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INFLUENCE OF HYDROGEN-METHANE GAS MIXTURES ON THE PHYSICAL AND CHEMICAL STRUCTURE OF POLYETHYLENE PIPES OF THE OPERATING GAS-DISTRIBUTION NETWORKS OF UKRAINE

M.V. Iurzhenko[1,2], M.O. Kovalchuk[1], V.Yu. Kondratenko[1], V.L. Demchenko[1,2], K.G. Gusakova[2], V.S. Verbovskyi[3], G.V. Zhuk[3], K.P. Kostogryz[4], I.A. Gotsyk[5]

[1]E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine
[2]Institute of Macromolecular Chemistry of NASU
48 Kharkiv Hwy, 02160, Kyiv, Ukraine
[3]Gas Institute of NASU
39 Dekhtyarivs'ka Str., 03113, Kyiv, Ukraine
[4]"Naftogasbudinformatyka" Company
5b Kudryavsky Uzviz, 04053, Kyiv, Ukraine
[5]"Regional Gas Company" LLC
32/2 Princes of Ostroh Str., Kyiv, Ukraine

ABSTRACT

The work is a study of the influence of mixtures of gaseous hydrogen with natural gas with the ratios of 10 % H_2/90 % CH_4 and 20 % H_2/80 % CH_4 on PE-80 polymer pipes. The paper presents the results of complex structural investigations of the material of polyethylene pipes from PE-80, which were used earlier in the operating gas distribution networks of Ukraine, after 6 months of their hydrogenation. The influence of gas mixtures on the material structure was established, which is manifested in reduction of the quantity of the crystalline phase, polyethylene crystallite dimensions and their orderliness. No changes in the chemical structure of the polyethylene pipe material were found.

KEYWORDS: polyethylene, PE-80, natural gas mixtures, hydrogen mixtures, hydrogen transportation

INTRODUCTION

Existing ecological trends for substitution of natural gas as the main type of fuel for both industry as well as household consumers present new challenges for polymer materials science and science as a whole. In terms of armed aggression of the Russian Federation against Ukraine, the problem of using alternative fuel sources is currently more than relevant for both Ukraine and the world. In this work, the effect of mixtures of hydrogen with natural gas on the physical and chemical structure of the material of polyethylene pipes from PE-80 as the most widespread material in the operating gas distribution networks of Ukraine was studied. The presented results are the basis for a future large-scale study, whose aim is to study the possibility of transporting pure hydrogen and hydrogen mixtures with natural gas by gas distribution networks operating in Ukraine and the EU.

MATERIALS

For complex studies, two gas mixtures of hydrogen with methane were used with the ratios of 10 % H_2/90 % CH_4 and 20 % H_2/80 % CH_4. To study the influence of gas mixtures on the structure of the material of polyethylene pipes using their full-scale specimens, a research bench was constructed (Figure 1). For research works, specimens of polyethylene pipes from PE-80 with an outer diameter of 63 mm, wall thickness of 3.6 mm, SDR 17.6 were selected, which served in operating gas pipelines during 15 years [1], produced by the companies LLC Plastkonstruktsiya (Figure 2, *a*) — marked further as ST1 and LLC Plastpipe (Figure 2, *b*) — marked further as ST2.

Rewelding with polyethylene thermistor plugs from PE-100 for pipes with an outer diameter of 63 mm and SDR range of 11–17 of Trans Quadro production was performed using the Optima 231 welding unit produced by LLC Terpolymergaz in accordance with acting standards and instructions for welding equipment [2].

For hydrogenation in the specified thermistor plugs piped transition pieces of the polyethylene PE-80 (with an outer diameter of 20 mm) — metal (with an outer diameter of 2/3 inches) with a milled thread were preliminary welded-in. The tightness of the joints was checked up pneumatically by a compressed air at a pressure of 8 bar.

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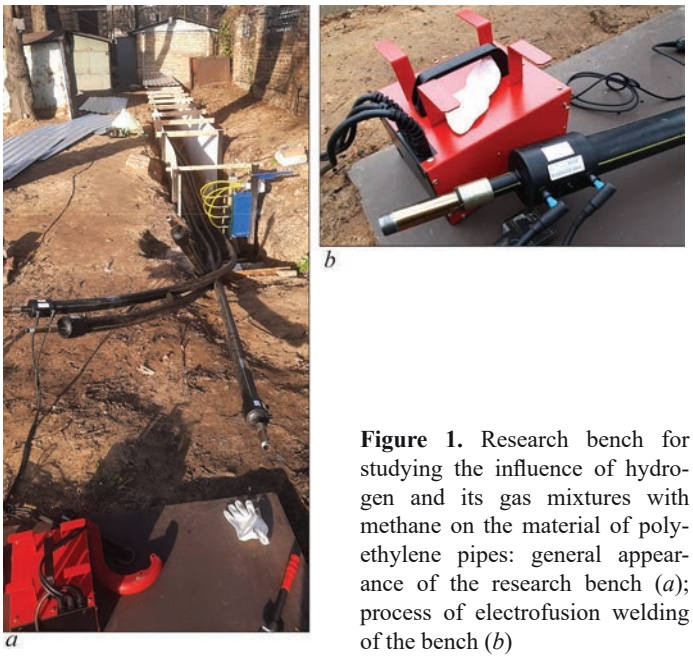

Figure 1. Research bench for studying the influence of hydrogen and its gas mixtures with methane on the material of polyethylene pipes: general appearance of the research bench (*a*); process of electrofusion welding of the bench (*b*)

METHODS OF RESEARCH

For structural studies, from the walls of polyethylene pipes, specimens of 1 mm thick were cut out, as is shown in Figure 3.

Structural studies of the material of the inner surface of the wall of polyethylene pipes in a longitudinal direction to the main axis of the pipe were carried out by the method of wide-angle scattering of X-rays on reflection by means of the X-ray diffractometer XRD-7000 (Shimadzu, Japan) according to the X-ray Bragg–Brentano scheme on reflection of the primary beam by the tested specimen using CuK_α-radiation (λ = 1.54 Å) and a graphite monochromator. The study was carried out by the method of automatic step-by-step scanning in the mode of 30 kV, 30 mA in the interval of scattering angles (2θ) 3–60° per exposure time of 5 s [3, 4]. The temperature of studies was 20 ± 2 °C.

The infrared spectroscopy of the material of the inner surface of the walls and the volume (at a depth of 1 mm from the inner surface of the wall) of polyethylene pipes was carried out on reflection in the Tensor 37 spectrometer with the Fourier transformation of the Bruker Corp. production (Germany) in the range of wavelengths of 600–3800 cm^{-1} [5] at a temperature of 20 ± 2 °C in the mode for reflection on both sides of the specimens. According to the certificate of the device, the relative measurement error was <2 %. At the second stage of works, polyethylene pipes, hydrogenated with gas mixtures, were dehydrogenated and purged with gaseous nitrogen.

To transport specimens of polyethylene pipes with the least influence of the environment, they were vacuum packed directly at the testing ground (Figure 4), then transported to laboratories in the box, which also excluded the action of light.

Figure 2. Specimens of polyethylene pipes from PE-80: ST1 (*a*) and ST2 (*b*)

RESEARCH RESULTS.
4.1. X-RAY STRUCTURAL ANALYSIS

Figure 5 shows the results of X-ray structural analysis of the material of polyethylene pipes before hydrogenation. The analysis of wide-angle X-ray diffraction patterns of the specimens of polyethylene pipe material showed that they all have an amorphous crystalline

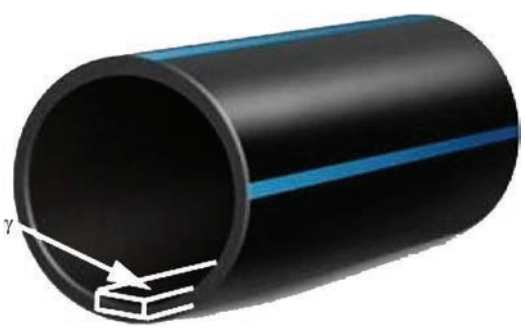

Figure 3. Direction of cutting out sections γ from the walls of polyethylene pipes for structural and thermophysical studies

Figure 4. Specimens of vacuum packed polyethylene pipes for structural studies

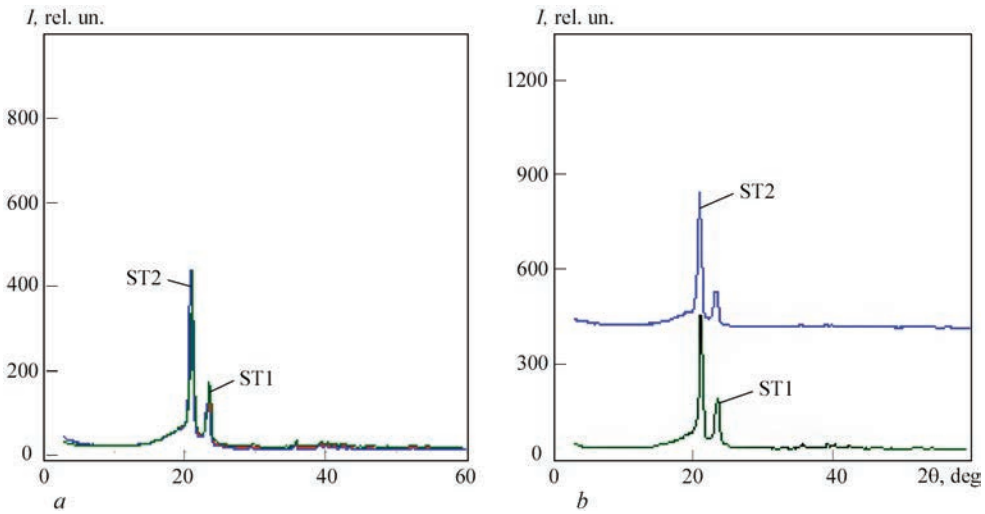

Figure 5. Wide-angle diffraction curves of X-ray structural analysis of the material of polyethylene pipes before hydrogenation (*a*) and their comparative diagram (*b*): *I*, rel. un. — relative intensity of reflected X-ray beam

structure, which is indicated by the presence of crystalline diffraction maxima on the background of imaginary amorphous halo with a vertex at $2\theta_{max} \approx 20°$ [6].

The relative level of crystallinity (X_{cr}) of the studied polymer specimens was calculated by the Mathew's method [7]:

$$X_{cr} = Q_{cr}(Q_{cr} + Q_{am})^{-1} \cdot 100, \quad (1)$$

where Q_{cr} is the area of diffraction maxima that characterize the crystalline structure of the polymer; $Q_{cr} + Q_{am}$ is the area of the entire diffraction pattern in the interval of scattering angles ($2\theta_1 \div 2\theta_2$), in which the amorphous crystalline structure of the polymer is revealed.

The results of the calculation of the degrees of crystallinity of the material of polyethylene pipes are given in Table 1. The evaluation showed that for the specimen of the ST1 polyethylene $X_{cr} = 63.18$ %, and for the specimen and ST2 $X_{cr} = 62.38$ %.

The evaluation of effective size of crystallites (L) of the specimens was carried out by the Scherrer method [8]:

$$L = K\lambda(\beta\cos\theta_{max})^{-1}, \quad (2)$$

where K is the constant associated with the shape of crystallites (their shape being unknown $K = 0.9$), and β is the angular half-width (width at a half of the height) of the diffraction maximum, showed that the average value $L \approx 17.22$ nm and 14.39 nm for ST1 and ST2, respectively. The size of the crystallites by individual diffraction maxima for ST1 and ST2 specimens is given in Tables 2, 3, respectively, where FWHM is the full width at a half of the maximum (width of the spectral curve, measured between those points on Y axis, which are the half of the maximum amplitude), FWHM tot. is the total full width at a half of the maximum, FWHM instr. is the instrumental full width at a half of the maximum.

The results of X-ray structural analysis of the material of polyethylene pipes after 6 months of hydrogenation are shown in Figure 6. It was established that specimens of polyethylene pipes ST1 and ST2, which were under the action of gas mixtures, as well as the initial specimens, are characterized by amorphous crystalline structure, which is indicated by the presence of crystalline diffraction maxima on the background of an imaginary amorphous halo with a vertex at $2\theta \approx 20°$. It was found that under the action of gas

Table 1. Degree of crystallinity of the material of polyethylene pipes, calculated according to the data of X-ray structural analysis

Specimen	X_{cr}, %	L, nm
ST1	63.18	17.22
ST2	62.38	14.39

Table 2. Sizes of crystallites according to diffraction maxima of ST1 pipe specimen

2θ, deg	*d*, Å	Attempts	FWHM tot., deg	FWHM instr., deg	FWHM of the specimen, deg	Size of crystallites, Å
21.100	4.2106	19324	0.4000	0.1303	0.2697	299.9
23.500	3.7858	10260	0.6000	0.1303	0.4697	172.9
29.700	3.0081	640	0.8000	0.1267	0.6733	122.2
35.800	2.5083	899	0.6000	0.1132	0.4868	171.6
39.300	2.2926	1127	0.8000	0.1074	0.6926	121.9
40.300	2.2380	2986	2.6000	0.1059	2.4941	43.0
42.500	2.1271	692	0.8000	0.1029	0.6971	122.4
46.400	1.9570	428	0.8000	0.0984	0.7016	123.3
52.600	1.7400	607	0.8000	0.1011	0.6989	126.9

Table 3. Sizes of crystallites according to diffraction maxima of ST2 pipe specimen

2θ, deg	*d*, Å	Attempts	FWHM tot., deg	FWHM instr., deg	FWHM of the specimen, deg	Size of crystallites, Å
20.900	4.2505	29650	0.6000	0.1313	0.4697	172.1
23.250	3.8259	7690	0.6000	0.1313	0.4697	172.8
35.550	2.5253	534	0.4000	0.1137	0.2863	291.6
39.100	2.3039	800	0.8000	0.1077	0.6923	121.9
40.050	2.2514	462	0.6000	0.1063	0.4937	171.9
40.950	2.2039	557	0.9000	0.1050	0.7950	106.8
42.300	2.1367	529	0.8000	0.1032	0.6968	122.3

mixtures in the material of polyethylene pipes, their crystalline structure changes, in particular, new crystalline peaks appear at $2\theta_{max} \approx 15.9°$, as well as the intensity of peaks grows at $2\theta_{max} \approx 29.5°$ and 35.5°, which is associated with an increase in the crystallinity of polyethylene [9]. It was established that the relative degree of crystallinity X_{cr} of the material of polyethylene pipes ST1 and ST2, which were under the action of gas mixtures 10 % H_2/90 % CH_4 and 20 % H_2/80 % CH_4 respectively, is higher compared to the source material (Table 4).

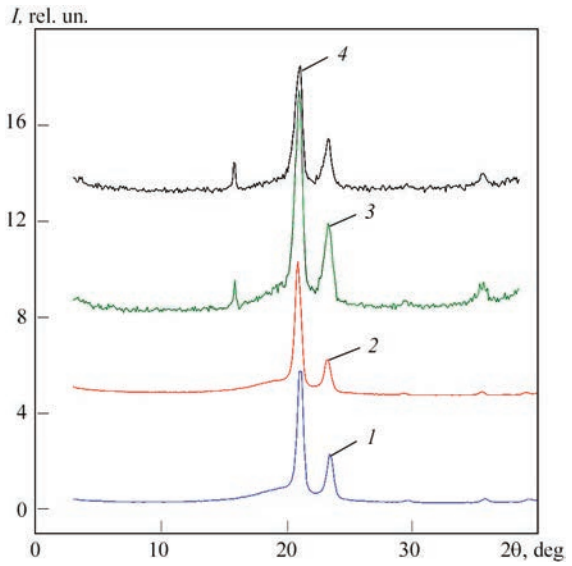

Figure 6. Comparative diagram of wide-angle diffraction curves of X-ray structural analysis of material of polyethylene ST1 and ST2 pipes before and after hydrogenation: *1* — ST1; *2* — ST2; *3* — ST1 10 % H_2; *4* — ST2 20 % H_2

The analysis of the results of X-ray structural analysis showed that under the action of gas mixtures, the crystalline structure changes, in particular, the average size of crystallites L is reduced (specimens of ST1 and ST1 10 % H_2). For calculations, diffraction maxima at $2\theta_{max} \approx 21.0°$ and 23.4° were used. The size of crystallites and interplanar distances at individual diffraction maxima for the specimens of ST1 10 % H_2 and ST2 20 % H_2, which were under the action of gas mixtures of 10 % H_2/90 % CH_4 and 20 % H_2/80 % CH_4 respectively, are given in Tables 5, 6.

4.2. INFRARED SPECTROSCOPY

Figure 7 shows the spectra of infrared (IR) spectroscopy of the material from the inner surface and volume of walls of the specimens of ST1 (Figure 7, *a*), ST2 (Figure 7, *b*) pipe before hydrogenation.

It is seen that the absorption spectra for all the specimens are similar and typical of polyethylene. However, it is necessary to focus the attention here on the appearance of additional absorption lines on the spectra of the specimen material from the inner surface of the walls of ST1 and ST2 pipes compared

Table 4. Degree of crystallinity of the material of polyethylene pipes, calculated according to data of X-ray structural analysis

Specimen	X_{cr}, %	*L*, nm
ST1	63.18	17.22
ST2	62.38	14.39
ST1 10 % H_2	68.91	13.19
ST2 20 % H_2	76.01	15.81

Table 5. Sizes of crystallites according to diffraction maxima of ST1 specimen 10 % H_2

2θ, deg	*d*, Å	Attempts	FWHM tot., deg	FWHM instr., deg	FWHM of the specimen, deg	Size of crystallites, Å
17.250	5.1386	8	0.2000	0.1303	0.0697	1153.7
22.400	3.9658	821	0.7000	0.1303	0.5697	142.3
24.750	3.5943	321	0.8000	0.1303	0.6697	121.5
37.050	2.4246	61	0.8000	0.1110	0.6890	121.7

Table 6. Sizes of crystallites according to diffraction maxima of ST2 specimen 20 % H_2

2θ, deg	*d*, Å	Attempts	FWHM tot., deg	FWHM instr., deg	FWHM of the specimen, deg	Size of crystallites, Å
17.250	5.1355	21	0.2000	0.1303	0.0697	1153.7
22.450	3.9571	269	0.4000	0.1303	0.2697	300.5
24.700	3.6012	149	0.6000	0.1303	0.4697	173.3
37.050	2.4245	47	0.8000	0.1110	0.6890	121.7
39.000	2.3076	6	0.4000	0.1078	0.2922	288.7

to the spectra of the material from the volume of the walls of these pipes. The presence of absorption lines near the wavelength of 2400 cm^{-1}, which are responsible for oscillations of CO_2 groups, may be an artefact of measurements, which is associated with the environment and carbon dioxide present in it. The emergence of new abovementioned absorption lines in the specimens from the inner surface of the walls of ST1 and ST2 pipes and their absence in the specimens from the volume of the walls of these pipes may indicate a certain effect of natural gas, which for 15 years was transported through these pipes, on the chemical structure of polyethylene, from which ST1 and ST2 pipes are manufactured. This fact should be taken into account during further studies of all the pipes after the next stages of work, i.e. after their hydrogenation.

The results of infrared spectroscopy after 6 months of hydrogenation are presented in Figure 8. From the comparative IR spectra before and after 6 months of hydrogenation of the specimens of all materials of polyethylene pipes, it is seen that the chemical structure of polyethylene did not undergo changes that follows

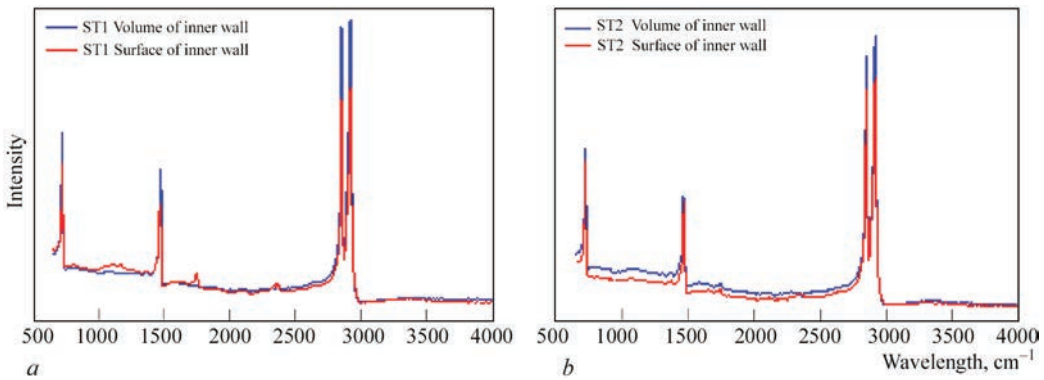

Figure 7. IR spectra of the material of the inner surface and volume of the walls of pipe specimens before hydrogenation: *a* — ST1; *b* — ST2

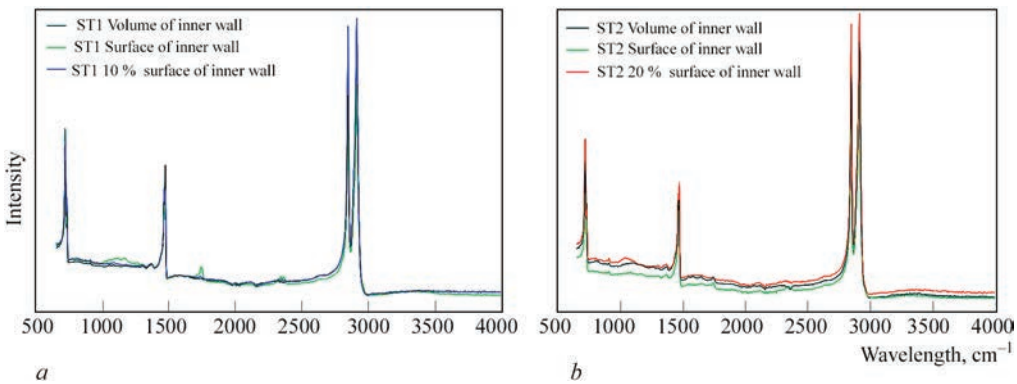

Figure 8. Comparative IR spectra of the material of the inner surface and volume of the walls of pipe specimens before and after hydrogenation: *a* — ST1 (10 % H_2/90 % CH_4); *b* — ST2 (20 % H_2/80 % CH_4)

from the absence of new peaks or displacement of existing peaks responsible for chemical bonds or groups of atoms. It is worth noting that after hydrogenation, the spectra from the surface of the inner wall of the pipe specimens being in operation, are similar to the spectra of the specimens of the material of these pipes from the volume, i.e., it can be said that the chemical structure of the material of the surface of these pipes became identical to the structure of the volume material.

Separately it should be noted that on the spectra of the specimens under the action of the gas mixture of 20 % H_2/80 % CH_4, the intensity of peaks in the wavelength range of 1000–1200 and 3300–3500 cm^{-1}, which are responsible for the oscillations of the C–O–H and –OH groups grows, that can indicate a certain interaction of hydrogen molecules with polymer chains of polyethylene, probably of a dipole in nature with their lateral groups of atoms [10].

CONCLUSIONS

In the work, complex investigations of the influence of gas mixtures of hydrogen with methane with two ratios of 10 % H_2/90 % CH_4 and 20 % H_2/80 % CH_4 on the physical and chemical structure of the material of polyethylene pipes from PE-80, which served in the operating gas distribution networks of Ukraine for 15 years were carried out.

It was established that pipe materials, that were in operation for 15 years have undergone certain structural changes, probably under the action of natural gas, which is manifested in the reduced number of crystalline phase and sizes of crystallites of polyethylene, as well as in the emergence of additional chemical groups in the material of the inner pipe surface.

The presence of influence of gas mixtures of 10 % H_2/80 % CH_4 and 20 % H_2/80 % CH_4 on the crystalline phase was established. A decrease in the sizes of polyethylene crystallites and their orderliness under the action of gas mixtures in the volume of pipes was found. At the same time, the emergence of crystallites of a new shape was found on the surface of the inner wall of the pipes. The influence of gas mixtures on the material of polyethylene pipes has a physical nature.

Changes in the chemical structure of the material of polyethylene pipes were not detected.

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ORCID

M.V. Iurzhenko: 0000-0002-5535-731X,
M.O. Kovalchuk: 0000-0003-2161-643X,
V.Yu. Kondratenko: 0009-0003-3521-9639,
V.L. Demchenko: 0000-0001-9146-8984

CONFLICT OF INTEREST

The Authors declare no conflict of interest

CORRESPONDING AUTHOR

M.V. Iurzhenko
E.O. Paton Electric Welding Institute of the NASU
11 Kazymyr Malevych Str., 03150, Kyiv, Ukraine.
E-mail: 4chewip@gmail.com

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