

## In-service degradation diagnostics of low-alloyed steels and aluminum alloys properties by electrochemical methods

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### Abstract

The effect degradation in-service and in-laboratory conditions of the low-alloyed steels and aircraft aluminum alloys on its electrochemical conditions has been investigated. It is shown that the structural changes over degradation causes not only material embitterment, but also an activation of anodic and cathode electrode reactions and, correspondingly, a decrease of corrosion resistance. Such electrochemical characteristics as anodic current at constant potential and polarization resistance are the most sensitive to degradation. Fair correlation between the connected with degradation changes of electrochemical and mechanical properties were obtained. It allows to monitor structural changes in-bulk metal during long-term service and it opens prospects for an application of the electrochemical methods to diagnostics of in-service degradation.

**Key words:** low-alloyed steels, aluminum alloys, degradation, brittle fracture, plasticity, corrosion current, polarization resistance

### Introduction

The processes of degradation proceed in metal of important structures (shells of sea and air crafts, pipelines, rigdeworks, portal cranes etc.) over long-term exploited loading and it increases sharply a risk of further service. Problem of aging is especially important for transit oil and gas pipelines since most of them is in service more than the normative term - 33 years. Facts of degradation is confirmed by enough high intensity of transit pipelines failures.

In the last time the problem of degradation of in-bulk metal properties, caused by microstructures processes of deformation aging [1], an increase of internal stresses [2] and a development of micro damages [3] becomes especially actual. In-service degradation of transit pipelines and oil storage tanks was revealed in the first turn in a decrease of resistance of brittle fracture and hydrogen cracking [3]. The problem of in-service degradation is concerned also to a reliability of aircraft elements since long-term service of the aircraft aluminum alloys is accompanied by its change of structural-phase state and, correspondingly, the mechanical properties [4].

The structural-sensitive physical methods like internal friction [5], specific resistance, coercive force, modulus of elongation and its amplitude dependence [6] are usually used. However most of the mentioned methods of diagnostics are oriented on a monitoring of the integral properties of all volume of metal whereas the microstructures changes, an increase of internal stresses and development of damages proceed in its local volumes and it causes often its low sensitivity. The other methods, namely, the method of international friction, are practically unfeasible in field conditions. In this sense the methods, based on investigation of electrochemical properties of metal have prospects since they are sensitive to changes of microstructure, hardening, damages [7].

The aim of this work is investigation of the changes of the mechanical and electrochemical properties of low-

alloyed steels of ferrite-pearlite structure and aluminum alloys of the Al-Cu-Mg system because of its long-term service and determination of correlation between these properties in respect to a usage of electrochemical characteristics as parameters of degradation level.

The investigated alloys were the following:

1. Power steam pipeline 12KH1MF. The stationary technological regime of service occurs at the temperature of 500...560 °C and steam pressure of 10...14 MPa. The steel was investigated in as-received state and after exploitation during 140 000 and 190 000 hours, the last was corresponded to critical level of degradation [8]. The electrochemical tests were carried out in tap water, 3%NaCl solution and aqueous solution of H<sub>2</sub>SO<sub>4</sub> (pH0).
2. Transit oil pipeline steel of the 10GS type. Pipes in as-received state (reserve pipe) and after 28 years of service were used. Top and low fragments of the pipe were separately distinguished. Corrosion tests were carried out in residual water from the oil storage tank of the working petroleum refinery [9].
3. St.3sp steel of a large volume oil storage tank. The specimens were cut from: 1 – upper part of the wall, which contacts constantly during service with air and condensed water; 2 – the wall part, which contacts constantly with oil; 3 – wall part at the storage bottom; 4 – storage bottom; parts 3 and 4 contact constantly only with residual water [10]. The comparative tests of the corrosion resistance of the different parts were carried out in residual water from the working oil storage tank.
4. Transit gas pipeline 17G1S steel. The material was selected from pipelines after 29 and 40 years (1220 and 529 mm in diameter correspondingly) and a reserve pipe [11]. Electrochemical investigations in tap water were carried out.

5. Transit gas pipeline X52. The material was selected from pipelines (275 mm in diameter and wall thickness 10 and 12 mm, marking X52-10 and X52-12, relatively) and a reserve pipe (marking X52) [3]. Corrosion tests were carried out in the special solution, which modeled the internal water condensate.
  6. Cleaned D16chT aluminum alloy (0,2 mas. % Si; 0,3% Fe) in as-received state (quenching and natural aging) and after artificial aging (cyclic loading  $10^5$  cycles in the range of 80 MPa at the temperature of 190°C), and also uncleaned D16T alloy (0,5% Si; 0,5% Fe) after quenching, natural aging and 25 years of service [4]. Electrochemical tests in 0.1 and 3.5%NaCl solutions were carried out.
- The mechanical properties of the tested materials in as-received state and after service are presented in Table 1. They can be considered as the parameters of degradation level.

Table 1. The mechanical properties of the tested materials

Material	State of material	$\sigma_Y$	$\sigma_{UTS}$	$\Delta$ , elongation	$\Psi$ , RA	KCV	$J_{IC}$ ( $\Delta K_{Ic}^{**}$ )
		MPa		%		Joule/cm <sup>2</sup>	МПа√m
10GS	As-recieved	555	650	36	77	180	-
	Exploited, top	-	-	-	-	95	-
	Exploited, bottom	520	620	28	56	-	-
St.3sp	Part 1	277	485	-	52	72	-
	Part 2	263	440	-	54	153	-
	Part 3	273	476	-	50	62	-
	Part 4	268	430	-	50	84	-
12KH1MF	As-recieved	280	465	31	76	-	486
	Exploited, (140·10 <sup>3</sup> h)	295	500	29	74	-	170
	Exploited, (190·10 <sup>3</sup> h)	270	445	34	76	-	73
17G1S	As-recieved	378	595	-	79	200	322
	Exploited 29 years	345	547	-	71	138	205
	Exploited 40 years	302	515	-	69	125	-
X52	As-recieved	355	475	22.7	72,9	350	412
	Exploited 30 years, X52-12	261	455	21.9	63.4	186	127
	Exploited 30 years, X52-10	349	537	29.3	54.8	142	79
D16chT (D16T)	As-recieved, D16chT	322	453	19	-	-	45**
	Exploited 28 years, D16T <sub>expl</sub> )	363	495	11	-	-	38**
	Artificially degraded (D16chT <sub>te</sub> )	375	442	7	-	-	35**

The change of the different electrochemical parameters because of the materials service was determined: corrosion potential  $E_{cor}$ , corrosion current  $j_{cor}$ , Tafel constants of anodic  $b_a$  and cathodic  $b_c$  part of polarization curve, current at the certain anodic potential  $j_a$  and polarization resistance  $R_p$ .

### Effect of long-term service on degradation of the mechanical properties of structural materials

Long term service of transit pipelines causes, as a rule, to some decrease of strength and properties of steels. The characteristics of brittle fracture – fracture toughness and impact strength – are especially sharply decreased. Such clear peculiarity was not observed in the case of a high temperature in-service degradation of the steam pipeline steel, but impact strength and fracture toughness drop almost by order. The characteristics of plasticity of degraded aluminum alloys are strongly decreased in comparison for the as-received state. Correspondingly, these characteristics can be considered as the mechanical parameters of an in-service material degradation.

### Comparison of the electrochemical characteristics sensitivity to in-service degradation

Electrochemical characteristics have the different sensitivity to the in-service degradation. Therefore it is necessary to compare theirs, showing a relative change for the same level of degradation. It was done using the relation  $P_d/P_0$ , a level of the certain characteristic of degraded material  $P_d$  to its in-received state  $P_0$  for the case, when the absolute level of this characteristic is decreased: Tafel constants, polarization resistance. In the case when the characteristic levels increased with the degradation level rise, the reverse level of this relation  $(P_d/P_0)^{-1}$  was used: corrosion potential, corrosion current, current at the certain anodic potential.

The similar tendencies of the electrochemical parameters changes for all investigated materials are seen from the generalized tests results (Fig. 1). The relative change of  $E_{cor}$  is not essential. Tafel constants are changed stronger, more for anodic reaction. The current  $j_{cor}$  is enough sensitive to degradation.

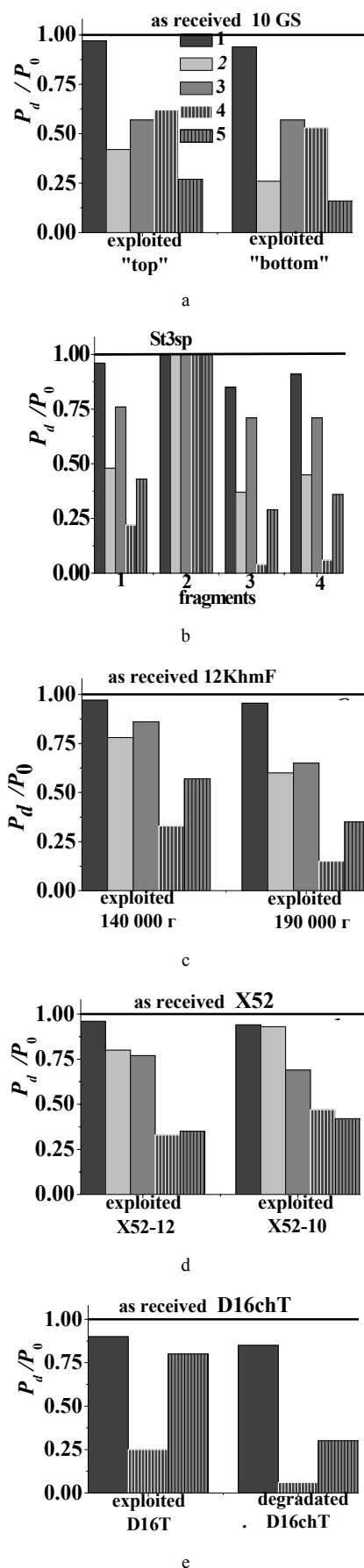
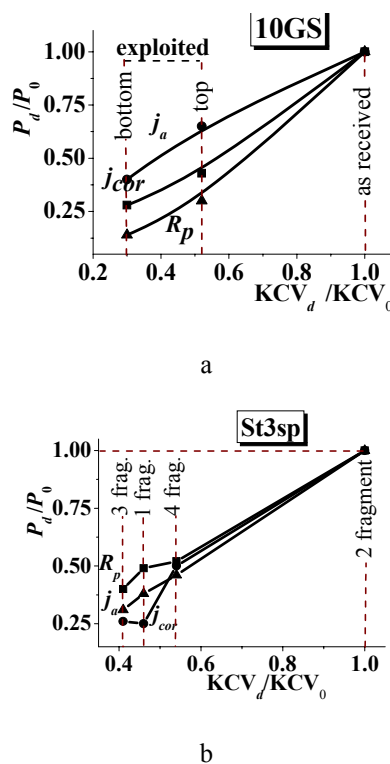


Fig. 1. Relative change of the electrochemical characteristics of the steels 10GS (a), St3sp (b), 12Khmf (c) and X52 (d) and aluminum alloys D16chT(D16T) (e) because of its in-service degradation: 1 -  $E_{cor}$ , 2 -  $b_a$ , 3 -  $j_{cor}$ , 4 -  $j_a$ , 5 -  $R_p$

The most sensitive to degradation are anodic current at the constant potential  $j_a$  and the polarisation resistance  $R_p$ . The high sensitivity of  $j_a$  parameter to degradation of the tested materials is caused by simultaneous action of two factors: a shift of the corrosion potential of exploited materials to the negative direction and also anodic reaction intensification of solution of the degraded metal. The method of  $j_a$  evaluation consists of a support of the certain anodic potential  $E_a$  correspondingly to  $E_{cor}$  for as-received material (the levels of polarization potential  $E_a$  were chosen specifically for the every system metal-environment). It is simple in application and avoids subjective estimation of the given parameter, what is peculiar at determination of the Tafel constants and the corrosion current. Furthermore, the method of polarization resistance evaluation excludes a researcher's influence, therefore a usage of this parameter is enough prospective for an evaluation of the degradation level.

It should be drawn that the change of electrochemical properties in-bulk material but not of surface of the structure after its in-service degradation, was analyzed in the work. However, there are only the first estimations of a possibility of application of the electrochemical methods for a diagnostics of the properties degradation. For more well-grounded conclusions it is desirable to carry out the substantial investigations concerning selection of a corrosion environment of the electrochemical tests, which should not be necessarily the same like exploited (technological) one but should provide a maximum sensitivity of the electrochemical characteristics to a metal degradation. Such parameters can be used for not only qualitative but also quantitative estimation of in-bulk material degradation. The prospect of such approach is confirmed by the obtained results, which show a good correlation between the changes of the mechanical and electrochemical parameters (Fig. 2).



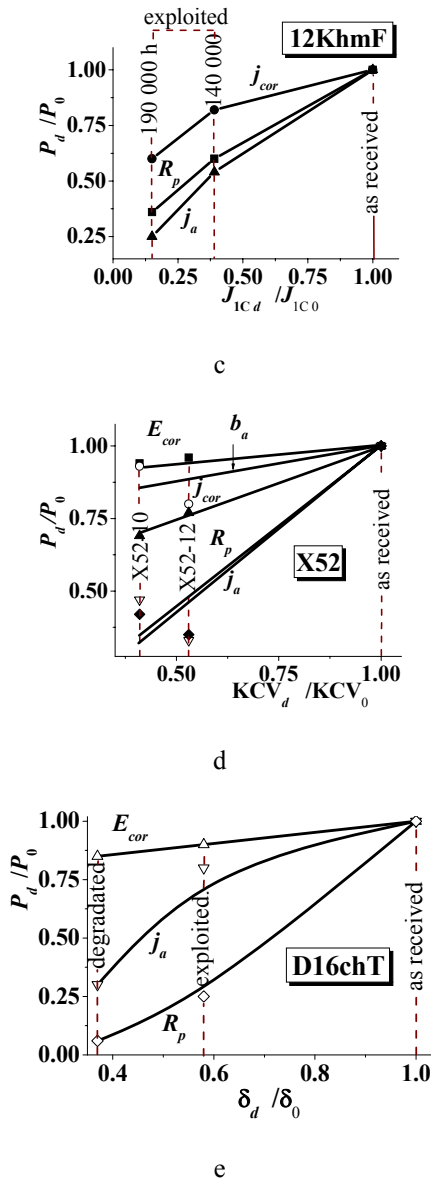


Fig. 2. Correlation between the relative change of electrochemical characteristics of degraded structural materials and the relative change of the mechanical parameters of degradation

**Conclusions**

Degradation of the mechanical properties of low-alloyed steels and aluminum alloys causes also an activation of the anodic and cathodic reactions.

The anodic current at a constant potential and the polarization resistance are the most sensitive to in-bulk material degradation.

Good correlation between the changes of electrochemical and mechanical characteristics of material degradation is observed.

It is possible to monitor in-bulk material properties changes by measurements of electrochemical characteristics and it opens up possibilities for an application of electrochemical methods for diagnostics of in-service degradation.

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**Mažai legiruotų plienų ir aliuminio lydinių savybių menkėjimo (degradacijos) eksploataavimo metu diagnostika elektrocheminiais metodais**

**Reziumė**

Tirtas mažai legiruotų plienų ir aviacinių aliuminio lydinių degradacijos poveikis elektrocheminėms savybėms. Parodyta, kad medžiagų struktūros pokyčiai dėl degradacijos ne tik veikia medžiagų trapumą, bet ir aktyvina anodinę-katodinę reakciją, atitinkamai mažina atsparumą korozijai. Tokios elektrocheminės charakteristikos kaip anodinė srovė esant pastoviam potencialui ir poliarizacijos varža itin jautrios degradacijai. Gauta puiki koreliacija tarp elektrocheminių ir mechaninių savybių pokyčių dėl degradacijos. Tai leidžia stebėti ilgai eksploatuojamo tūrinio metalo struktūrinius pokyčius ir atveria galimybes eksploatacinės degradacijos diagnostikai taikyti elektrocheminius metodus.

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