes No. 1 (a), No. 2 (b) and No. 3 (c): 1) thermocyclic hardening zone; 2) heat-affected zone; 3) base material.

In any case, TEPT results in formation of a zonal structure comprising three areas with different microstructure and hardness - thermocyclic hardening layer, heat affected layer, and basic metal (Fig. 2). At the end of regime No. 1 the thickness of hardening layer reaches approximately 400 μm and comprises martensite (Fig. 2a, area 1), while below it there is an HAZ where there is a smooth change from martensite to initial ferrite – pearlite structure (Fig. 2a, areas 2 and 3); at the end of regime No. 2 - a hardening layer up to ~500 μm thick (Fig. 2b, zone 1) is formed as well, mainly consisting of martensite; in the heat affected zone there are bainite and ferrite present (Fig. 2b, zones 2 and 3); Regime No. 3 results in the largest depth of hardness, roughly 600 μm . Here, the transition from martensite through bainite to heat affected zone occurs (Fig. 2c). With increasing heat input of the regime, the thickness of martensite increases accordingly to approx. 600 μm .

In order to determine phases, X - ray phase analysis was carried out for surface of specimens before and after TEPT (Fig. 3). Before treatment there is only α - Fe in the steel that corresponds to ferrite - pearlite microstructure. Following the TEPT all specimens contain martensite (α' - Fe) plus cementite (Fe_3C), hardening agent of steels. Results are consistent with the SEM data.

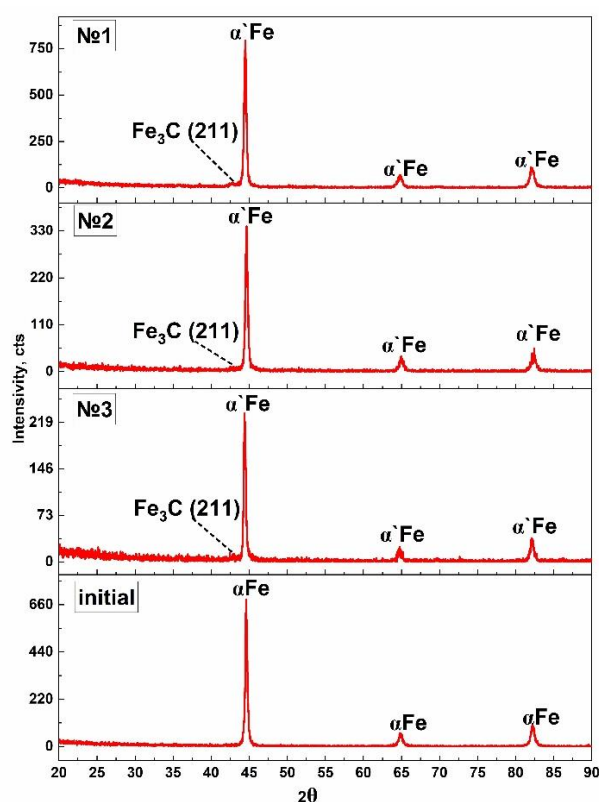


Fig. 3. X-ray diffraction patterns of 12Kh1MF steel before and after TEPT in different regimes.

The surface microhardness results are given in Table 3. Microhardness rose from 205 $\text{HV}_{0.1}$ in the initial state to 345, 365 and 373 $\text{HV}_{0.1}$ after regimes No. 1, No. 2 and No. 3. This is about 1.7–1.8 times higher and

is due to the formation of martensite. Microhardness increases slightly from regime to regime, following the growth of the hardened layer.

Figure 4 shows the results of the tribological tests. The friction coefficient of the untreated steel is 0.627. After TEPT, it decreases to 0.617, 0.596 and 0.613 for regimes No. 1, No. 2 and No. 3, respectively. The lowest value is for regime No. 2, about 5% below the initial state. Wear resistance improves much more. Wear intensity falls from $4.7 \cdot 10^{-4}$ to $4.4 \cdot 10^{-4}$, $3.0 \cdot 10^{-4}$ and $2.7 \cdot 10^{-4}$ mm³/(N·m), which means wear resistance is 1.1, 1.5 and 1.8 times higher, respectively. Wear resistance increases along with microhardness, so the harder martensitic layer resists wear better.

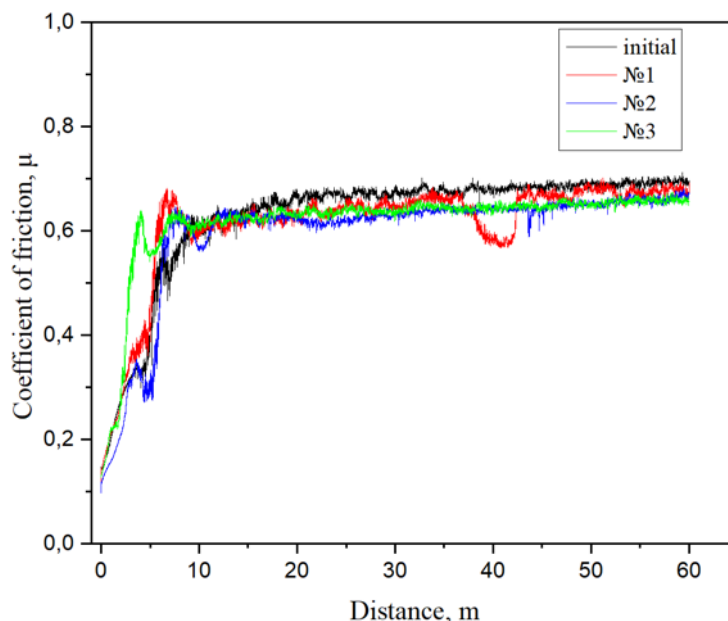


Fig. 4. Tribological test results before and after TEPT.

The results of the salt-spray corrosion tests are presented in Table 3. Losses in mass per unit surface were determined using eq. (1) - they reduced following treatment in each case – approximately 32 % for regime No. 1; 43 % for regime No. 2 and 20 % for regime No. 3. The corrosion rate follows a similar pattern. It drops from 0.0024 mm/year for the non-treated steel to 0.0016, 0.0013 and 0.0019 mm/year respectively. Best corrosion protection is provided by regime No. 2. Regime No. 3 has the largest amount of heat input, so it probably results in greater residual stresses. This may account for localised corrosion, and thus explains why regime No. 3 is more susceptible to corrosion than regime No. 2 despite having a higher hardness value.

Table 2. Results of corrosion tests of samples before and after TEPT.

Sample	Mass before testing, g	Mass after testing, g	Loss of mass, g	Loss of mass per unit area Δm , kg/m ²
Initial	9.5391	9.5299	0.0092	0.0191
Cycle No.1	11.2293	11.2198	0.0095	0.0129
Cycle No.2	8.4946	8.4883	0.0063	0.0109
Cycle No.3	7.0022	6.9941	0.0081	0.0152

Table 2 summarises all the results. The regimes affect the properties in different ways. Regime No. 3 gives the thickest hardened layer and the highest microhardness and wear resistance. Regime No. 2 gives the lowest friction coefficient and the best corrosion resistance, together with high hardness and wear resistance. Overall, a 10% Na₂CO₃ electrolyte combined with regimes No. 2 and No. 3 provides steady power supply and regulated heat treatment, resulting in an optimal set of mechanical and tribocorrosion characteristics for 12Kh1MF steel.

Table 3. Phase composition, microhardness, tribological and corrosion properties of samples before and after TEPT.

Sample	Phase composition	Microhardness, HV _{0.1}	TRB3		Corrosion rate, mm/year
			μ	Wear intensity, mm ³ /N×m	
Initial	α Fe	205±30	0.627	0.0004706	0.0024
Cycle No.1	α' Fe, Fe ₃ C	345±30	0.617	0.0004391	0.0016
Cycle No.2	α' Fe, Fe ₃ C	365±34	0.596	0.0003047	0.0013
Cycle No.3	α' Fe, Fe ₃ C	373±31	0.613	0.0002672	0.0019

4. Conclusion

Based on the results, the following conclusions were drawn:

1. TEPT of 12Kh1MF steel in an electrolyte of 10% Na₂CO₃ in distilled water produces a zonal structure in the surface layer. It consists of a thermocyclic hardening zone, a heat-affected zone and the base material. The hardened layer grows with the number of cycles, from about 400 μ m for regime No. 1 to about 600 μ m for regime No. 3.
2. X-ray phase analysis and SEM showed that the initial ferrite-pearlite structure (α -Fe) turns into martensite (α' -Fe) with cementite (Fe₃C) in all regimes. As a result, microhardness rises from 205 to 345–373 HV_{0.1}, which is about 1.7–1.8 times higher.
3. TEPT improves the tribological properties of the steel. The friction coefficient falls from 0.627 to 0.596–0.617, and wear intensity drops from $4.7 \cdot 10^{-4}$ to $2.7 \cdot 10^{-4}$ mm³/(N·m), which means wear resistance is up to 1.8 times higher. Wear resistance increases along with microhardness and the thickness of the hardened layer.
4. Salt spray tests showed better corrosion resistance after treatment. The corrosion rate fell from 0.0024 to 0.0013–0.0019 mm/year, a reduction of 21–46%. Regime No. 2 was the most corrosion-resistant. The weaker result for regime No. 3 is likely due to higher residual stresses caused by its greater heat input.
5. The recommended TEPT regime for 12Kh1MF steel is a 10% aqueous Na₂CO₃ electrolyte, with the voltage alternating between 300 V (30 A) and 150 V (8 A), and 2–3 thermocycles, each lasting 19 s, at a maximum surface temperature of 850–900 °C. Regime No. 2 gives the best balance of hardness, low friction and corrosion resistance. Regime No. 3 gives the highest hardness and wear resistance. The choice between them depends on the service conditions of the part.

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Conflict of interest statement

The authors declare that they have no competing interests.

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