

## The properties of chromium electrodeposited with programmed currents. Part I. Direct current

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The electrodeposition of chromium in programmed direct current (DC) was investigated in the regime of high current density ( $77 \text{ A dm}^{-2}$ ). Chromium was deposited in a system of plane-parallel electrodes in chromic-sulphuric acid solution, on specimens of steel, during one hour. The basic properties of deposits, the appearance, thickness, morphology, microhardness and brightness were investigated. Thicknesses of the coatings (between 28 and 82  $\mu\text{m}$ ) were measured at 36 points on the surface of the specimens by the non-destructive ferromagnetic method. Based on these results, graphic models of the surface distribution of the deposits were made. Three ranges of thickness could be seen on the model (range 1 – average thickness 29.87  $\mu\text{m}$ , range 2 – average thickness 42.0  $\mu\text{m}$  and range 3 – thickness 67.87  $\mu\text{m}$ ). For the whole specimens, the average thickness was 50.8  $\mu\text{m}$  with a coefficient of variation of 0.3281. The basic properties of the coating, morphology and brightness changed depending on the deposit thickness being very different at different points of one and the same specimen. For this reason these chromium deposits should not be considered reliable protection against aggressive gases at high pressures and temperature of systems from corrosion, wear and erosion.

**Keywords:** electrodeposition of chromium, programmed direct current, properties of the deposits, thickness, morphology, microhardness, brightness, distribution of the deposits on the surface, modelling.

Programmed electrodeposition is process controlled and led by a computer. The computer controls the electrodeposition by regulation of basic input parameters within limited values. The basic program has three sequence. The first is pretreatment of the surface, the second is electrodeposition and the third is the final treatment. The input parameters are: solution temperature, cathodic and anodic current, time of treatment, free-time between operation, concentration and volume of solution, *etc.*<sup>1,2</sup>

The properties of chromium deposits are primarily determined by the current density and solution temperature. By variation of these two parameters matt-gray, bright or milk deposit can be achieved.<sup>3,4</sup> Together with chromium, hydrogen

develops on the cathode. This makes the current efficiency lower (between 10 and 15 % for chromic–sulphuric acid solution).<sup>5,6</sup> The deposition rate increases with increasing current density, which results in an increase of the current efficiency and, consequently, a change of the properties and throwing power of the deposits.<sup>7,8</sup>

The purpose of this work was the examination of programmed electrodeposition of chromium with DC. Special regard was given to the surface distribution of the deposits and its effect on others properties of the coating. The results obtained in the present study will be of reference value for the results obtained in reversing current regime.

#### EXPERIMENTAL

The specimens used in the experiments were in the form of plates (dimensions: 0.5 · 0.8 · 0.025 dm). The specimens were placed vertically in the bath and point 42.5 was on the bottom of the bath. Chromium was deposited on the working area of 0.18 dm<sup>2</sup> (0.4 · 0.45 dm). The steel specimens contained 0.28 % C, 0.10 % Si, 0.40 % Mn, 3.1 % Cr, 1.1 % Ni, 0.1 % V and 0.45% Mo.

All specimens were mechanically polished. Specimens on which the morphology was observed were electropolished in a phosphoric–sulphuric–chromic acid solution (60 g dm<sup>-3</sup> H<sub>3</sub>PO<sub>4</sub>, 50 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, 50 g dm<sup>-3</sup> CrO<sub>3</sub>).

The basic surface treatment prior to plating was an acetone degrease. The part of the surface on which it was not intended to deposit chromium was protected by vinylplast. The specimens were electrolytically cleaned in an alkaline solution (30 g dm<sup>-3</sup> NaOH, 35 g dm<sup>-3</sup> Na<sub>3</sub>PO<sub>4</sub>, 30 g dm<sup>-3</sup> Na<sub>2</sub>CO<sub>3</sub>) for 2 min, at a current density of 20 A dm<sup>-2</sup> at a temperature of 65 °C. The specimens were then etched from 30 to 60 s in a 20 % H<sub>2</sub>SO<sub>4</sub> solution. Between these operations the surface of the specimens were rinsed in running cold water.

The programmed computer controlled process consisted of the regulation of the anodic etching and of the chromium electrodeposition. The basic input parameters are given in Table I. A personnel computer and additional equipment maintained the basic input parameters within the limited values.

TABLE I. Basic input parameters in the chromium plating bath in the DC regime

No.	Parameters of electrolysis	Sequence I	Sequence II
		Anodic etching of the substrate	Chromium deposition
1	Anodic current density/ A dm <sup>-2</sup>	55	
2	Cathodic current density/ A dm <sup>-2</sup>		77
3	Anodic time/ s	45	
4	Cathodic time/ s		3600
5	Temperature/°C	50–1	50–1

The programmed anodic etching and the chromium electrodeposition were performed in chromic–sulphuric acid solution (250 g dm<sup>-3</sup> CrO<sub>3</sub>, 2.5 g dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>). Insoluble anodes were used, the lead alloy contained 10 % tin. The anode and cathode were situated 5 cm apart.

After deposition the specimens were rinsed in running cold and hot water, and than dried in a hot air current.

The thickness of the deposit was measured by a magnetic method (Dermatron 3000). The thickness of the deposit was measured at 36 points on the surface of specimens, as is shown in Fig. 1a. The method of measurement with 6 rows and 6 columns was used.

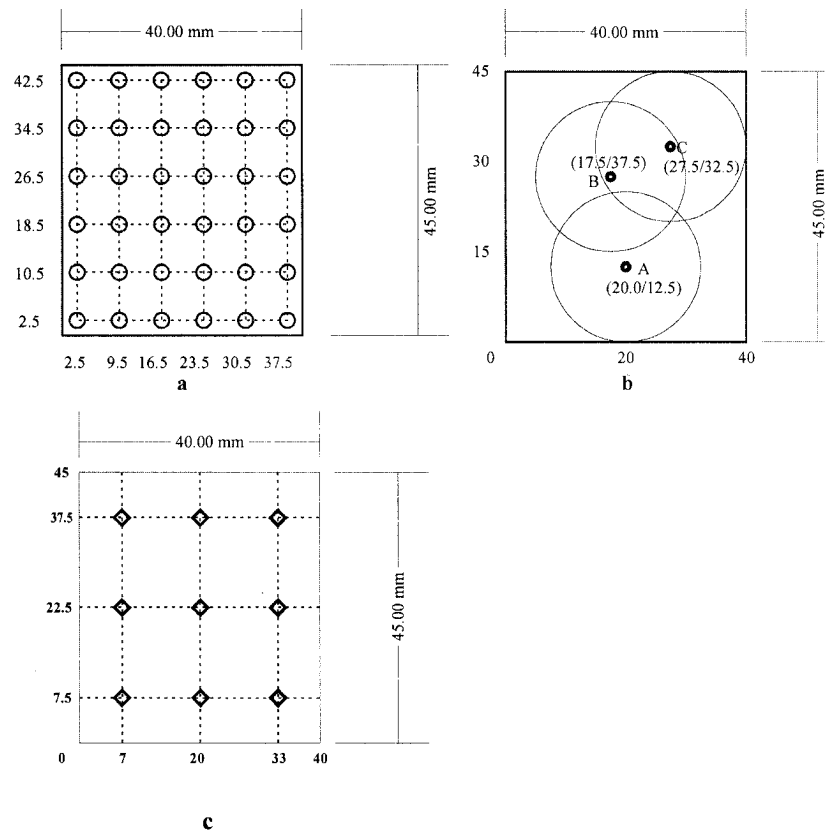


Fig. 1. Graphic model of the positions for measurement on the specimens: a – for thickness; b – for reflection; c – for microhardness.

The reflection of the deposit was measured by a spectrophotometer (Beckman UV 5240). Three different locations on the surface of the specimens were chosen for the reflection measurements (Fig. 1b). The circular measurement area had a diameter of 2.5 cm. The hardness of each specimen was determined by an average of nine measurements. The selection was made with a net (Fig. 1c). A Vickers tester with a load of 100 g (Duriment) was used for the hardness measurements. Surface morphology was examined by optical microscopy (Metaloplan Leitz).

## RESULTS AND DISCUSSION

The chromium coatings deposited in the programmed DC regime with  $77 \text{ A dm}^{-2}$  at a solution temperature  $50^\circ \text{C}$  were bright, with a pronounced edge effect. Visible rough and burnt deposits were visible on the surface at the edges, especially on the lower edge and on the corners.

The distribution of the thickness of the deposits is presented in Fig. 2. A pronounced edge effect can be seen in the latitude profile. The last row (longitude 42.5 mm) has a deformed profile and the highest values of the deposit thickness.

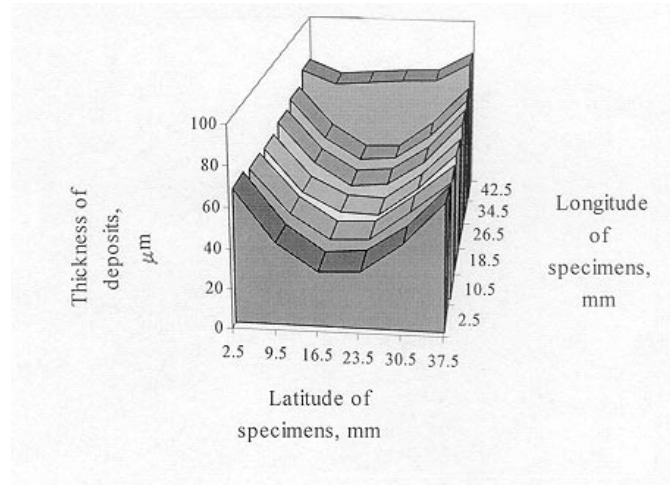


Fig. 2. Latitude profile of the deposit thickness in different rows of measurement.

The longitude profiles are presented in columns in Fig. 3 and as can be seen they are non-uniform. The columns at latitudes 2.5 mm and 37.5 mm, along the side edges have thicknesses from 60 to 80 mm. The middle columns at latitudes 16.5 mm and 23.5 mm have thicknesses from 28 to 70 mm. The largest values of the thickness were measured on the lower edge (the last value in the columns). The ratio between the minimum thickness and the maximum thickness in the middle columns is 2.4. Statistical analysis of the measured deposits thickness was made. The analysis included determination of the interval of variation ( $I$ ), the average thickness ( $\bar{d}$ ), the standard deviation ( $sd$ ) and the coefficient variation ( $cv$ ). According to this, the latitude profiles are non-uniform. The average thickness of the points belonging to

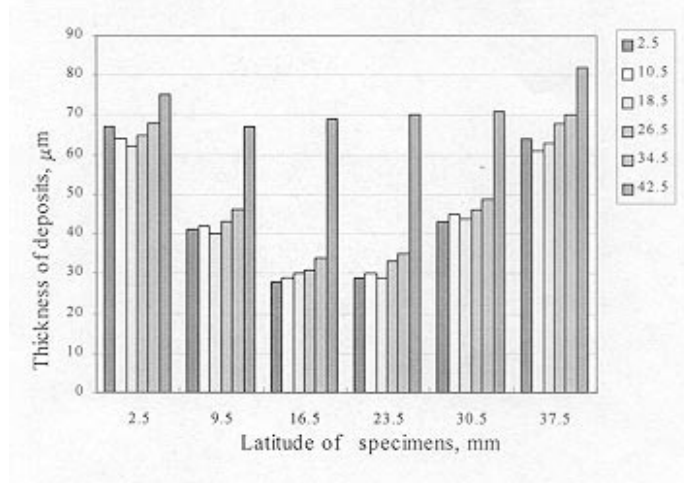


Fig. 3. Longitude profile of the deposit thickness.

row with longitude 2.5 mm was  $\bar{d} = 45.33$  mm and the corresponding value for the row with longitude 42.5 mm was  $\bar{d} = 72.33$  mm.

The biggest interval of variation ( $I$ ) existed between the points belonging to the row with longitude 2.5 mm and the row with longitude 42.5 mm:

$$I = d_{\max} - d_{\min} = 82 - 28 = 54 \text{ mm} \quad (1)$$

On the basis of the results from Fig. 2, Fig. 4 can be derived, assuming a linear change of the thickness of the deposit between two neighbours points.

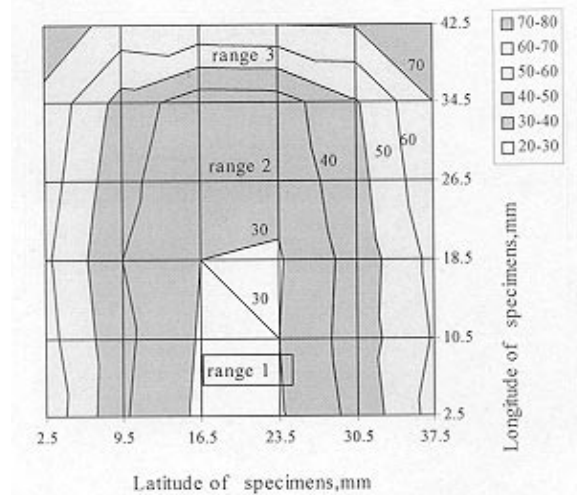


Fig. 4. Graphic model of the surface deposit distribution (electrodepositions in the DC regime with  $77 \text{ A dm}^{-2}$  at a solution temperature  $50^\circ\text{C}$ ). Range 1 – thickness from 20 to 30 mm; range 2 – thickness from 30 to 50 mm; range 3 – thickness from 50 to 70 mm.

The specimens latitude is presented on the abscissa and the specimens longitude is presented on the ordinate. The distribution of the deposit on the surface was determined in three ranges of thicknesses. The first range is limited by a line marking 30, which means that this line connects the points on the surface with thickness 30 mm. The first range contained thicknesses from 20 to 30 mm. The second range is limited by lines marking 30 and 50. The third range is limited by lines marking 50 and 70. The thickness on the corners was over 70 mm.

Statistical analysis of measured thicknesses is given in Table II. Range 1 with the smallest  $\bar{d} = 29.87$  mm was uniform with fine grains.

Range 2 has middle thickness  $\bar{d} = 42$  mm, larger grains and excessive cracks. Range 3 is the edge and the deposits were rough and burnt.

Investigation of the morphology was performed by optical microscopy. The finest structure with small grains and few cracks was observed in the first range (Fig. 5a). Bigger grain with larger cracks was observed in the second range (Fig.

5b). The morphology of the edges of the specimens is presented in Fig. 5c, from which it can be seen that the deposits in range 3 are rough and burnt. Especially burnt deposits could be seen on the lower corners (Fig. 5d).

TABLE II. Results of the statistical analysis of the measured thickness

	Average thickness/ mm	Standard deviation of the thickness/ mm	Coefficient of variation
Range 1	29.87	1.55	0.0518
Range 2	42	4.32	0.1031
Range 3	67.87	5.26	0.0776
Whole surface of the specimens	50.80	16.68	0.3281

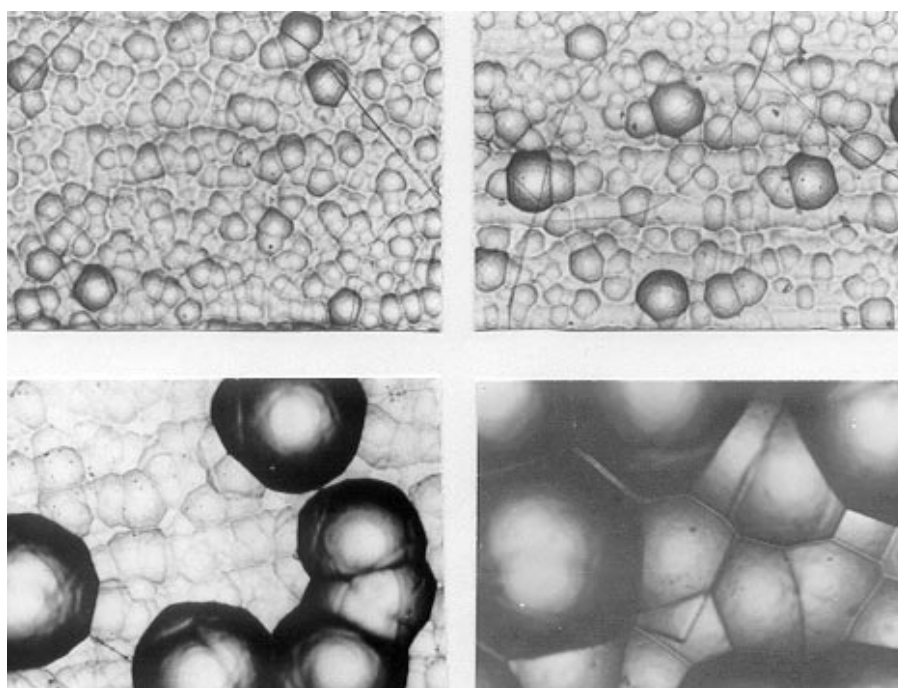


Fig. 5. Morphology of the deposits in different ranges of thickness (electrodeposition in the DC regime with  $77 \text{ A dm}^{-2}$  at a solution temperature  $50^\circ\text{C}$ ). Magnification  $640\times$ . a) Range 1 – thickness from 20 to 30 mm; b) range 2 – thickness from 30 to 50 mm; c) range 3 – thickness from 50 to 70 mm; d) corner – thickness 82 mm.

Reflection from the surface of the deposits was measured at three location on the specimens (Fig. 1b). The total and diffuse reflection was measured and their difference is the mirror reflection. The mirror reflection is an indicator of the surface brightness. A reflective spectrophotometer in the visible wavelength range (from 400 to 700 nm) was used for the measurements. Nine curves are presented in Fig. 6. The

top three curves show the total reflection at all three location on the specimens. The three curves in the middle represent the diffuse reflection and the last three curves the mirror reflection at all three location on the specimens. As can be seen from Fig. 6, there is a difference in the reflection at different points of the specimen due to the differences in the surface morphology. Obviously, these results are only qualitative, because there are different morphologies in each region under consideration.

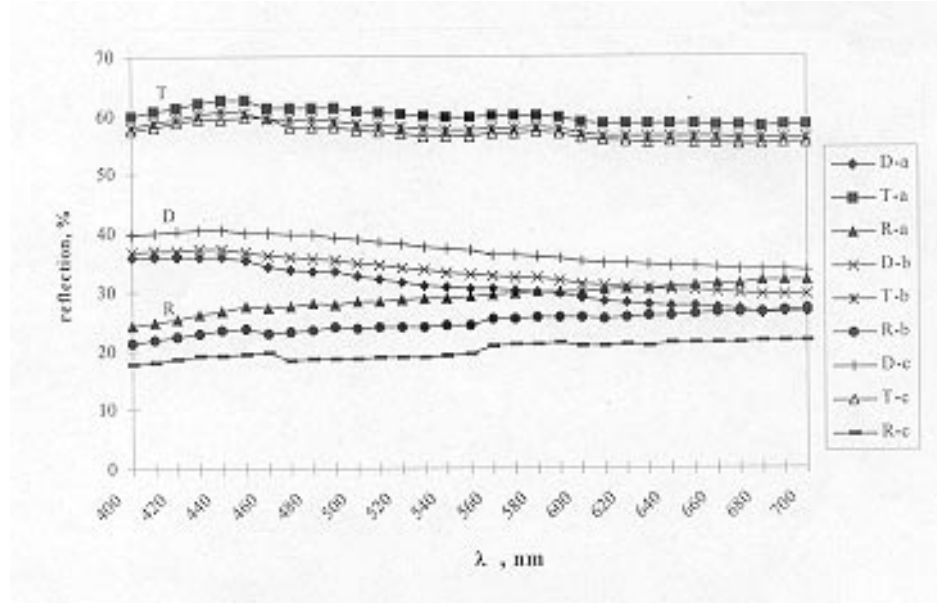


Fig. 6. Reflection of chromium deposits dependence on wavelength in the visible range (electrodepositions in the DC regime with  $77 \text{ A dm}^{-2}$  at a solution temperature  $50^\circ\text{C}$ )  $D$ -a,  $D$ -b,  $D$ -c diffuse reflection at locations A, B and C;  $T$ -a,  $T$ -b,  $T$ -c total reflection at locations, A, B and C;  $R$ -a,  $R$ -b,  $R$ -c – mirror reflection at locations A, B, and C (Fig. 1b).

The results of the microhardness measurements are presented in Table III. The measurements were performed at nine selected points on the surface. It seems that the microhardness at the different points depends on the deposit thickness, being higher with increasing thickness.

TABLE III. Results of the measurements of the microhardness of the deposits (electrodeposition in the DC regime with  $77 \text{ A dm}^{-2}$  at a solution temperature  $50^\circ\text{C}$ )

Microhardness $HV_{0.1}$	I column	II column	III column	Average $HV_{0.1} \pm sd$
1 row	946	920	933	
2 row	950	946	988	
3 row	946	1003	967	955–26

For the whole specimens  $\bar{d} = 50.8 \text{ mm}$  with a  $cv = 0.3281$ . This makes the deposit non-uniform in the distribution of the thickness. Because of the important

variations in the thickness, the morphology and the reflection of the deposits in all three ranges, this kind of protection cannot be taken as reliable under aggressive atmosphere conditions.<sup>9</sup> Also, range 3, with burnt and fragile deposits, is unreliable in systems with high dynamic pressure and precise dimensions. The results of the microhardness measurements (Table III) showed that the hardness is high  $HV_{0.1} = 955 - 26$  and stable. According to the literature,<sup>7,8</sup> bright chromium coatings deposited at temperatures between 50 to 56 °C with thickness variations from 30 to 70 nm have stable microhardnesses.

On the basis of these results and the literature, programmes for deposition with reversing current will be proposed. The purpose of these programmes will be obtaining deposits with fine grain, cracks-free structures, free and with a more uniform thickness distribution of the deposits on the surface.

### CONCLUSION

Chromium deposited with a programmed DC regime in the range of high current density ( $77 \text{ A dm}^{-2}$ ) at a temperature of 50 °C was bright with a pronounced edge effect.

Graphic models based on the measurement of the thickness of the deposits showed three different ranges of thickness with specific corners (range 1 – average thickness 29.87 mm, range 2 – average thickness 42 mm and range 3 – thickness 67.87 mm).

The morphology and structure was different in the different ranges of the specimen, from fine in range 1 to rough and burnt in range 3. The reflection was different in the different ranges, and decreased from the middle to the edge of the specimens (total reflection from 59.92 % to 56.93 %, mirror reflection from 28.96 to 19.8 %). The microhardness is stable over the whole specimens and has a value of  $HV_{0.1} = 955 - 26$ .

Statistical analysis was performed to define the coefficient of variation for the whole specimens, 0.3281. The latitude profiles of the thickness of the deposits are non-uniform, and the longitude profiles, presented as columns, are also non-uniform. It was shown that the distribution of the deposit is non-uniform.

### ИЗВОД

#### СВОЈСТВА ЕЛЕКТРОХЕМИЈСКИ ИСТАЛОЖЕНОГ ХРОМА ПРОГРАМИРАНИМ СТРУЈАМА. ДЕО I. ЈЕДНОСМЕРНА СТРУЈА

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Електролитичко таложење хрома у програмираном режиму једносмерне струје испитивано је у области високих густина струје ( $77 \text{ A dm}^{-2}$ ). Хром је таложен из хроматно-сулфатног електролита на узорке од челика, у току једног часа. Електроде су



постављене у систем план-паралелних плоча. Испитивана су основна својства превлака хрома: изглед, дебљина, морфологија, микротврдоћа и рефлексација. Дебљина превлаке (од 28 до 82  $\mu\text{m}$ ) мерена је на површини узорка на 36 места. Коришћена је неразарајућа феро-магнетна метода. На основу резултата мерења урађени су графички модели расподеле талоба по површини узорка. На моделима су уочене три области дебљина превлаке (област 1 – средња дебљина 29,87  $\mu\text{m}$ , област 2 – средња дебљина 42  $\mu\text{m}$ , област 3 – средња дебљина 67,87  $\mu\text{m}$ ). Испитивањем основних својстава превлаке (морфологије и рефлексације) утврђено је да се мењају по површини превлаке у зависности од дебљине превлаке хрома. У средини узорка област 1 структура је фина (ситно зрно са танким прскотинама), потом се зрно укрупњава и појављују се веће прскотине област 2, да би на крајевима узорка област 3, талоб био груб и прегорео, посебно на угловима узорка. Статистичком анализом измерених резултата за дебљину утврђено је да је превлака хетерогена са великим интервалом варијације (54  $\mu\text{m}$ ) и коефицијентом варијације 0,3281. Резултати ових испитивања доводе у питање поузданост ових превлака хрома у заштити од корозије, ерозије и хабања система који раде са агресивним гасовима на високим температурама и притисцима.

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